Chemical
SAFETY AND SECURITY TRAINING

Industrial Waste Management - II

SAND No. 2011-0486P
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Sandia National Laboratories

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

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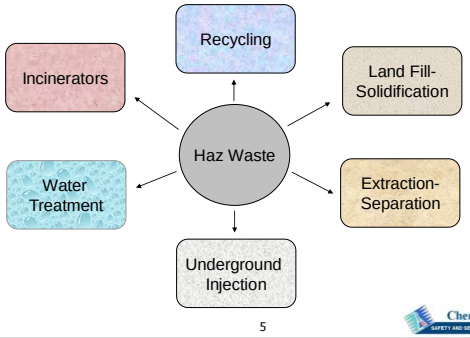
Industrial and Agricultural Solid Waste are Application Specific

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



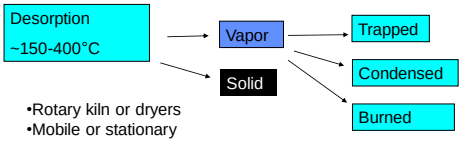
Thermal Hazardous Waste Treatment Technologies

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



- •Rotary kiln or dryers
- •Mobile or stationary
- •Co-current or countercurrent
- •Feed and product handling equipment

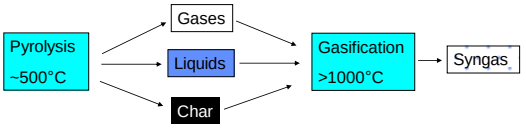
•Desorbed vapor
- •Trapped onto activated carbon
- •Condensed
- •Burned in afterburner or oxidizer

•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



Gas %	Purox (FB-MSW)
H_2	23.4
CO	39.1
CO_2	24.4
CH_4	5.5

Higher Heating Value ~ 19 MJ/kg

Waste Management 24 (2004) 633–639

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 synfuel 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.

Gasification Pros and Cons

- **Advantages**
  - Beneficial use of waste to produce syngas, energy or useable 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.

Reactions Occurring in the Gasifier

		ΔH
$C + O_2 \rightarrow CO_2$	Combustion	-
$C + CO_2 \rightarrow 2\,CO$	Boudouard	+
$C + H_2O \rightarrow CO + H_2$	Carbon-steam	+
$CO + H_2O \rightarrow CO_2 + H_2$	Water-gas Shift	-
$C + 2H_2 \rightarrow CH_4$	Hydrogenation	-

Synthesis Gas Reactions

Combustion

$H_2 + CO \rightarrow CO_2 + H_2O$

Fischer Tropsch Synthesis

$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$

Direct Methanol Synthesis

$2\ H_2 + CO \rightarrow CH_3OH$

$3\ H_2 + CO_2 \rightarrow CH_3OH + H_2O$

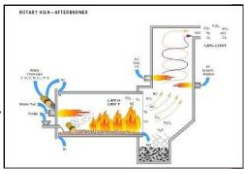
$H_2 + CO_2 \rightarrow CO + H_2O$

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



Source :http://www.pollutionissues.com/

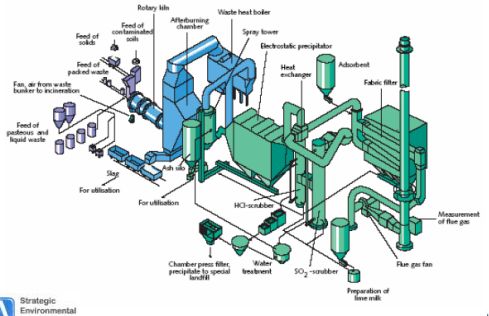
Incineration is not the Same as Open Burning

	Open Burn (µg/kg)	Municipal Waste Incinerator (µg/kg)
PCDDs	38	0.002
PCDFs	6	0.002
Chlorobenzenes	424150	1.2
PAHs	66035	17
VOCs	4277500	1.2

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

Waste to Energy =WTE

Rotary Kiln Incineration Specifically for Waste Disposal

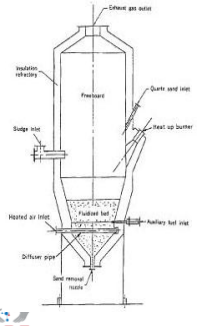


Strategic Environmental Analysis, L.C.

Incineration Pros and Cons

- **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



- Fluidized sand recirculated
- 1,000 units operated world wide
- 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

Fluidized Bed Combustion Pros and Cons

- **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

(US EPA regulates 200 constituents)

Pollutant	Standard
Benzene	<10 mg/kg
Trichloroethylene	<6 mg/kg
Cresols	<5.6 mg/kg
Dioxins	<0.0025 mg/kg
Pesticides	<0.087mg/kg
Leachable Metals	<0.1-0.75 mg/L*

* 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% SO_2
Selective Catalytic Reduction -80-90% NO_x

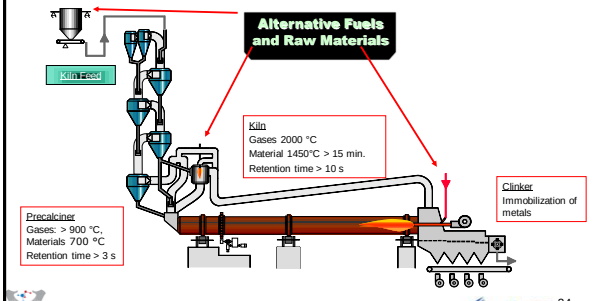
Emissions also affected by feed and combustion conditions

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



Boiler, Furnace and Cement Kiln Pros and Cons

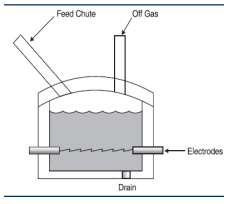
- **Advantages:**
  - Displace other fuels improve economics
  - Waste producers may pay for service
  - Can be applied to a waster oils and other solid waste (tires).
  - APC equipment in place
  - Residence times in kilns are high
  - Steady state is the rule
- **Disadvantages**
  - Industrial process and products may not permit
  - Waste feed mechanisms add complexity
  - Admixture rate may be low
  - Waste destruction may upset industrial process

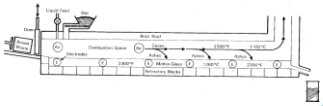
Molten Glass Processes

- 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.

Glass Processes can use Joule Heating

- Electrical current produces melt
- Wastes fed to pool of molten glass (1000°C to 1200°C)
- Glass is contained within the melting cavity, airtight steel lined with insulating refractory.
- Initial heat-up of the melt cavity usesnatural gas burners or electric heaters
- The molten glass/encapsulated waste residual is drained through an overflow



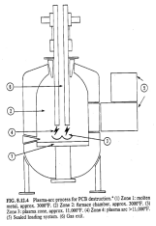


Molten Glass Processes Pros And Cons

- **Advantages**
  - Permanent treatment and encapsulation of waste in geologically stable form
  - Final material is delistable as "non-hazardous" under EPA regulations.
  - High degree of volume reduction; up to factors of 100.
  - No CO is generated.
  - DRE's of 99.9999% demonstrated for PCBs.
- **Disadvantages**
  - High capital and operating costs, because of electricity.
  - Costs for radioactive waste have been as high as $3.90/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

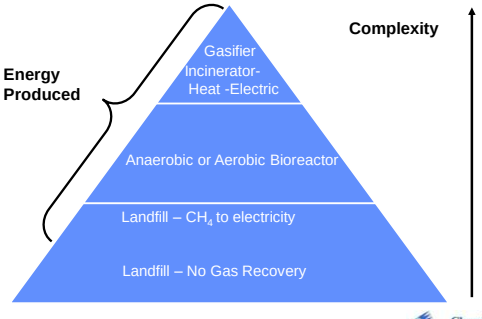
- **Advantages**
  - **Plasma systems can transfer heat much faster than conventional flames.**
  - **Very effective for organic halogens, (PCBs and Dioxins). Eight "9's" DRE has been observed.**
- **Disadvantages**
  - **Extremely high temperatures, material durability of equipment**
  - **High capital 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.**

- Advantages: low cost, low technology, suitable for many types of waste
- Disadvantages: increases volume, may leak

Waste Treatment Options –Energy Considerations



Comparison of 95 U.S. WTE plants with EPA Standard - (2001Success story!)

Pollutant	Average Emission	EPA standard	Unit
Dioxin/Furan (TEQ basis)	0.05	0.26	ng/dscm
Particulate Matter	4	24	mg/dscm
Sulfur Dioxide	6	30	ppmv
Nitrogen Oxides	170	180	ppmv
Hydrogen Chloride	10	25	ppmv
Mercury	0.01	0.08	mg/dscm
Cadmium	0.001	0.020	mg/dscm
Lead	0.02	0.20	mg/dscm
Carbon Monoxide	33	100	ppmv

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

Source: http://www.energyanswers.com/pdf/awma_final.pdf

Example: Anaerobic Biosolid Digestion Reduces Solids - Makes Methane

Anaerobic sludge digestors produce methane

(65% CH_4 - 35% CO_2)

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

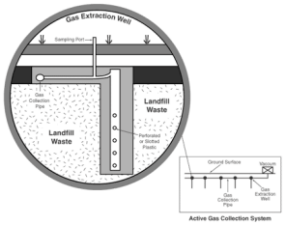
Recogen-Badalgama Sri Lanka-8 MW

http://www.eurocarb.com/

Example: Palm Oil Mill Effluent and Waste to Energy Plant

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**



http://www.epa.gov/tmop/basic-info/lfg.html#01

Landfill Design and Construction

Landfill Liners
- Clay
- Flexible membrane
- Liner/waste compatibility

Landfill Cap

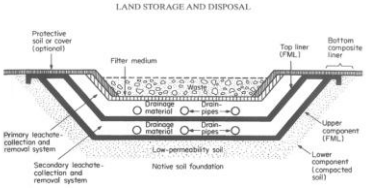
Leachate
- Collection-Removal-Recirculation
- Primary leachate
- Leak detection

Surface water collection

Gas collection and removal

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

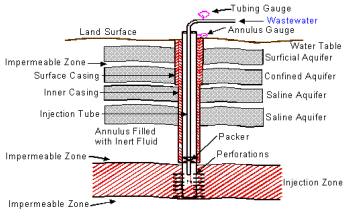
Landfill with Flexible Membrane Liner Plus Compacted Soil Double Liner



http://www.epa.gov/wastes/hazard/tsd/td/disposal.htm

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 !!!

http://www.epa.gov/safewater/uic/index.html

Play Movie for Underground Injection Wells - USEPA