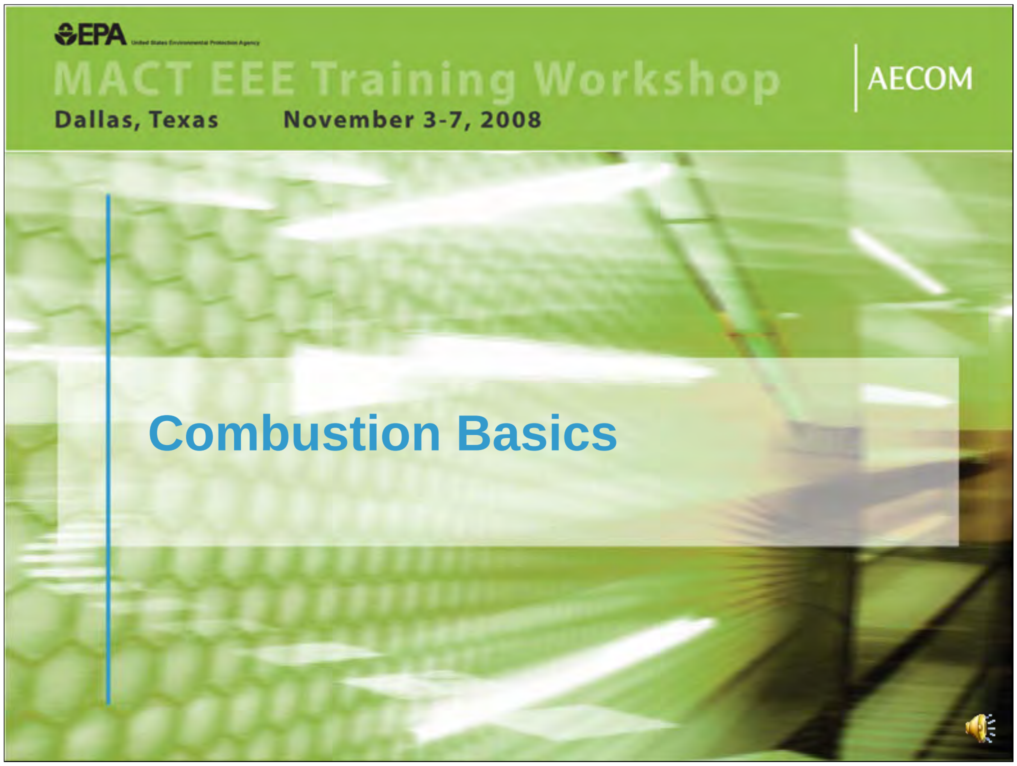

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MACT EEE Training Workshop

Dallas, Texas November 3-7, 2008

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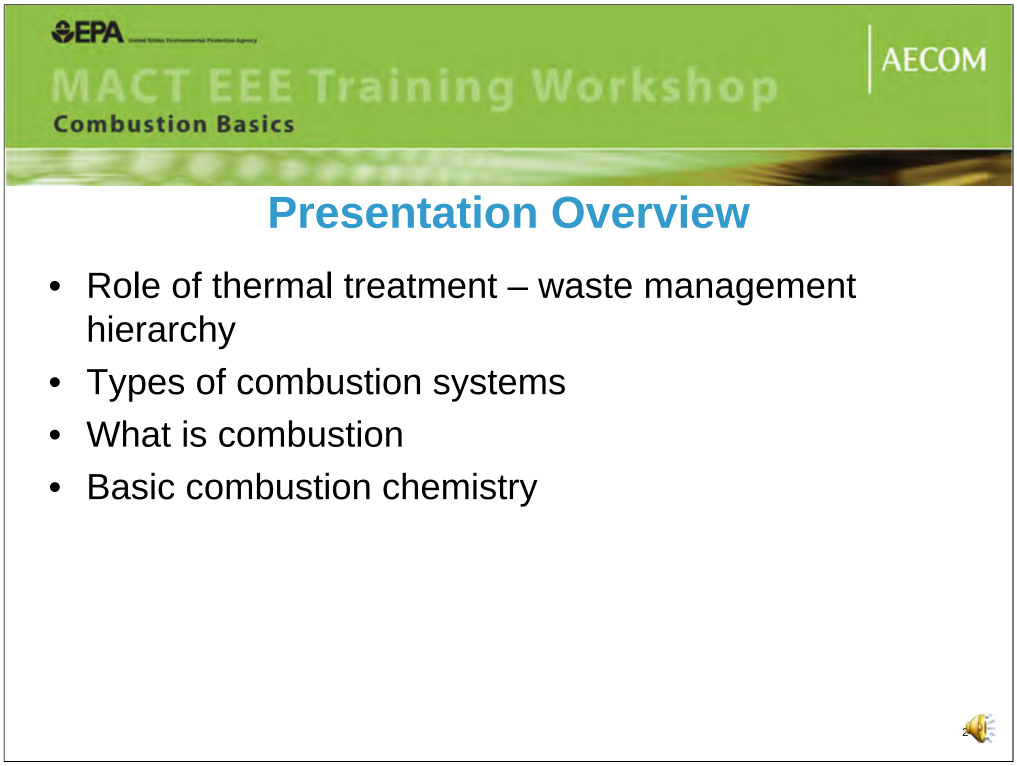
Combustion Basics

Welcome to US EPA's hazardous waste combustion on line training program. This program is intended to assist state and regional permit writers, inspectors and enforcement staff. This program is comprised of 30 individual modules to provide a comprehensive overview of waste combustion and its regulation here in the US.

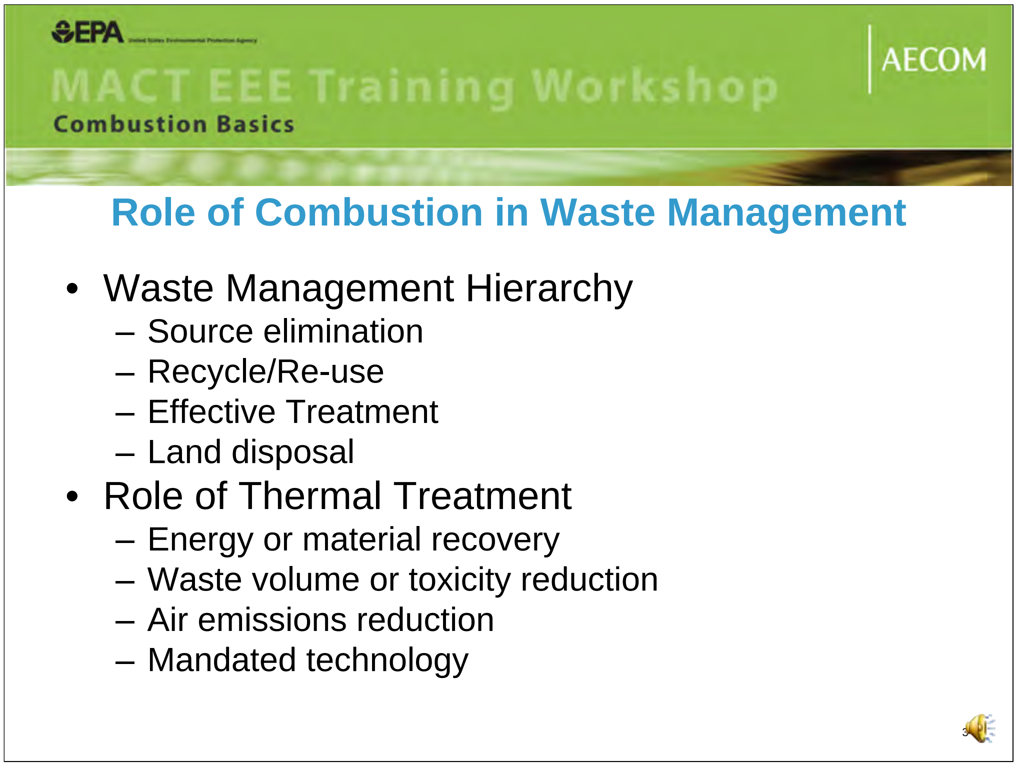
This first module is an introductory level discussion that focuses on the basics of combustion and basic technical principles that relate to it.



Presentation Overview

- Role of thermal treatment – waste management hierarchy
- Types of combustion systems
- What is combustion
- Basic combustion chemistry

The topics to be covered in this module include the overall role that thermal treatment can provide in the management of byproducts and wastes, the types of combustion systems that will be covered in this training program, an overview of combustions basics and its related chemistry.



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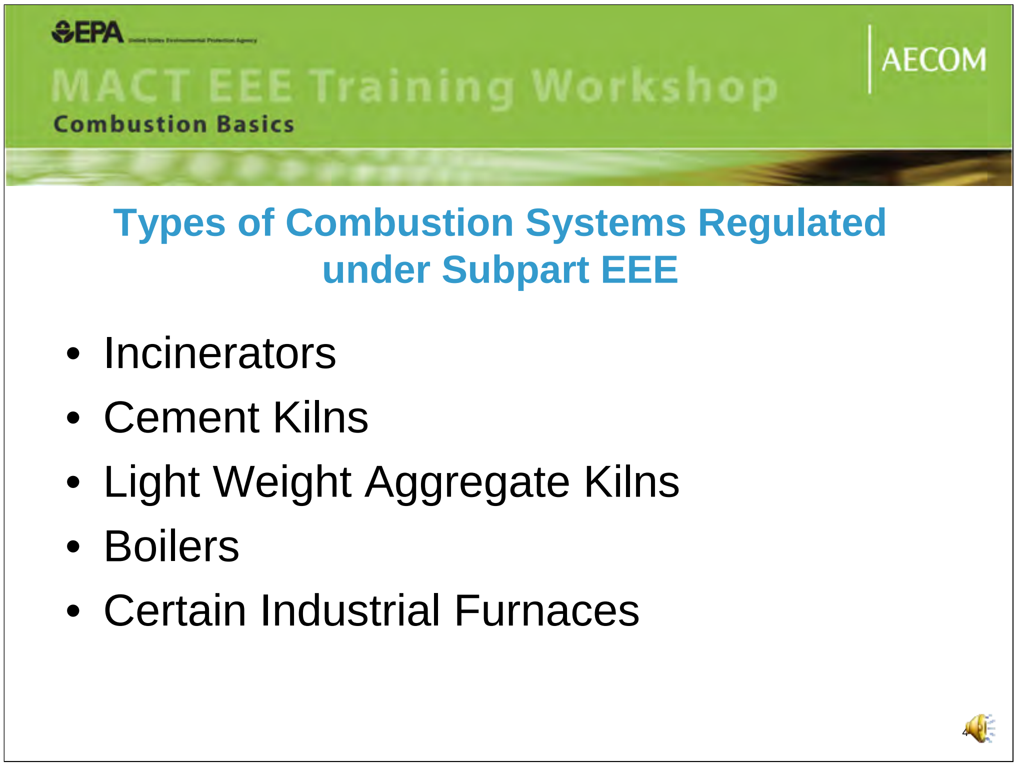
Role of Combustion in Waste Management

- Waste Management Hierarchy
  - Source elimination
  - Recycle/Re-use
  - Effective Treatment
  - Land disposal
- Role of Thermal Treatment
  - Energy or material recovery
  - Waste volume or toxicity reduction
  - Air emissions reduction
  - Mandated technology

It has long been recognized that in order to promote effective resource conservation, wastes in general, and industrial wastes in particular need to be managed in accordance with an established hierarchy. The objective of following this hierarchy is minimize industry's and therefore society's burden on the environment. Thus, the waste management hierarchy was developed. Elimination of waste at the source through efficient design is the first option that should be considered. This often eliminates the need for downstream waste management and can make manufacturing more economical by maximizing the amount of product made for the same amount of raw materials used. Recycling and reuse options are considered as the next option for managing byproducts or wastes as these approaches can often enable valuable components of potential waste streams to be recovered and re-used. Examples of this include recovering sulfur, chlorine or heavy metals from wastes or burning wastes to recover their heating value for use in making steam or providing other thermal energy to a manufacturing process. After source elimination and recycle/re-use options are considered, primary waste management approaches should include those that effectively treat the waste. Land disposal of a waste stream should be considered only after other options have been evaluated and determined to not be viable and this should only be done in units that meet applicable federal and/or state requirements for such disposal.

Combustion technologies used in the hazardous waste industry today generally fall into one of two categories above – either recycle/re-use or treatment. There are numerous facilities in the US that recovery energy in the form of Btu's to produce steam (e.g., boilers), heat their production processes (e.g., cement kilns and light-weight aggregate kilns) or recover valuable materials (e.g., halogen acid furnaces). The combustion portions of these technologies subject the waste streams fed to them to intense temperatures in direct flame systems, thus destroying the original waste streams and these technologies can significantly reduce both the volume and the toxicity of the original waste. In similar fashion, combustion technologies can and do serve as specific control devices to also achieve significant reduction of air emissions. Finally, for a number of different RCRA regulated wastes, combustion is a mandated technology under the Land Disposal Restrictions program codified at 40 CFR Part 268.



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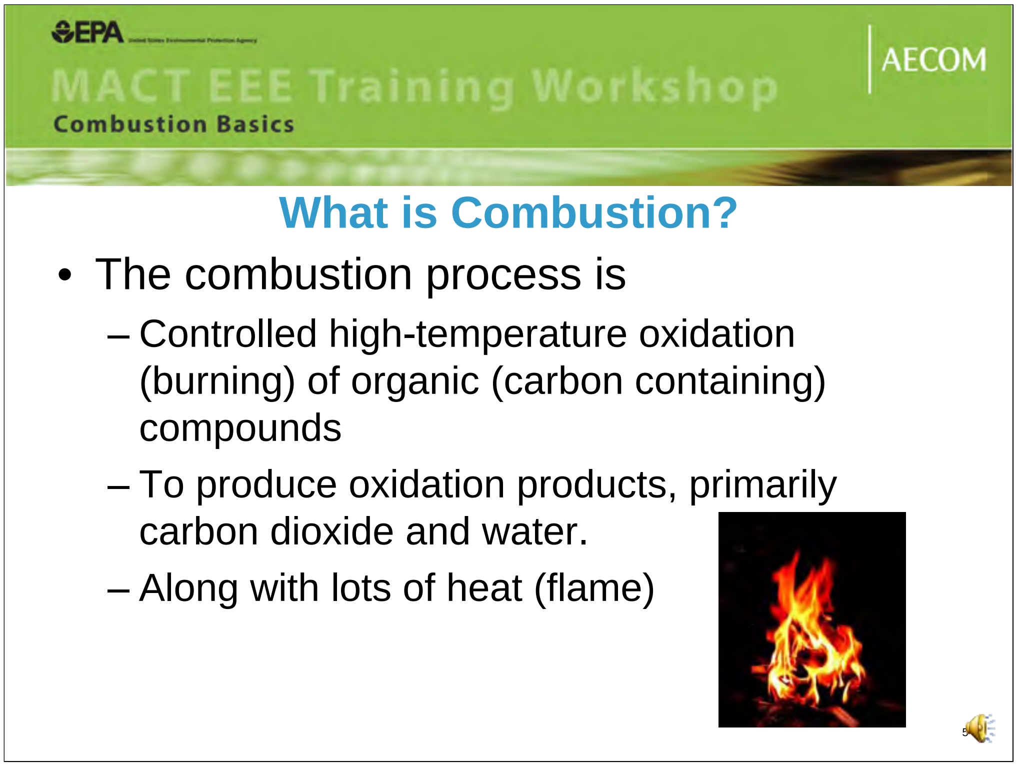
Types of Combustion Systems Regulated under Subpart EEE

- Incinerators
- Cement Kilns
- Light Weight Aggregate Kilns
- Boilers
- Certain Industrial Furnaces

There are five primary combustion technology types that are regulate under federal and state programs in the US. There are incinerators, which include several different basic types including liquid fired units, rotary kiln units and fluidized bed units. There are also waste burning cement kilns and light weight aggregate kilns that primarily produce either cement “clinker” for use in making cement or produce a light aggregate used in place of traditional stone in making concrete and burn waste in place of traditional fossil fuels. A third category of combustion system includes a variety of different solid and liquid fuel boilers that burn waste in lieu of or in addition to fossil fuels to either produce steam directly or to indirectly heat up heat transfer fluids to provide process heat. And finally, there are specially designed furnaces that enable the recovery of certain materials like chlorine from chlorinated organic waste streams or heavy metals such as silver or lead from wastes containing these materials



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Combustion Basics

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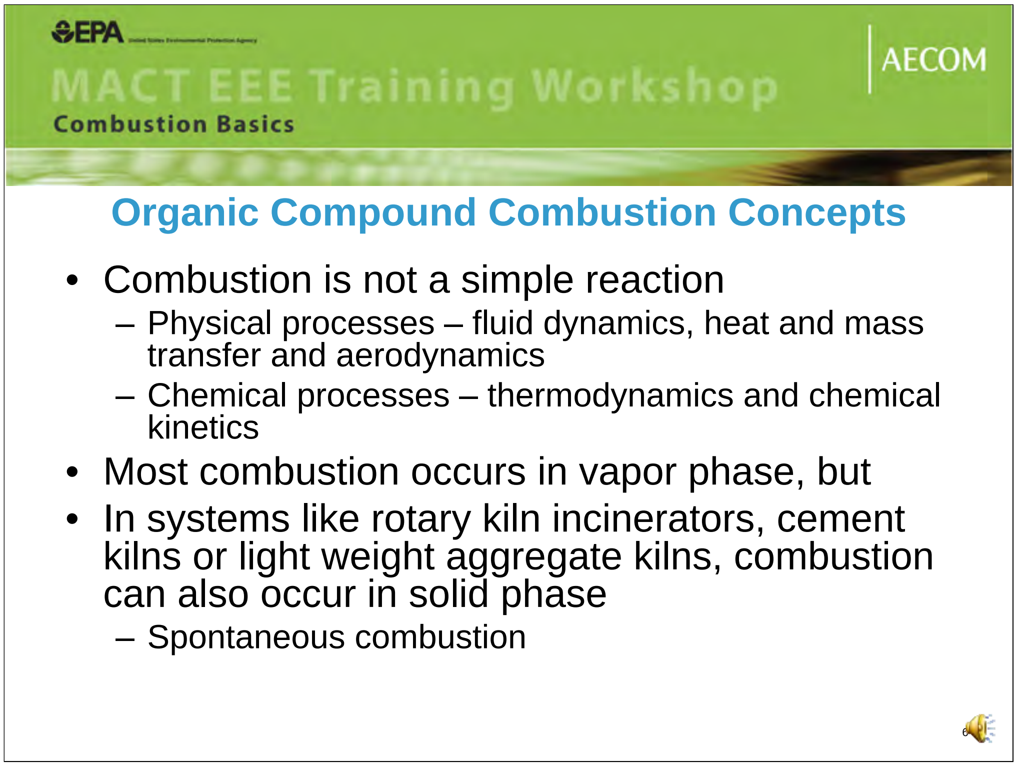
What is Combustion?

- The combustion process is
  - Controlled high-temperature oxidation (burning) of organic (carbon containing) compounds
  - To produce oxidation products, primarily carbon dioxide and water.
  - Along with lots of heat (flame)

So what actually is combustion? In the context within which much of the regulations have been developed, the combustion involved, although varying in its application, is fundamentally the same. Combustion involves high temperature oxidation or burning of an organic or carbon containing compounds in a manner that converts the original compounds to their oxidized forms, which under optimal conditions are carbon dioxide and water. This oxidation process requires both the carbon coming from the wastes or fossil fuels, along with large amounts of oxygen, typically supplied as air and involves the release of large amounts of heat, typically in the form of flames or fire.



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Combustion Basics

Organic Compound Combustion Concepts

- Combustion is not a simple reaction
  - Physical processes – fluid dynamics, heat and mass transfer and aerodynamics
  - Chemical processes – thermodynamics and chemical kinetics
- Most combustion occurs in vapor phase, but
- In systems like rotary kiln incinerators, cement kilns or light weight aggregate kilns, combustion can also occur in solid phase
  - Spontaneous combustion

Combustion though, is not a simple step or reaction, but rather involves several physical and chemical processes in order to complete. Most traditional combustion is vapor phase, meaning the carbon containing materials do not burn until they have been converted to a vapor. Thus, physical processes such as propelling solid or liquid waste through a feed nozzle at sufficient velocity and pressure must be accomplished in order to mix these materials with other already heated in the flame zone, to transfer heat and convert these materials to their vapor form. Then, once vaporized, sufficient interaction can occur between the waste and the supplied air to enable the chemical reaction to occur and cause the oxidation products of the original waste to be formed.

As stated, most combustion reactions occur in the vapor phase, however, certain waste streams fed to rotary kiln incinerators, cement or light weight aggregate kilns can ignite and burn vigorously without needing to be converted first to their vapor phase. This occurs when sufficient air or oxygen is available to allow combustion to occur and when the temperature of the material in question is raised above its "auto-ignition" temperature. This phenomena is also known as spontaneous combustion.

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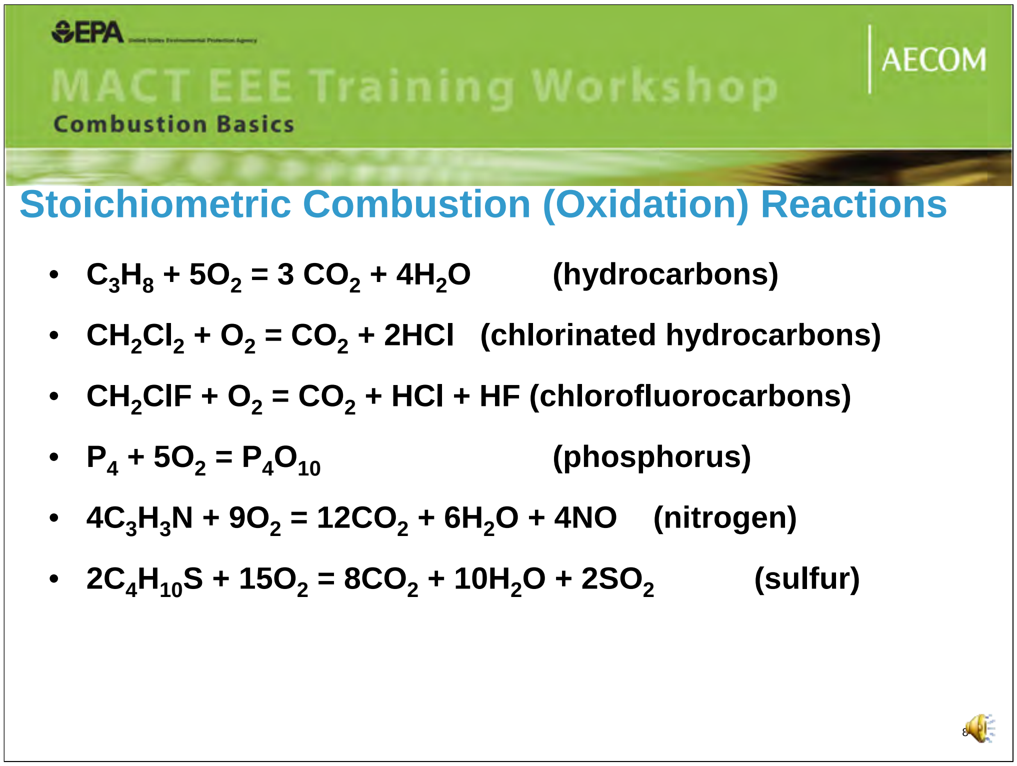
Operating Rotary Kiln Look at Front Face

Source: Heritage Environmental

This picture is a view of a rotary kiln incinerator looking from the discharge end of the kiln towards the front face. The yellow area on the left is the flame of one of the liquid waste burners and is approximately 4-6 feet in diameter and can extend much of the length of a typical 40 foot long kiln. The rectangular area to the right of the flame is the feed chute where both bulk solids and containerized wastes would be fed.



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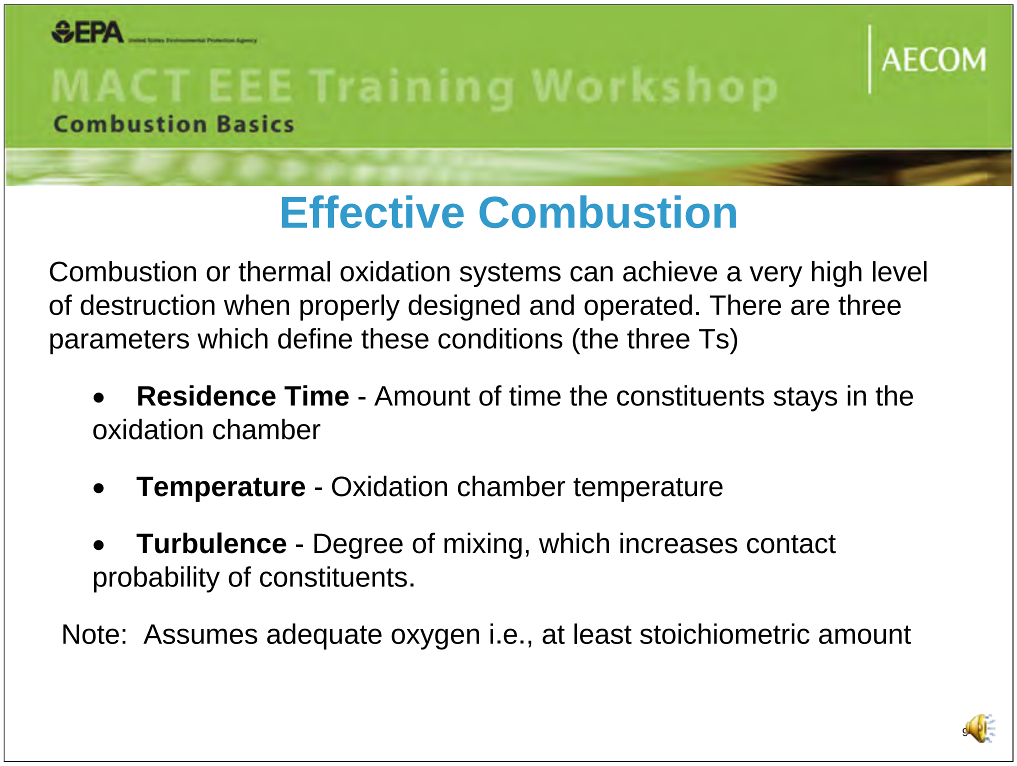
Stoichiometric Combustion (Oxidation) Reactions

- $C_3H_8 + 5O_2 = 3\ CO_2 + 4H_2O$ (hydrocarbons)
- $CH_2Cl_2 + O_2 = CO_2 + 2HCl$ (chlorinated hydrocarbons)
- $CH_2ClF + O_2 = CO_2 + HCl + HF$ (chlorofluorocarbons)
- $P_4 + 5O_2 = P_4O_{10}$ (phosphorus)
- $4C_3H_3N + 9O_2 = 12CO_2 + 6H_2O + 4NO$ (nitrogen)
- $2C_4H_{10}S + 15O_2 = 8CO_2 + 10H_2O + 2SO_2$ (sulfur)

The chemical equations shown on this slide depict what is referred to as stoichiometric combustion for a number of typical combustion reactions. Each reaction shows the amount in moles of oxygen that would be required to convert the compound being burned to their oxidized form. Note that the inorganic and halogen compounds are not destroyed, just converted to a different form.



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Effective Combustion

Combustion or thermal oxidation systems can achieve a very high level of destruction when properly designed and operated. There are three parameters which define these conditions (the three Ts)

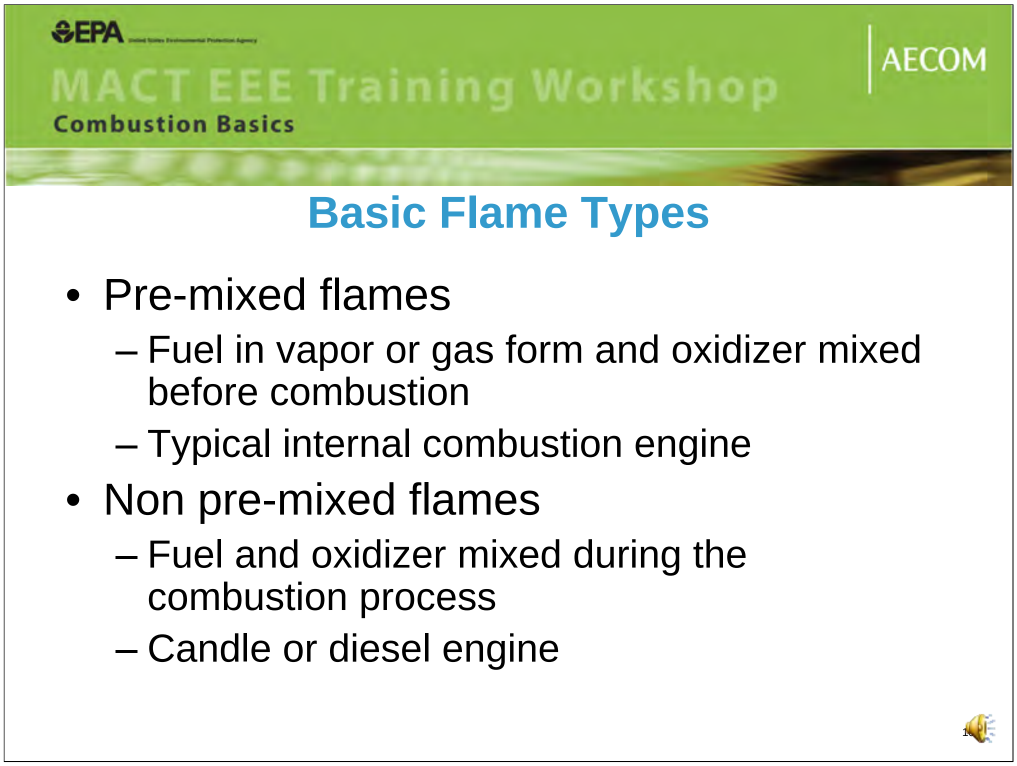
- **Residence Time** - Amount of time the constituents stays in the oxidation chamber
- **Temperature** - Oxidation chamber temperature
- **Turbulence** - Degree of mixing, which increases contact probability of constituents.

Note: Assumes adequate oxygen i.e., at least stoichiometric amount

The previous slide depicted the chemical reactions that occur when various are combusted into their oxidized form. However, there are a number of key factors that contribute to the efficiency of those reactions that have to do with design, equipment configuration and operating practices. The “three T’s” of combustion refer to several of the most important factors in effective combustion.

Adequate residence time is one of the three T’s refers to the amount of time either the solids remain in a solids processing combustor, like a rotary kiln incinerator or the amount of gas residence time in a liquids processing unit. Solids can require 30 minutes or more for organics contained in them to be volatilzed and combusted. This residence time is a function of the solids feed rate, kiln incline and rational speed and overall length. Gas residence time is a function of the feeds, fuels and air firing rates, chamber temperature and volume. Gas residence times of less then a second have been shown to meet required destruction and removal efficiencies (DRE) in many cases. However, for some, more difficult to destroy compounds and those requiring higher DREs like PCBs and dioxin containing, 2 seconds gas residence may be needed or required.

Combustion chamber temperature is also a key factor in assuring effective combustion occurs and there are established minimum temperatures that must be maintained during testing and operations to assure the require DRE is achieved. A third key factor in assuring that effective combustion occurs is turbulence and generally, the more turbulence that exists in a combustion system, the better the mixing of the waste, fuels and combustion air in the flame or combustion zone(s). And, although there are systems that are designed to use less air than what is stoichiometrically called for (these can be “starved air” or “pyrolysis” units and are outside the scope of this training program), the overall effectiveness of the combustion process is dependent on an adequate supply of available oxygen, usually supplied as air.



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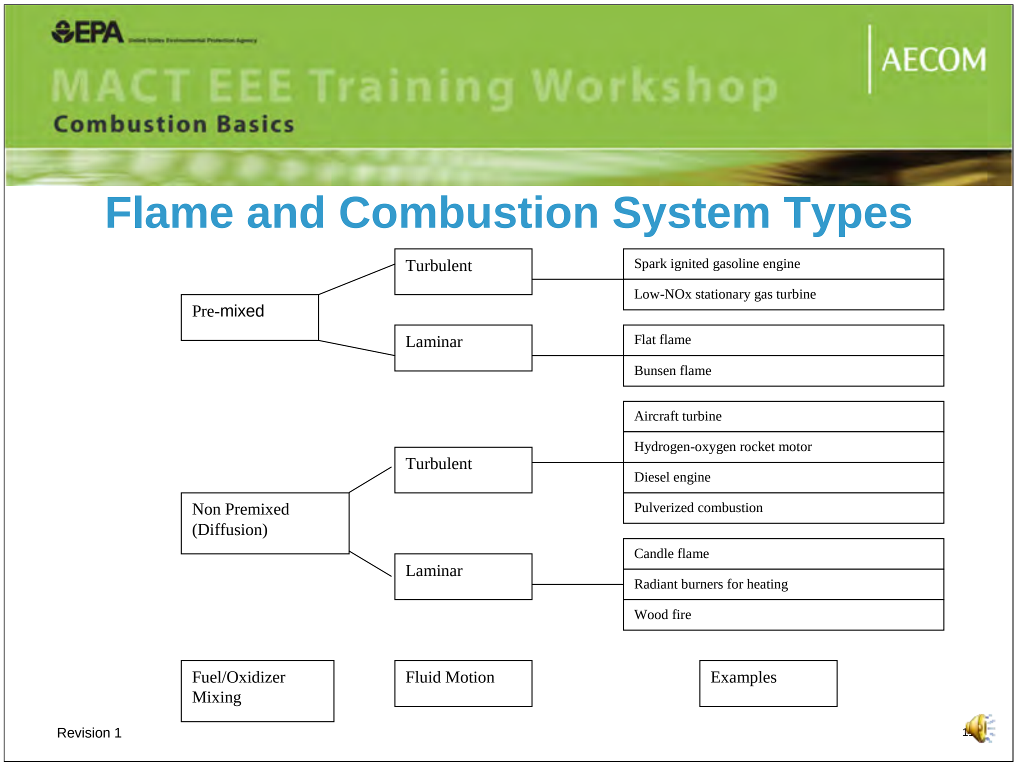
Basic Flame Types

- Pre-mixed flames
  - Fuel in vapor or gas form and oxidizer mixed before combustion
  - Typical internal combustion engine
- Non pre-mixed flames
  - Fuel and oxidizer mixed during the combustion process
  - Candle or diesel engine

We have established that combustion is the oxidation of organic compounds with the subsequent release of large amounts of energy in the form of heat. Generally, this occurs in the form of fire or flames and the presence of the flame is what continues to ignite new waste entering the combustor. In fact, start-up of combustion systems generally rely initially on a “pilot” flame from which a main flame is subsequently lit. As fuel (or waste) and air continue to be added, the flame becomes self sustaining and no longer needs the pilot flame to continue to burn. There are two principal types of flames in use in combustion systems today. These include “pre-mixed” and non-pre-mixed flames and these are fairly self-explanatory. For the “pre-mixed” type of flame, fuel and the oxidizer (generally air) are mixed together prior to being introduced into the combustion chamber. A prime example of this is the carburetor of an internal combustion engine, where gas and air are mixed and then flow into the cylinder to be ignited by the spark plug. Many hazardous waste combustion systems are designed as non pre-mixed flames in that the fossil fuel or waste fuel are kept separate from the combustion air supply right up until the point of injection into the flame zone itself such that the mixing itself occurs due to the design of the feed nozzle and the turbulence created by the burner and the flame.



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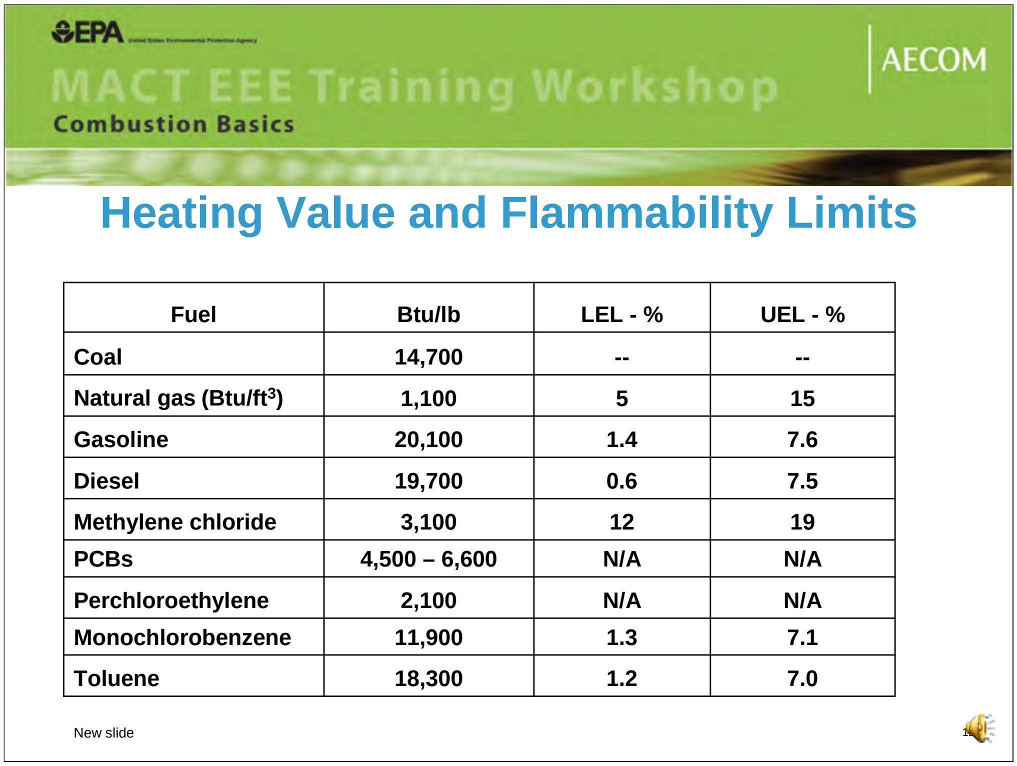
Flame and Combustion System Types

Fuel/Oxidizer Mixing	Fluid Motion	Examples
Pre-mixed	Turbulent	Spark ignited gasoline engine Low-NOx stationary gas turbine
	Laminar	Flat flame Bunsen flame
Non Premixed (Diffusion)	Turbulent	Aircraft turbine Hydrogen-oxygen rocket motor Diesel engine Pulverized combustion
	Laminar	Candle flame Radiant burners for heating Wood fire

Revision 1

This slides shows additional examples of the two flame types just discussed.



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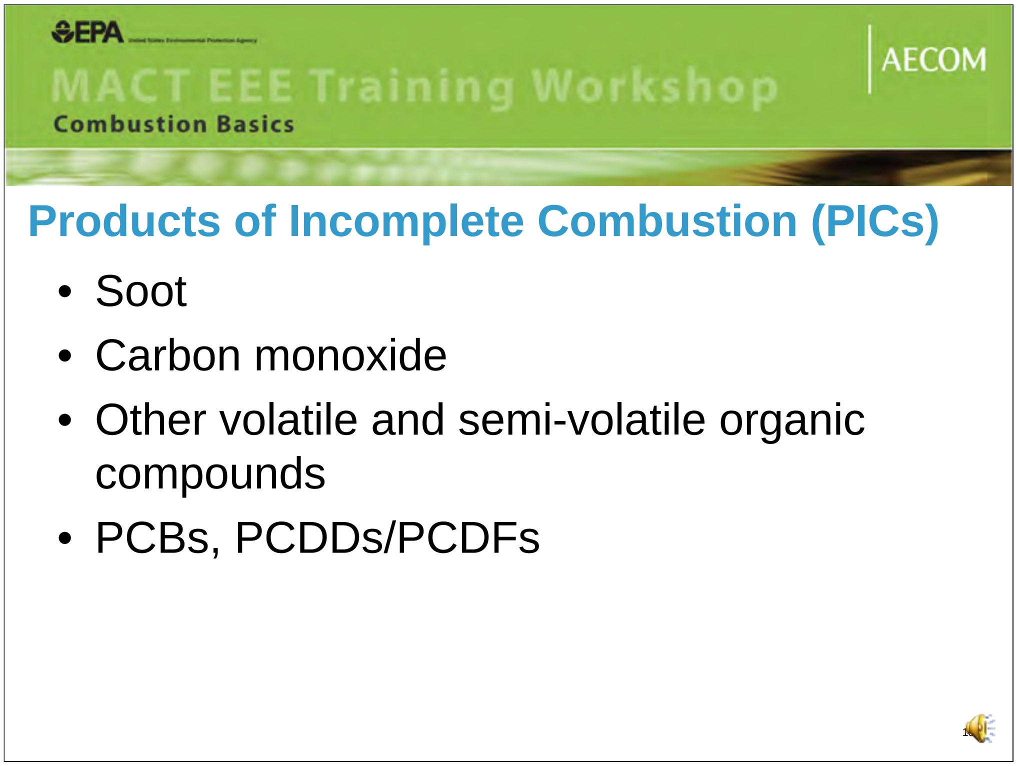
Heating Value and Flammability Limits

Fuel	Btu/lb	LEL - %	UEL - %
Coal	**14,700**	**--**	**--**
Natural gas (Btu/ft^3)	**1,100**	**5**	**15**
Gasoline	**20,100**	**1.4**	**7.6**
Diesel	**19,700**	**0.6**	**7.5**
Methylene chloride	**3,100**	**12**	**19**
PCBs	**4,500 – 6,600**	**N/A**	**N/A**
Perchloroethylene	**2,100**	**N/A**	**N/A**
Monochlorobenzene	**11,900**	**1.3**	**7.1**
Toluene	**18,300**	**1.2**	**7.0**

New slide

There are several different parameters that are used to evaluate how well various materials will burn. Heating value or heat of combustion, generally represented by the “higher heating value” is the amount of energy in Btu’s or calories released by a given mass of material, taking into account the heat of vaporization of any water present in the material. As can be seen, good fuels have high heating values. Flammability limits are also a measure of how well various materials will burn. The lower explosive limit (or LEL) and the Upper Explosive Limit (or UEL) represent the flammability range of a material as measured in air. Below the LEL, there is insufficient material present in air for the mixture to sustain combustion. Likewise, above the UEL, there is too much material present and combustion cannot be sustained either. If a material is present between the LEL and UEL in a mixture with air, and an ignition source is provided, it will burn.



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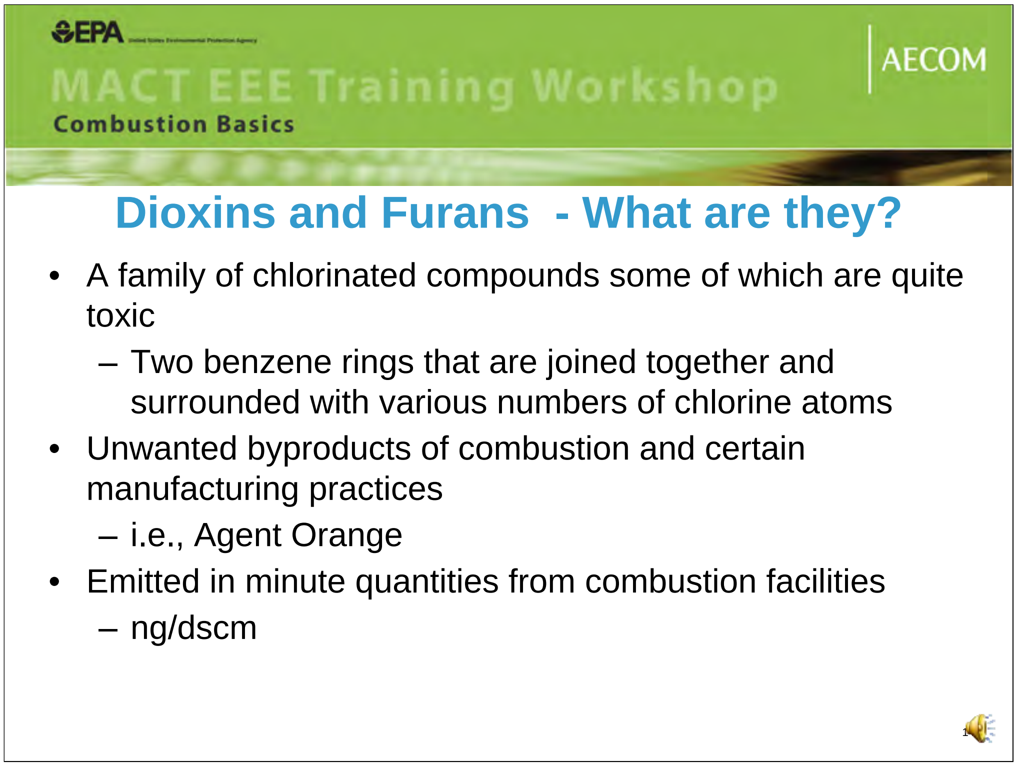
Products of Incomplete Combustion (PICs)

- Soot
- Carbon monoxide
- Other volatile and semi-volatile organic compounds
- PCBs, PCDDs/PCDFs

While waste combustion systems are designed to be very efficient, there are compounds called “Products of Incomplete Combustion” or PICs that can form in many systems. Soot, which is essentially unburnt carbon, carbon monoxide (CO) and other volatile (VOICs) and semi-volatile organic (SVOCs) compounds can be formed either during combustion or downstream if the combustion chamber in the air pollution control system. These PICs can also include compounds such as polychlorinated biphenyls (or PCBs) and polychlorinated dibenzo dioxins and/or dibenzo furans (PCDDs/PCDFs). While soot can be present in up to % levels in combustion emissions and CO can be present in ppm levels, VOCs and SVOCs are usually only present in microgram/cubic meter range or less and PCBs and PCDDs/PCDFs are generally present in low nanogram/cubic meter range



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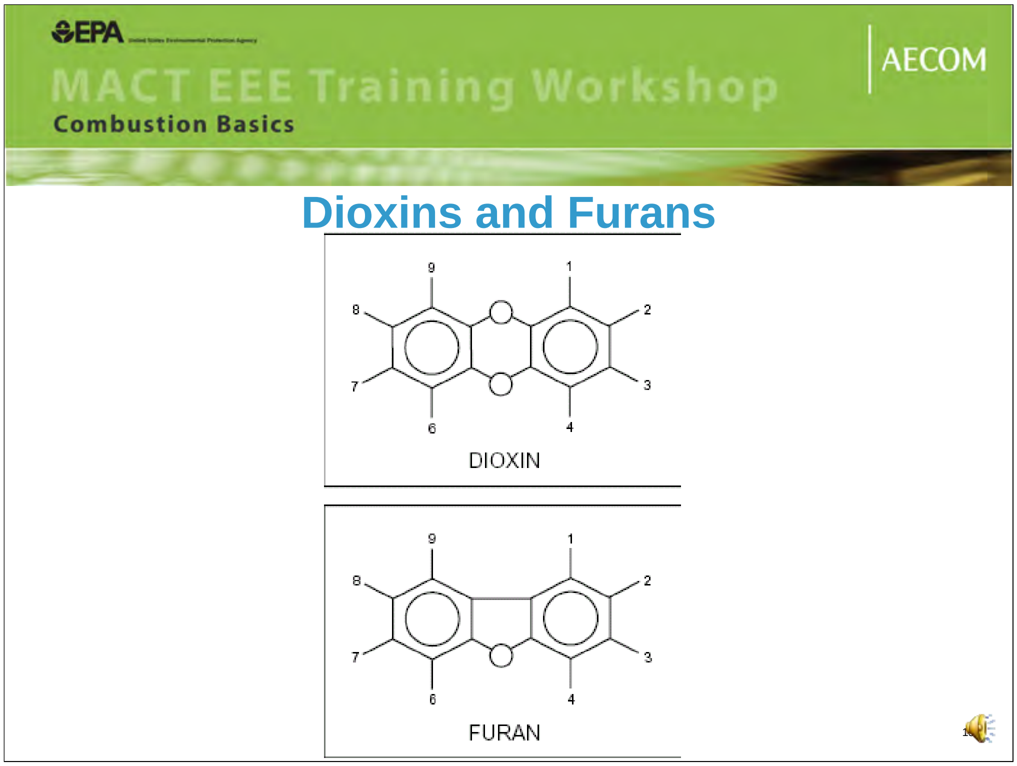
Dioxins and Furans - What are they?

- A family of chlorinated compounds some of which are quite toxic
  - Two benzene rings that are joined together and surrounded with various numbers of chlorine atoms
- Unwanted byproducts of combustion and certain manufacturing practices
  - i.e., Agent Orange
- Emitted in minute quantities from combustion facilities
  - ng/dscm

One PIC – PCDDs/PCDFs include a family of over 100 related but individual compounds that are of particular environmental concern as they have been shown be toxic. PCDDs and PCDFs are comprised of two benzene rings that are joined together and have various numbers of chlorine molecules attached around the rings. They were originally discovered to be unwanted byproducts that occurred in certain chlorinated compound products, such as Agent Orange, but also can be present in combustion emissions.



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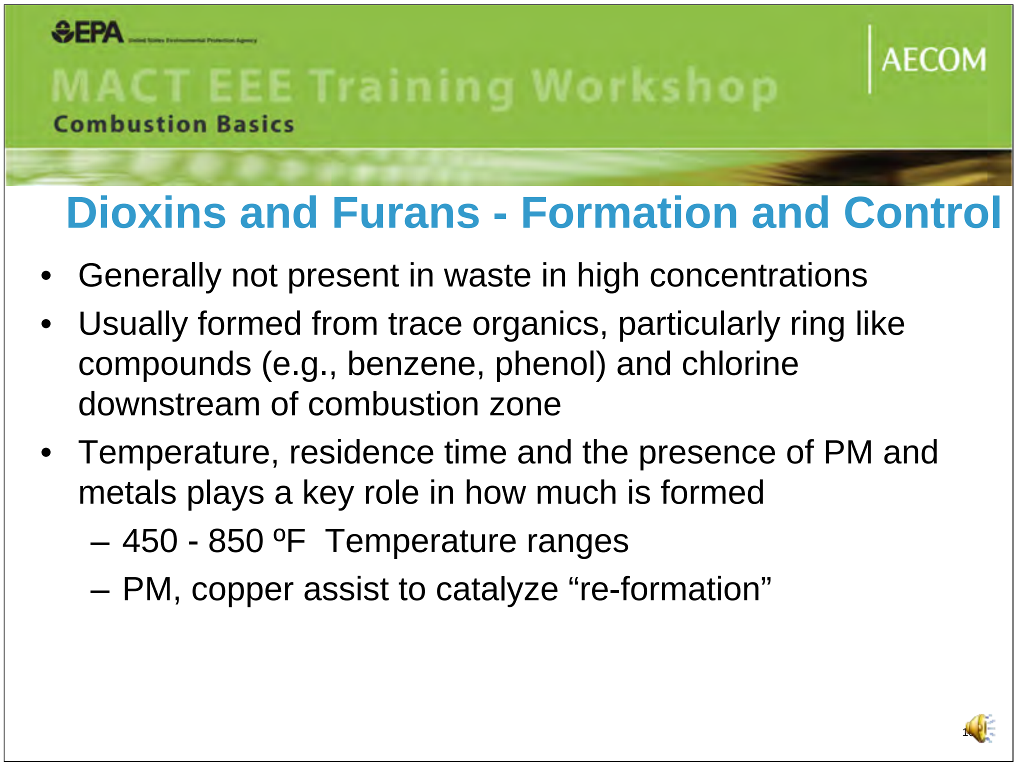
Dioxins and Furans

The two families are compounds are shown above and will have chlorines attached at the numbered locations.



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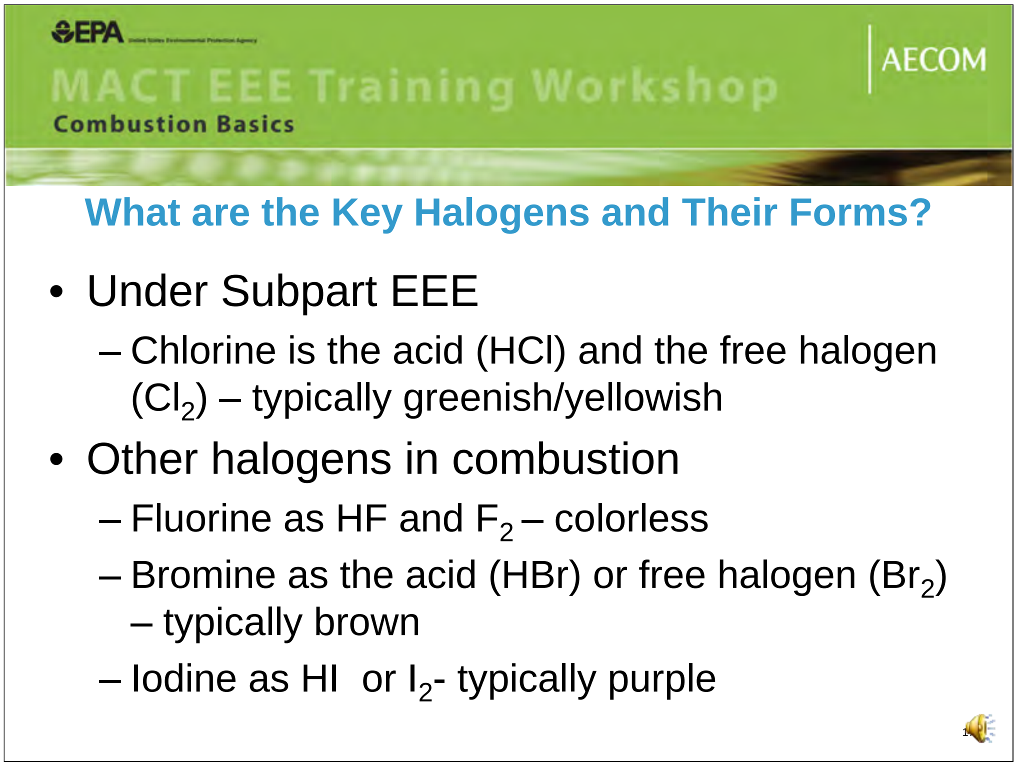
Dioxins and Furans - Formation and Control

- Generally not present in waste in high concentrations
- Usually formed from trace organics, particularly ring like compounds (e.g., benzene, phenol) and chlorine downstream of combustion zone
- Temperature, residence time and the presence of PM and metals plays a key role in how much is formed
  - 450 - 850 ºF Temperature ranges
  - PM, copper assist to catalyze “re-formation”

PCDDs and PCDFs are generally not present in waste streams in high concentrations, but rather they tend to form downstream of the combustion zone from other VOC PICs such as benzene and phenol where physical conditions are amenable, such as time and temperature and other materials such as particulate and certain metals are present to catalyze the reformation chemistry.



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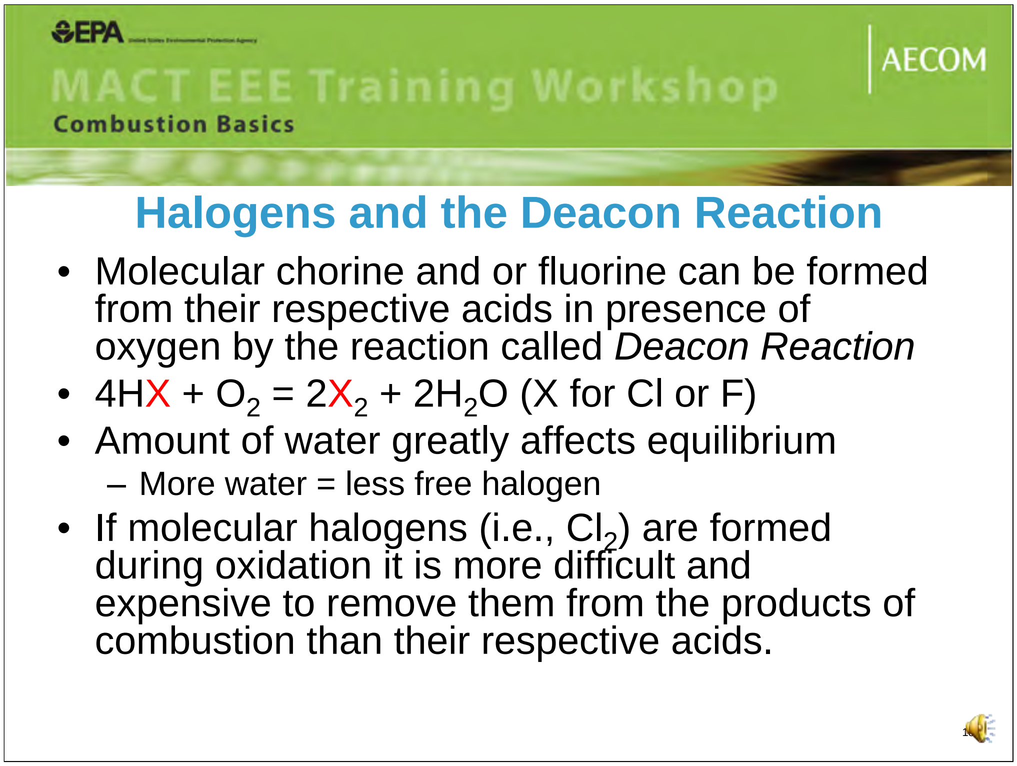
What are the Key Halogens and Their Forms?

- Under Subpart EEE
  - – Chlorine is the acid (HCl) and the free halogen (Cl_2) – typically greenish/yellowish
- Other halogens in combustion
  - – Fluorine as HF and F_2 – colorless
  - – Bromine as the acid (HBr) or free halogen (Br_2) – typically brown
  - – Iodine as HI or I_2- typically purple

There are also other inorganic compounds that are present in waste streams that are combusted and may need to be scrubbed and removed in the air pollution control system to limit their emissions. One group of such compounds are the halogens. Most common is chlorine and that generally has specific limits under Subpart EEE, but fluorine, bromine and iodine are other halogens that may be present in certain combusted waste streams.



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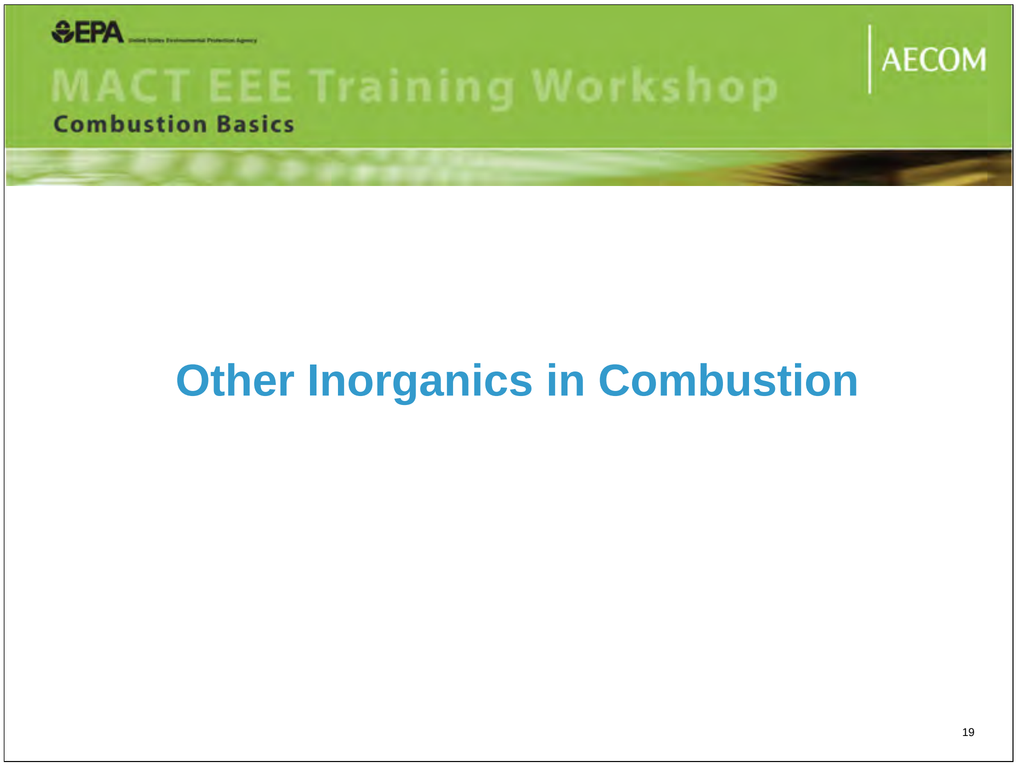
Halogens and the Deacon Reaction

- Molecular chorine and or fluorine can be formed from their respective acids in presence of oxygen by the reaction called *Deacon Reaction*
- $4HX + O_2 = 2X_2 + 2H_2O$ (X for Cl or F)
- Amount of water greatly affects equilibrium
  - More water = less free halogen
- If molecular halogens (i.e., Cl_2) are formed during oxidation it is more difficult and expensive to remove them from the products of combustion than their respective acids.

Halogens are generally present in emissions as either the acid form (i.e., HCl) or as the free halogen (Cl_2). The presence of water in the combustion system can affect the amount of the acid or the free halogen form through what is known as the "Deacon Reaction". The significance of this is that the acid form of the halogen is generally more soluble in water and therefore easier to scrub out and thus, facility operators often pay attention to how much water is present to minimize free halogen formation.



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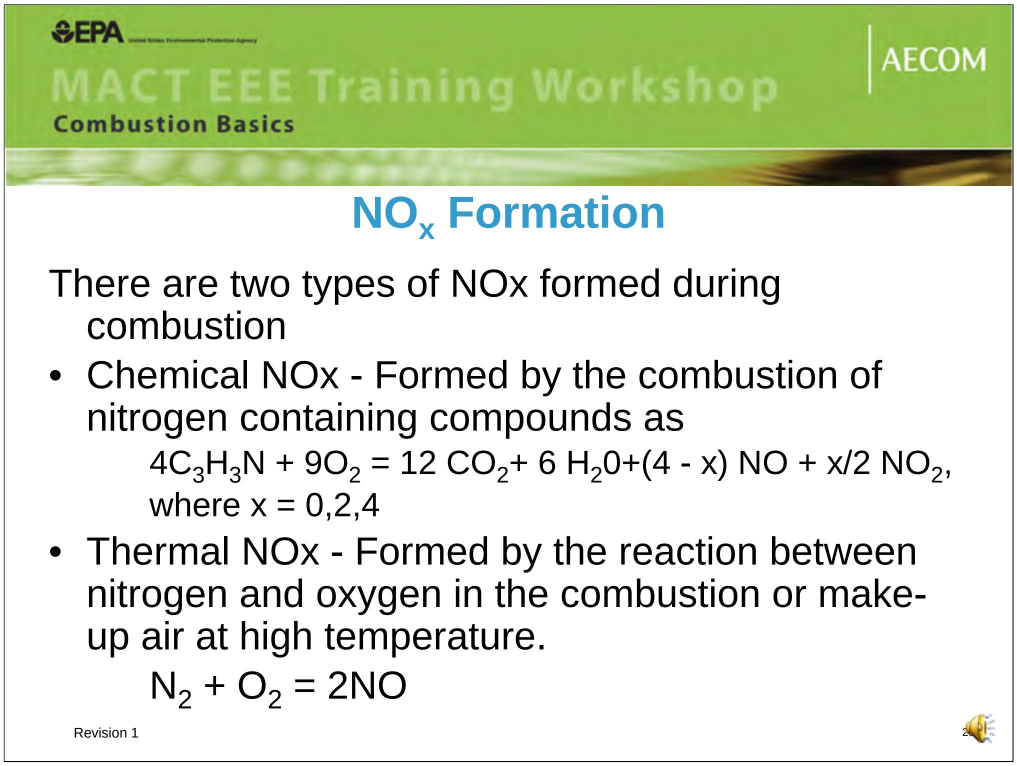
Other Inorganics in Combustion



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NO_x Formation

There are two types of NOx formed during combustion

- Chemical NOx - Formed by the combustion of nitrogen containing compounds as

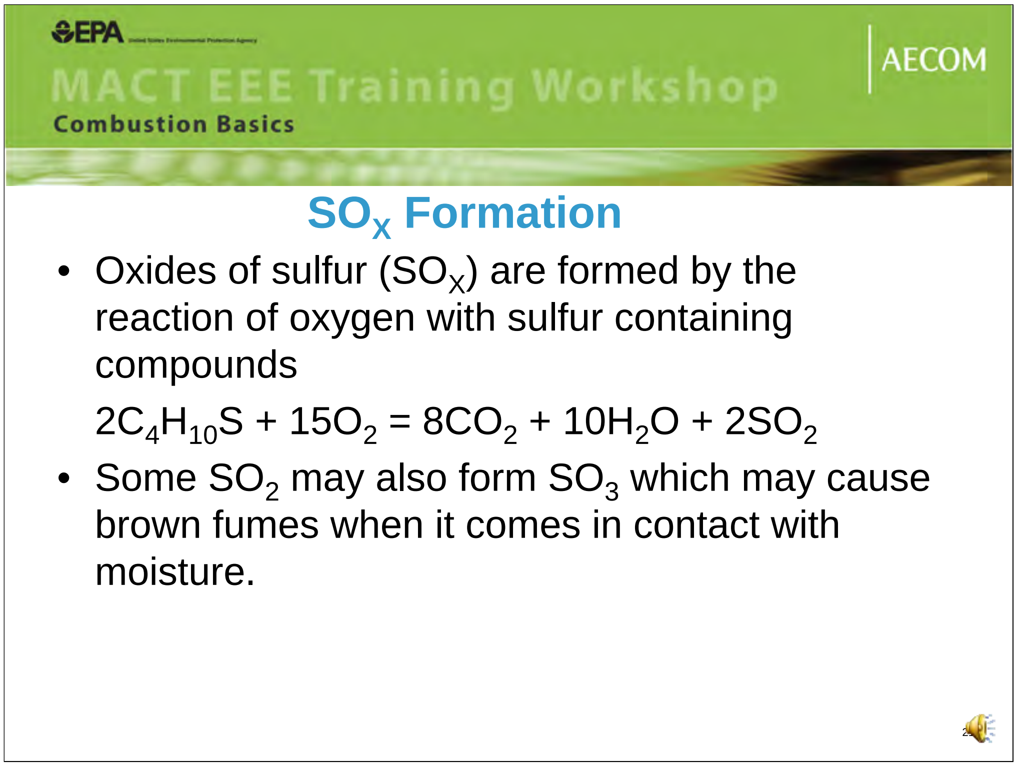
  $4C_3H_3N + 9O_2 = 12\ CO_2 + 6\ H_20 + (4 - x)\ NO + x/2\ NO_2$,
  where x = 0,2,4

- Thermal NOx - Formed by the reaction between nitrogen and oxygen in the combustion or make-up air at high temperature.

  $N_2 + O_2 = 2NO$

Revision 1

Nitrogen compounds can form during combustion and these are generally categorized as either chemical or thermal NOx compounds. Thermal NOx is termed is that which is formed from nitrogen contained in the fuel or waste, while thermal NOx is formed nitrogen present in atmospheric used in combustion or make-up air systems.



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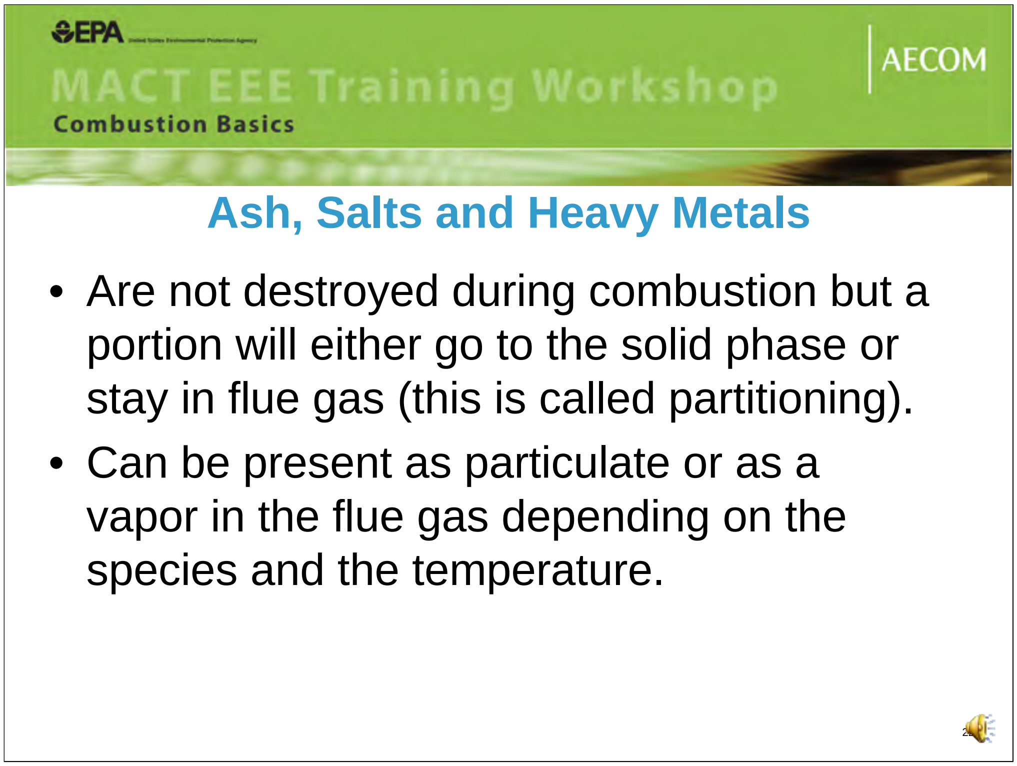
SO_X Formation

- Oxides of sulfur (SO_X) are formed by the reaction of oxygen with sulfur containing compounds

  $2C_4H_{10}S + 15O_2 = 8CO_2 + 10H_2O + 2SO_2$
- Some SO_2 may also form SO_3 which may cause brown fumes when it comes in contact with moisture.

Similarly, sulfur oxides can form from the combustion of sulfur containing compounds in either the fuel or waste.



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Ash, Salts and Heavy Metals

- Are not destroyed during combustion but a portion will either go to the solid phase or stay in flue gas (this is called partitioning).
- Can be present as particulate or as a vapor in the flue gas depending on the species and the temperature.

Ash, salts and/or heavy metals present in waste streams or fuels are not destroyed during combustion but rather partition out to both any solid or liquid streams that exit combustion, such as bottom ash or scrubber blowdown or are emitted. Flue gas temperatures downstream of the combustion chamber will affect the physical state these exist as and they can be present as either particulate or as a vapor depending on the specific species and what the properties of those compounds are.