Pesticides POPs waste from Inventory to Elimination: Part 3 Environmental Disposal of (pesticides) POPs waste

Stockholm Convention Regional training workshop on PCBs and POPs wastes
Kingston 2-5 February 2009
John Vijgen
IHPA
Updated Technical Guidelines on ESM of POPs

Welcome to Module c of Guideline 1

Environmentally Sound disposal of POPs

This module will provide you with information on environmentally sound disposal of POPs waste. Information for this module was taken from the ‘Updated general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (POPs)’, p.27-46. You can find this guideline and others on POPs wastes at the following address:
http://www.basel.int/meetings/sbc/workdoc/techdocs.html

Please close this window to start this module.
SBC Training Manual:  
http://www.basel.int/meetings/sbc/workdoc/techdocs.html  
See under Training manuals
The graphic below shows the link between the available guidelines. Guideline I contains information that is relevant to all the other individual POPs wastes guidelines.

**Guideline I**
- Updated general technical guidelines for the ESM of POPs wastes
  - a. Basel and Stockholm Convention mandates on POPs wastes
  - b. Environmentally sound management of POPs wastes
  - c. Environmentally sound disposal of POPs wastes
  - d. POPs wastes: Remediation of contaminated sites, health and safety, emergency response and public participation

**Guideline II**
- Technical guidelines on PCBs
- Additional specific information

**Guideline III**
- Technical guidelines on DDT
- Additional specific information

**Guideline IV**
- Technical guidelines on unintentionally produced PCDDs, PCDFs, HCB and PCBs
- Additional specific information

**Guideline V**
- Technical guidelines on POPs pesticides
- Additional specific information
Treatment strategies

1. Dedicated Hazardous Waste treatment Plants

2. Local Treatment
   Modern Cement Kilns
   Small size alternative methods

3. Only in Exceptional cases:
   Specially designed Landfills
Combustion ------ Non-combustion

Destruction and irreversible transformation methods

There are many different destruction technologies, which can be grouped into two main categories - combustion and non-combustion methods.

The following operations are currently in commercial use:

<table>
<thead>
<tr>
<th>Combustion methods</th>
<th>Non-combustion methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste incineration</td>
<td>Alkali metal reduction</td>
</tr>
<tr>
<td>Cement kiln co-incineration</td>
<td>Base-catalysed decomposition (BCD)</td>
</tr>
<tr>
<td></td>
<td>Gas-phase chemical reduction (GPCR)</td>
</tr>
<tr>
<td></td>
<td>Plasma arc</td>
</tr>
</tbody>
</table>

SBC Training manual contains Fact Sheets of these technologies + Autoclave
Overview technologies mentioned in guidelines:

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Pre-treatment

Environmentally sound disposal of POPs wastes

There are two processes to complete ESM:

1. Pre-treatment
2. Destruction or irreversible transformation methods

Pre-treatment:

Normally, waste is treated before destruction can take place.
Treatment may include:

- Adsorption and absorption
- Dewatering
- Mechanical separation
- Mixing

- Oil-water separation
- pH adjustment
- Size reduction
- Solvent washing
- Thermal desorption
Lets go to Training Tool Guideline I: Module C  
Environmentally sound disposal of POPs waste

- Hazardous Waste incineration → Alwin Booij
- Cement kiln co-incineration
- Alkali Metal Reduction → Michael Müller
Cement kiln co-incineration

Cement kilns are designed to produce cement. However, due to the high temperature, which reaches 1,400°C- 1,500°C, these kilns are able to destroy POPs waste.

Cement kilns are particularly used for the destruction of PCBs as the destruction and removal efficiency is higher than in hazardous waste incinerators. These kilns can also be used for other POPs in liquid and solid form. The use of POPs as a fuel will also reduce fuel costs for the production of the cement.

Pre-treatment may include thermal desorption of solid waste and homogenization of solid and liquid wastes. The treatment of POPs waste has to be properly designed and operated in order to be relatively safe.

Cement kilns are large plants that require a lot of space compared to non-combustion techniques. Cement kilns are fixed installations.
The cement manufacturing process in a nutshell

**Raw materials**
- Quarry

**Raw meal preparation**

**Clinker burning**

**Cement grinding and dispatch**

**Raw meal**
- Ca: limestone
- Si: e.g. sand
- Fe: e.g. pyrite
- Al: e.g. clay

**Clinker**
- Calcination & burning at 1,450 °C
- Formation of clinker minerals
  - C2S, C3S
  - C3A, C4AF

**Cement**
- Grinding with gypsum (OPC)
- Blended cement with
  - slag, fly ash
  - filler...

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Holcim Group Support

Holcim co-processing experience

17.10.2007/LDS
Technical characteristics of the cement kiln

**Precalcer**
- Gases: $> 900 \degree C$
- Retention time: $> 3$ s
- Raw meal: $700 \degree C$
- (Non)-hazardous AFR: liquid, solid, coarse particles,

**Kiln main burner**
- Flame: $1800 - 2000 \degree C$
- Combustion gases: $>1100 \degree C$
- Retention time: $> 10$ s
- Material: $1450 \degree C > 15$ min.
- (Non)-hazardous AFR: liquid, fine solid particles, readily combustible

**Preheater cyclones**
- Act like a dry scrubber for acid gases and metals

**Clinker**: Thermal, macromolecular immobilization of metals

**Mineral wastes**:
- CaO, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$

Holcim Group Support
Holcim co-processing experience

17.10.2007/LDS
...but it is also an opportunity as the example from the European Union clearly shows

Alternative fuels by source classes and respective quantities 2002

<table>
<thead>
<tr>
<th>Source class</th>
<th>%</th>
<th>Quantity [t/a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste management</td>
<td>36.0</td>
<td>534'600</td>
</tr>
<tr>
<td>Agricultural</td>
<td>13.1</td>
<td>194'500</td>
</tr>
<tr>
<td>Thermal processes</td>
<td>19.5</td>
<td>289'600</td>
</tr>
<tr>
<td>Chemical</td>
<td>10.3</td>
<td>153'000</td>
</tr>
<tr>
<td>Petroleum</td>
<td>5.0</td>
<td>81'700</td>
</tr>
<tr>
<td>Metal</td>
<td>6.5</td>
<td>96'500</td>
</tr>
<tr>
<td>Wood</td>
<td>5.0</td>
<td>74'200</td>
</tr>
<tr>
<td>Tires</td>
<td>1.3</td>
<td>19'300</td>
</tr>
<tr>
<td>Pharmaceutical</td>
<td>1.3</td>
<td>19'300</td>
</tr>
<tr>
<td>Automotive</td>
<td>1.0</td>
<td>5'300</td>
</tr>
<tr>
<td>Electronics/photographic</td>
<td>0.2</td>
<td>3'000</td>
</tr>
<tr>
<td>Glass</td>
<td>0.1</td>
<td>1'500</td>
</tr>
<tr>
<td>Mechanical</td>
<td>0.1</td>
<td>1'500</td>
</tr>
<tr>
<td>Plastics, paints, miscellaneous</td>
<td>0.1</td>
<td>1'500</td>
</tr>
<tr>
<td>TOTAL Europe</td>
<td>100.0</td>
<td>1'475'500</td>
</tr>
</tbody>
</table>

A large variety of wastes, hazardous or not, can be co-processed
Strengths and weaknesses of cement kiln co-incineration for POPs waste treatment

- Can treat hazardous wastes as fuel to a maximum of 40% of heat requirement
- Cement kilns with high throughput may treat significant quantities of waste PCBs demonstrated, should be applicable to other POPs
- Can treat liquid and solid wastes
- Pre-treatment by thermal desorption or blending of waste
- Fixed plants - no mobility costs
- Much experience and success with reliable expertise and logistics
- DREs greater 99.99998%
- Comparable cost-effectiveness

- Remainder may require disposal at specially engineered landfill
- Modifications to rotary kiln may be required for waste treatment
- Chlorine levels in waste can be critical; if blended down sufficiently, highly chlorinated hazardous waste can be treated
- Huge space requirements
**BCD Technology description**

Hydrogen Donor

PCB (POP) (Hydrocarbon oil) Base

\[ \text{ClyCl}_x + R' - H + \text{NaOH} \]

Carbon

\[ \text{Cly} \]

>320°C

\[ \rightarrow \]

Biphenyl

Salt

Steam

\[ \text{Cl}_y \]
Mexico PCB plant
Major Breakthrough
Spolana Neratovice, Czech Republic

- Big project, large amounts
- Excellent period for technical optimization
- Extremely difficult
- Ideal project to eliminate all “problematic” issues
- Sufficient budget
- Ideal to combine with thermal desorption
- This is often lacking for alternative technologies
**Strenghts and Weaknesses → Training Tool**

**Strengths and weaknesses of BCD for POPs waste treatment**

- Simple process
- Proven technology
- Re-use 90-95% of donor oil
- Treatment of POPs with high concentrations possible
- DEs greater than 99.99% achievable
- Capacity of 1000 t/y
- Modular, transportable and fixed plants
- Relatively low energy consumption
- Air emissions expected to be relatively minor
- Potential for PCDDs/PCDFs formation relatively low

- Pre-treatment needed with solvent extraction for transformers and capacitors
- PCDDs eventually formed from chlorophenols under alkaline conditions at 150°C
- If remaining sludges cannot be treated for use as a neutralizing agent, then disposal in a landfill is necessary
GCPR: Gase Phase Chemical Reduction

Front-End Waste Feed
- Liquid Waste Injection
- Gaseous Waste Injection
- Thermal Reduction Batch Processor (TRBP)
- Treated Solids

Waste Destruction
- Mixer
- Gas-Phase Chemical Reduction (GPCR™) Reactor
- Hydrogen and Steam Preheater
- Recirculation Gas
- Water
- Treated Solids

Output Recovery
- Gas Scrubbing System
- Fuel for Front-end Systems
- Auxiliary Burner
- Product Gas Compression and Storage
Principal chemistry

Reduction of a PCB Molecule

\[ \text{Cl} - \text{C} - \text{Cl} + 5 \text{H}_2 \rightarrow 4 \text{HCl} + 2 \text{CH}_4 \]

Reduction of a Chloro-Alkane

\[ \text{Cl} - \text{C} - \text{H} + 4 \text{H}_2 \rightarrow 3 \text{HCl} + 2 \text{CH}_4 \]

Steam Reforming of Benzene

\[ \text{C} + 6 \text{H}_2 \text{O} \rightarrow 6 \text{CO} + 9 \text{H}_2 \]

Steam Reforming of Methane

\[ \text{CH}_4 + \text{H}_2 \text{O} \rightarrow \text{CO} + 3 \text{H}_2 \]

Steam Reforming of Carbon Monoxide

\[ \text{CO} + \text{H}_2 \text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]
Drummed HCB waste placed inside of the SBV in Kwinana, Australia
SBV used in Kwinana, Western Australia
Kwinana plant Australia
Strenghts and Weaknesses → Training Tool

Strengths and weaknesses of GPCR for POPs waste treatment

- Handles all kind of wastes
- Proven technology
- High destruction rates (99.9999%)  
- Minimum operator exposure
- Mobile and fixed units
- Possibility of PCDD/PCDF formation is considered limited

- Not cost-effective for wastes with low POP concentrations
- Costly to operate
- Pre-treatment required
- High power use
- Complex and labour intensive
- Need for hydrogen which requires a need for high quality risk management
- Residuals require off-site disposal
Plasma Arc (Plascon)

DESTRUCTION OF TYPICAL PCB WASTE

**HEXACHLORO-BIPHENYL**

**PLASMA SPECIES**

12 C atoms
12 O atoms
4 H atoms
6 Cl atoms

**FLIGHT TUBE SPECIES**

12 CO
4 HCl + Cl₂

**DISCHARGE PRODUCTS**

12 CO₂
6 NaCl
5 H₂O
0.5 O₂

Pyrolysis

6 O₂

Thermal Oxidation

Quench

6 NaOH
ARGON STORAGE TANK
OXYGEN STORAGE TANK
PCB FEED TANK
POWER SUPPLY
DATA ACQUISITION & PROCESS CONTROL
PROCESS GAS TO FLARE
PACKED COLUMN
PLASMA COOLANT TANK
50% NaOH TANK

IN FLIGHT PLASMA OVERVIEW
Close up of torch
PLASCON- ODS Unit
Strengths and weaknesses of PLASCON for POPs waste treatment

- Proven technology
- Handles all wastes
- No pre-treatment for gas and liquid wastes
- Easy set-up and handling
- Few operators required
- Limited space required
- POPs with high concentrations can be destroyed
- High destruction rates (99.9999 - 99.999999%)
- Fixed and mobile units available
- Low amount of residues
- Simple gas treatment

- Small capacity
- Argon use required
- High electrical power usage
- Generally costly to operate
- Metal-like compounds may cause problems for residue disposal
Only when both irreversible transformation and destruction are not the environmentally preferable option
How much obsolete Pesticides have been destroyed?
Not yet updated

- Obsolete pesticides: last 7-10 years
- *Incinerators in Europe* 25-30 000 t
- *Alternative technologies* 5 000 t
- PCB’s:
  - *Incinerators in Europe* 100 -115 000 t
  - *Alternative technologies* 15 000 t
- *Chlorphenols Alt tech* 7000 t
Status on destruction

- More than 75-90% of all pesticides are destroyed by the dedicated incinerators mainly in Europe.

- Major interest by international Cement industry to cut energy costs by co-incineration of waste and also POPs and pesticides in the future.

- Cement industry will start competition with hazardous waste incinerators, as they can save money on production costs for cement by co-incineration of high energy waste.

- Alternative technologies: smaller part of market and work in specialised niches.