



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.



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



2



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



3



Industrial and Agricultural Solid Waste are Application Specific

Industrial Solid Waste

- Petroleum waste
- Packaging waste
- Metal waste
- Hazardous waste



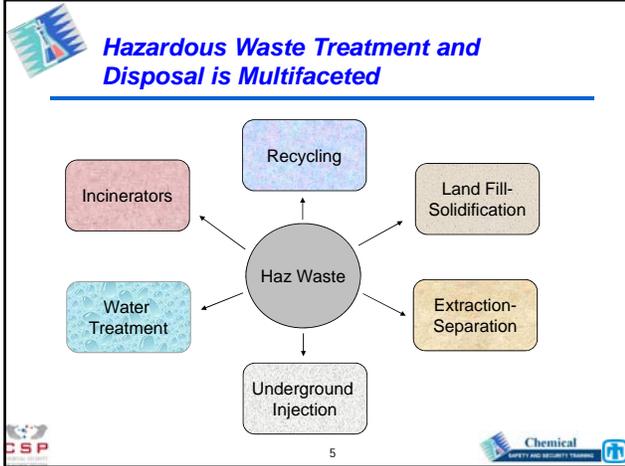
Agricultural Solid Waste

- Cellulosic-plant waste
- Manure - high nitrogen
- Food waste

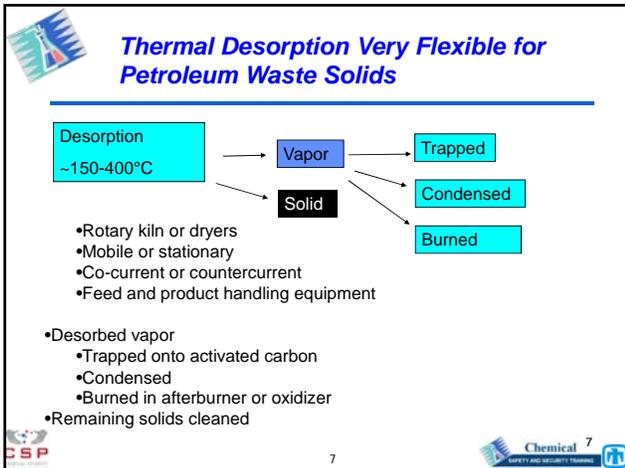


4

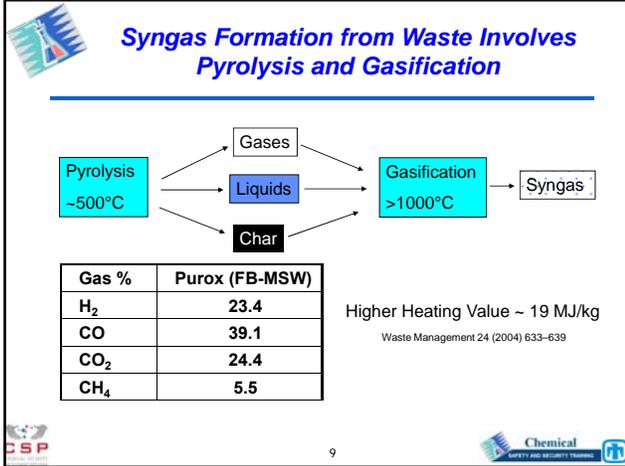




- ### Thermal Hazardous Waste Treatment Technologies
- Thermal Desorption**
- Incineration**
- Dedicated (no power or product)
 - High temperature oxidation
 - Air pollution control (APC)
- Industrial Furnaces**
- Boilers – produces steam for power
 - Kilns – produces product and reduces fuel
 - Furnace – provides process heat
 - APC part of industrial process
- Pyrolysis Gasification**
- Specialized Methods**
- Molten glass
 - Plasma arc
- 6
- Chemical SAFETY AND SECURITY TRAINING



- ### 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.
- 8
- Chemical SAFETY AND SECURITY TRAINING



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.

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

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



Incineration Pros and Cons

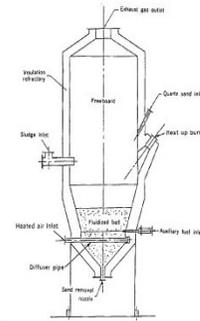
- **Advantages:**
 - Can be applied to a wide variety of hazardous wastes.
 - Provides destruction and volume reduction of the waste.
- **Disadvantages**
 - Not amenable to waste containing high concentration of heavy metals (> 1%).
 - Waste feed mechanisms often complex
 - High capital cost due to extensive Air Pollution Control (APC) system and sophisticated controls required to meet emission standards.
 - Ash must be treated for leachable metals prior to land disposal.



17



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



18



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 1/2 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.



19



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)



20





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% NO_x

Emissions also affected by feed and combustion conditions

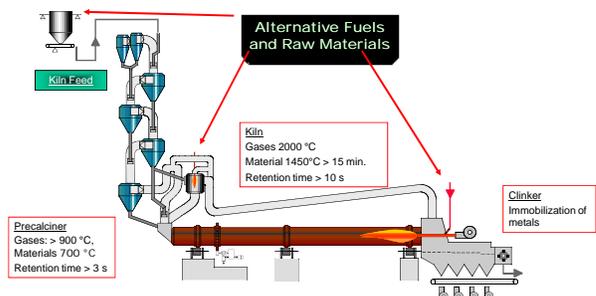


Industrial Furnaces: Kilns and Boilers (APC part of industrial process)

- 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 wider 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



25



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.

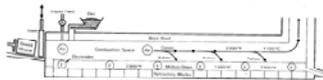
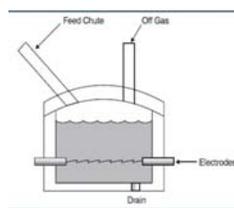


26



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 uses natural gas burners or electric heaters
- The molten glass/encapsulated waste residual is drained through an overflow



27



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.



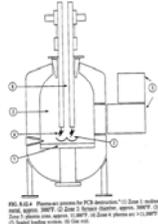
28





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.



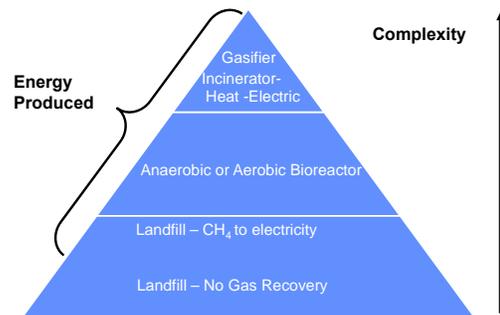
Solidification and Stabilization Processes

- 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 - (2001 Success 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



33



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)

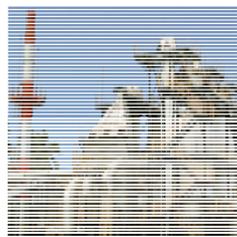
Source: Albuquerque NM Waste Water Treatment Plant



34



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



Recogen-Badalgama Sri Lanka-8 MW

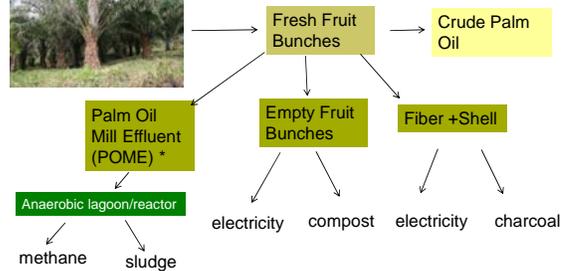
<http://www.eurocarb.com/>



35



Example: Palm Oil Mill Effluent and Waste to Energy Plant



36



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/mop/basic-info/fg.html#01>

CSP Chemical SAFETY AND SECURITY TRAINING

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

CSP Chemical SAFETY AND SECURITY TRAINING

Landfill with Flexible Membrane Liner Plus Compacted Soil Double Liner

LAND STORAGE AND DISPOSAL

<http://www.epa.gov/wastes/hazard/tsd/ld/deposal.htm>

Groundwater and leachate monitoring important

CSP Chemical SAFETY AND SECURITY TRAINING

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>

CSP Chemical SAFETY AND SECURITY TRAINING



Movie for Underground Injection Wells - USEPA

