**Industrial Waste Management - II**

**Hazardous Waste Management**

- Hazardous solid waste treatment
- Thermal desorption
- Pyrolysis gasification
- Combustion
  - Incineration
- Industrial furnaces/ Cement kiln
- Molten glass / Plasma
- Waste to Energy
- Solidification-Stabilization
- Land Disposal

**Transitioning from Land Disposal To Treatment**

Government policy is essential for managing hazardous waste (HW)

- Alone HW will be handled in cheapest way
- No natural market forces for HW
- Government provides incentive for management
- Without regulation dumping will prevail
- Even the best designed landfills leak
- Cleanup is always more costly than proper management

**Industrial and Agricultural Solid Waste are Application Specific**

**Industrial Solid Waste**
- Petroleum waste
- Packaging waste
- Metal waste
- Hazardous waste

**Agricultural Solid Waste**
- Cellulosic-plant waste
- Manure - high nitrogen
- Food waste
Hazardous Waste Treatment and Disposal is Multifaceted

- Incinerators
- Land Fill-Solidification
- Recycling
- Water Treatment
- Extraction-Separation
- Underground Injection

Thermal Hazardous Waste Treatment Technologies

- Thermal Desorption
- Incineration
  - Dedicated (no power or product)
  - High temperature oxidation
  - Air pollution control (APC)
- Industrial Furnaces
  - Boilers – produces steam for power
  - Kilns – produces product and reduces fuel
  - Furnace – provides process heat
  - APC part of industrial process
- Pyrolysis Gasification
- Specialized Methods
  - Molten glass
  - Plasma arc

Thermal Desorption Very Flexible for Petroleum Waste Solids

- Desorption ~150-400°C
- Vapor
  - Trapped
- Solid
  - Condensed
  - Burned
- Rotary kiln or dryer
- Mobile or stationary
- Co-current or countercurrent
- Feed and product handling equipment
- Desorbed vapor
  - Trapped onto activated carbon
  - Condensed
  - Burned in afterburner or oxidizer
- Remaining solids cleaned

Thermal Desorption Pros and Cons

- Advantages
  - Low capital operating cost compared to other thermal technologies.
  - Low regulatory hurdles for permitting.
  - Can be applied in the field.
  - Allows for both destruction and recovery of organic contaminants.
- Disadvantages
  - Material larger than 2 inches needs to be crushed or removed.
  - Plastic soils tend to stick to equipment and agglomerate.
  - Pretreatment- shredding- blending with friable soils/ gypsum.
  - Highly contaminated soils will require multiple cycles.
  - Not amenable to semi-volatile or non-volatile, chlorinated hazardous constituents. (Example: PCBs, pesticides)
  - Fugitive emissions may present exposure risk to workers and environment.
Syngas Formation from Waste Involves Pyrolysis and Gasification

**Pyrolysis**
- Gases
- Liquids
- Char

Pyrolysis

- $\approx 500^\circ C$

Gasification

- $>1000^\circ C$

Syngas

**Gas % Purox (FB-MSW)**

<table>
<thead>
<tr>
<th>Gas</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>23.4</td>
</tr>
<tr>
<td>CO</td>
<td>39.1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>24.4</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Higher Heating Value ~ 19 MJ/kg


**Advantages**
- Lower temperature process compared to incineration, increasing refractory life and reducing costs.
- High feed rates, up to 5 tons/hour.
- Downstream APC equipment needs reduced since metals and PM tend to be retained in char.
- Degree of pyrolytic reaction can be controlled to yield syngas or products for recovery. Condensable vapors with economic value can be recovered. Non-condensable vapors can be used for energy.

**Disadvantages**
- High capital cost.
- Char still retains hazardous constituents and metals, requiring subsequent treatment and controlled disposal.
- Fume incineration needed to destroy Products of Incomplete Combustion (PICs), and other hazardous organic constituents.

**Reactions Occurring in the Gasifier**

\[
\begin{align*}
C + O_2 & \rightarrow CO_2 & \text{Combustion} & \Delta H^o \\
C + CO_2 & \rightarrow 2 CO & \text{Boudouard} & + \\
C + H_2O & \rightarrow CO + H_2 & \text{Carbon-steam} & + \\
CO + H_2O & \rightarrow CO_2 + H_2 & \text{Water-gas Shift} & - \\
C + 2H_2 & \rightarrow CH_4 & \text{Hydrogenation} & - \\
\end{align*}
\]

Gasification Pros and Cons

**Advantages**
- Beneficial use of waste to produce syngas, energy or usable products.
- High temperature process provides for destruction of hazardous constituents.

**Disadvantages**
- Extremely high capital cost $30 – 50M. Large scale operation required to make economics work.
- Must be integrated into a chemical or petroleum refining plant. Not a free-standing technology like incineration.
- Off-gas treatment still required, including downstream fume incineration.
- Residues are generated which, like pyrolysis, may contain hazardous metals that require subsequent managed treatment and disposal.

Pyrolysis Pros and Cons

**Advantages**
- Lower temperature process compared to incineration, increasing refractory life and reducing costs.
- High feed rates, up to 5 tons/hour.
- Downstream APC equipment needs reduced since metals and PM tend to be retained in char.
- Degree of pyrolytic reaction can be controlled to yield syngas or products for recovery. Condensable vapors with economic value can be recovered. Non-condensable vapors can be used for energy.

**Disadvantages**
- High capital cost.
- Char still retains hazardous constituents and metals, requiring subsequent treatment and controlled disposal.
- Fume incineration needed to destroy Products of Incomplete Combustion (PICs), and other hazardous organic constituents.
**Synthesis Gas Reactions**

*Combustion*
\[ \text{H}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

*Fischer Tropsch Synthesis*
\[(2n+1) \text{H}_2 + n \text{CO} \rightarrow \text{C}_n\text{H}(2n+2) + n \text{H}_2\text{O} \]

*Direct Methanol Synthesis*
\[ 2 \text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{OH} \]
\[ 3 \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \]
\[ \text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \]

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**Incineration is the Controlled Combustion of Waste**

Requires 3 “T’s”:
- **Time**: 2 seconds minimum
- **Temperatures**: 1000°C-1200°C
- **Turbulence**: Mixing during burn

Rotary Kiln or Fixed Grate
Secondary Combustion Chamber (afterburner)
Rapid cooling of ash to prevent PCDD and PCDF

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**Incineration is not the Same as Open Burning**

<table>
<thead>
<tr>
<th></th>
<th>Open Burn (µg/kg)</th>
<th>Municipal Waste Incinerator (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDDs</td>
<td>38</td>
<td>0.002</td>
</tr>
<tr>
<td>PCDFs</td>
<td>6</td>
<td>0.002</td>
</tr>
<tr>
<td>Chlorobenzenes</td>
<td>424150</td>
<td>1.2</td>
</tr>
<tr>
<td>PAHs</td>
<td>66035</td>
<td>17</td>
</tr>
<tr>
<td>VOCs</td>
<td>4277500</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Source: EPA/600/SR-97/134 March 1998

Waste to Energy =WTE

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**Rotary Kiln Incineration Specifically for Waste Disposal**

Source: http://www.pollutionissues.com/
Advantages:
- Can be applied to a wide variety of hazardous wastes.
- Provides destruction and volume reduction of the waste.

Disadvantages
- Not amenable to waste containing high concentration of heavy metals (> 1%).
- Waste feed mechanisms often complex
- High capital cost due to extensive Air Pollution Control (APC) system and sophisticated controls required to meet emission standards.
- Ash must be treated for leachable metals prior to land disposal.

Fluidized Bed Combustion

Pros and Cons

- Fluidized sand recirculated
- Up to 140 million Btu/hr (2460 MJ/min)
- Transportable fluidized bed systems
  - Halogenated waste (> 99.99% DRE at 1300 F)
  - Lower capital and operating than rotary kiln
  - Refractory life longer than rotary kiln

Advantages:
- Well suited to refinery waste, pumpable sludges and halogenated waste.
- Excellent contact between gas and solid high DRE.
- Stable control temperature, residence time
- Vary air velocity at the bottom of bed.
- Better than other thermal methods for heat recovery.

Disadvantages
- Cannot feed containerized waste directly or non-pumpable solids.
- Pre-processing (homogenization) of waste is required so that all solids are less than ½ inch.
- Waste must have heat content > 3500 BTU/lb.
- Bed agglomeration and failure of the fluidized system can occur in the presence of > 2% sodium or other alkali salts.

Incineration: Ash Treatment Standards

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>&lt;10 mg/kg</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>&lt;6 mg/kg</td>
</tr>
<tr>
<td>Cresols</td>
<td>&lt;5.6 mg/kg</td>
</tr>
<tr>
<td>Dioxins</td>
<td>&lt;0.0025 mg/kg</td>
</tr>
<tr>
<td>Pesticides</td>
<td>&lt;0.087 mg/kg</td>
</tr>
<tr>
<td>Leachable Metals</td>
<td>&lt;0.1-0.75 mg/L *</td>
</tr>
</tbody>
</table>

* Toxic Characteristic Leaching Procedure (TCLP)
Incineration: Air Emission Standards

- Particulate Matter < 34 mg/dscm
- Dioxin < 0.2 ng TEQ/dscm
- Pb & Cd < 240 ug/dscm
- As, Be & Cr < 87 ug/dscm
- HCl < 77 ppm
- Hydrocarbons < 10 ppm
- CO < 100 ppm
- DRE > 99.99%
- PCB and Dioxin waste incinerators must demonstrate a minimum of 99.9999% Destruction Removal Efficiency (DRE)
- Products of Incomplete Combustion (PICs) must be evaluated in a Human Health and Ecological Risk Assessment.

Air Pollution Control Equipment Essential for Hazardous Waste Incineration

- Fabric filters – fly ash – 99% efficient
- Electrostatic precipitators – fly ash - 99% efficient
- Absorbers – Liquid/gas-70-99% acid gases
- Adsorbers Activated carbon/gas -95-98% organics
- Wet Scrubbers-
  - Flue gas desulfurization – 80-90% SO₂
  - Selective Catalytic Reduction -80-90% NOₓ

Emissions also affected by feed and combustion conditions

Industrial Furnaces: Kilns and Boilers (APC part of industrial process)

- Kilns
  - Cement
  - Lightweight Aggregate
  - Lime
- Furnaces
  - Halogen Acid
  - Sulfuric Acid
- Industrial boilers.
- Waste types and amount limited
  - Protect product and process quality
  - Cement and lightweight aggregate kilns only liquid waste
  - Minimum heat content > 5000 BTU/lb
  - Thermal substitution rate is limited to 50%.

Typical Dry Process Cement Kiln

- Alternative Fuels and Raw Materials
- Precalciner
- Gases: > 900 °C,
- Materials 700 °C
- Retention time > 3 s
- Kiln
- Gases 2000 °C
- Material 1450°C > 15 min.
- Retention time > 10 s
- Clinker
- Immobilization of metals
**Boiler, Furnace and Cement Kiln Pros and Cons**

- **Advantages:**
  - Displace other fuels improve economics
  - Waste producers may pay for service
  - Can be applied to a waste oils and other solid waste (tires).
  - APC equipment in place
  - Residence times in kilns are high
  - Steady state is the rule

- **Disadvantages:**
  - Industrial process and products may not permit
  - Waste feed mechanisms add complexity
  - Admixture rate may be low
  - Waste destruction may upset industrial process

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**Molten Glass Processes**

- **Advantages:**
  - Used for the destruction and/or immobilization of hazardous wastes, particularly mixtures of hazardous waste and radioactive wastes.
  - Destroy combustible hazardous constituents and simultaneously encapsulate residuals (ash and metals) into a stable glass form.
  - Molten Glass process is known as “joule heating”
  - Electrodes in the molten glass apply a voltage passing current through alkaline ionic components in the glass. Electric resistance of the glass creates heat which is distributed evenly by convective currents in the fluid.
  - Two main applications:
    - Joule-heating glass melters
    - In situ vitrification.

- **Disadvantages:**
  - High capital and operating costs, because of electricity.
  - Costs for radioactive waste have been as high as $3.80/kg.
**Plasma Arc System-Batch Process**

- High voltage arc - two electrodes
- Inert gas under pressure injected sealed container of waste material
- Plasma temperature 6,000 °C
- Furnace chamber 1,800 °C
- Plasma destroys HW
- Operates at a slightly negative pressure
- Gas removal system to APC and/or production of syngas.

**Plasma Arc Pros and Cons**

- **Advantages**
  - Plasma systems can transfer heat much faster than conventional flames.
  - Very effective for organic halogens, (PCBs and Dioxins). Eight “9’s” DRE has been observed.
- **Disadvantages**
  - Extremely high temperatures, material durability of equipment
  - High capital costs.
  - Complex process control and highly trained professionals are required.
  - Electricity is required as an energy source. This is more expensive than most thermal processes.

**Solidification and Stabilization Processes**

- Solidification methods physically encapsulate hazardous waste into a solid material matrix of high structural integrity.
- Stabilization techniques chemically treat hazardous waste by converting them into a less soluble, mobile or toxic form.
- Principally used for metal-bearing wastes.
- Limited applicability to organic wastes.
- 2 Main types of processes: cement and pozzolanic.

**Waste Treatment Options – Energy Considerations**

- Energy Produced
- Complexity
- Gasifier - Inclinator - Heat - Electric
- Anaerobic or Aerobic Bioreactor
- Landfill – CH₄ to electricity
- Landfill – No Gas Recovery

**Advantages**: low cost, low technology, suitable for many types of waste
**Disadvantages**: increases volume, may leak
Comparison of 95 U.S. WTE plants with EPA Standard - (2001 Success story!)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Average Emission</th>
<th>EPA standard</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxin/Furan (TEQ basis)</td>
<td>0.05</td>
<td>0.26</td>
<td>ng/dscm</td>
</tr>
<tr>
<td>Particulate Matter</td>
<td>4</td>
<td>24</td>
<td>mg/dscm</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>6</td>
<td>30</td>
<td>ppmv</td>
</tr>
<tr>
<td>Nitrogen Oxides</td>
<td>170</td>
<td>180</td>
<td>ppmv</td>
</tr>
<tr>
<td>Hydrogen Chloride</td>
<td>10</td>
<td>25</td>
<td>ppmv</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.01</td>
<td>0.08</td>
<td>mg/dscm</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.001</td>
<td>0.020</td>
<td>mg/dscm</td>
</tr>
<tr>
<td>Lead</td>
<td>0.02</td>
<td>0.20</td>
<td>mg/dscm</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>3.5</td>
<td>100</td>
<td>ppmv</td>
</tr>
</tbody>
</table>

TEQ: Toxic Equivalents are used to report the toxicity-weighted masses of mixtures of dioxins (ng/dscm or mg/dscm): nanograms or milligrams per dry standard cubic meter (ppmv) parts per million by volume - Waste to Energy = WTE


Example: Anaerobic Biosolid Digestion Reduces Solids - Makes Methane

Anaerobic sludge digestors produce methane (65% CH₄ - 35% CO₂)

On-site electricity is produced with the methane 50% of plant power (2.2MW)

Source: Albuquerque NM Waste Water Treatment Plant

Example: Coconut Charcoal (WTE) Reduces Air Pollution Makes Electricity

Recogen-Badalgama Sri Lanka-8 MW

http://www.eurocarb.com/

Example: Palm Oil Mill Effluent and Waste to Energy Plant

Palm Oil Mill Effluent (POME) *

Fresh Fruit Bunches → Crude Palm Oil

Empty Fruit Bunches → Fiber + Shell

Anaerobic lagoon/reactor

methane → electricity, compost, electricity, charcoal

Sludge → compost
**Land Disposal Units (LDUs)** Consist of Landfills, Surface Impoundments and Underground Units

- Landfill
- Surface impoundment
- Waste pile
- Land treatment unit
- Injection well
- Salt dome formation
- Salt bed formation
- Underground mine
- Underground cave

**Landfill Design and Construction**

- **Landfill Liners**
  - Clay
  - Flexible membrane
  - Liner/waste compatibility
- **Landfill Cap**
- **Leachate**
  - Collection-Removal-Recirculation
  - Primary leachate
  - Leak detection
  - Surface water collection
  - Gas collection and removal

- **Leachate**
  - No free or bulk liquids
  - Mixed with sorbent
  - Small ampoules
  - Container is item–battery
  - Container is lab pack

**Landfill with Flexible Membrane Liner Plus Compacted Soil Double Liner**

- Groundwater and leachate monitoring important

**Deep Well Injection is an Important Technology**

- 550 Class I wells in the United States (22% for HW)
- 43% of all HW in United States !!!
Movie for Underground Injection Wells - USEPA