Destruction and Decontamination Technologies for PCBs and Other POPs Wastes

A Training Manual for Hazardous Waste Project Managers

Part III. Technology Selection Process
Foreword

This Training Manual has been prepared by the University of Auckland, New Zealand in the context of the convening of the First Continental Conference for Africa on the Environmentally Sound Management of Unwanted Stocks of Hazardous Wastes and their Prevention, Rabat, Morocco, 8-12 January 2001.

It has been designed to assist those governments or organisations, not only in Africa, charged with the task of managing the destruction or decontamination of POPs (Persistent Organic Pollutants) with procedures that assist with the planning and selection of appropriate technologies that suit the particular circumstances whilst complying with the need for environmentally sound management principles and the principles of sustainability. In that context special consideration should be given to the local national frameworks and the responsibilities of the relevant competent authority.

New ideas and technologies are emerging rapidly and good practices are still evolving. The Training Manual however will remain useful in providing a selection process allowing new technologies to be evaluated under the provisions of the Training Manual and enabling organisations to continue to adopt new technologies as they become available. There are four parts to this Training Manual. Part Four is a detailed Field Application Training Manual to the handling and environmentally sound management of POPs as wastes covering obsolete pesticides and PCB's in particular.

The Training Manual should be considered in conjunction with other technical guidelines adopted by the Conference of the Parties to the Basel Convention and governing the environmentally sound management of hazardous wastes, in particular the Technical Guidelines on Wastes.

Comprising or Containing PCB's, PCTs, and PBB's (Y10), Technical Guidelines for Incineration on Land,(D10), Technical Guidelines for Specially Engineered Landfill (D5), and Technical Guidelines on Wastes collected from Households (Y46). The document should be considered in conjunction with other important guidelines such as the FAO Pesticide series.

The writer refers in particular to the Draft Technical Guidelines on the environmentally sound management of POPs wastes which, at the time of printing of this document, are being negotiated under the Basel Convention. Furthermore, this Training Manual aimed at providing practical training for waste managers should not be interpreted as preempting any of the principles, guidance and recommendations that will form part of the Technical Guidelines on the ESM of POPs wastes mentioned hereabove.

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How to use this Training Manual

This Training Manual is designed as a desk top manual for planners, project managers and government department staff. Its style aims to provide for ease of reference and absorption of complex ideas and areas of uncertainty. The Training Manual has been designed as a complete technical Training Manual for the management of POPs as waste in an Environmentally Sound Manner. This Training Manual not only covers the basic principles of hazardous waste such as POPs but seeks to provide a step by step Training Manual as to how such wastes are to be managed, packaged, stored, transported, decontaminated and disposed of. The step by step strategy culminates in a set of Work Procedure Instructions that will allow a party to establish and manage a POPs waste project. At the end of Part IV there is a sample set of Tender and Contract documents that a party can use to create a contract for the management and handling of a POPs project. This technical Training Manual is based on the integrated matrix system of waste management and no part of the project can be initiated without the preceding parts being carried out. The reader must understand that all parts of this Training Manual have been consolidated to form a management programme.

The Training Manual is designed to be used in several complementary ways:

- In creating a project strategy for disposal or decontamination
- In establishing the appropriate technology to be used
- In establishing a set of rules and methods to actually perform a destruction of decontamination project.
- In providing the principles for site establishment and the basis for an operational manual.

The Training Manual can help with

Planning
- understanding background and principles
- correct inventory collation
- inventory analysis

Writing project Plans
- produce an overall plan for disposal or decontamination

Technology Decision making
- appraisal of appropriate technology
- selection of technology for destruction or decontamination

Writing tender documents
- produce tender documents for destruction or decontamination

Hazardous waste project Implementation
- produce implementation plans

Project manual
- produce comprehensive destruction or decontamination manual
Structure of the Training Manual

I BASIC PRINCIPLES AND BACKGROUND

This section covers the background to the POP's problem and the actions of international organisations to deal with the toxic waste problems.

II POPs PROJECT STRATEGIES

The formulation of strategies for destruction and decontamination depends on the inventory analysis. When the information is available then the strategy selection process commences.

III TECHNOLOGY SELECTION PROCESS

When the destruction and decontamination strategy is in place then the specific technology decisions can be made and the appropriate technology selected. Several destruction and decontamination technologies are presented in this section.

IV IMPLEMENTATION PROCESS

Tendering and project management documentation and plans. This section provides design guidance for site appraisals, packaging of hazardous wastes, storage, transportation as well as guidance for the destruction and decontamination processes.

Scope of the Training Manual

• The Training Manual can be used to prepare plans and strategies for the project management of hazardous waste projects involving intractable chemicals such as PCBs and other POP's.

• The scope is such that any organisation can use it to prepare simple plans for a small scale waste problem involving less than 5 tonnes of material or for a large scale operation involving say 5000 tonnes of material.

• In the final Part of the Training Manual there are planning guides so that large projects that demand a high standard of quality assurance are available.
PART III TECHNOLOGY SELECTION PROCESS

Step 6 Technology Selection
POPs, PCBs, Unwanted and Obsolete Pesticides

After the rationalisation strategy (Step 5) is complete and the basic areas of destruction and decontamination are known then the technology selection can commence. When the amount and nature of the contaminated material to be decontaminated on shore is known then the work can begin to look at what technologies are available and then select the appropriate technology from an environmental and economic point of view. There are many decontamination technologies to choose from either, on shore or off shore. The decision to go offshore is of course dependent on the rationalisation strategy (Step 5) and this decision is based on the best environmentally sound management approach which best meets the amount and nature of the POPs involved.

For destruction of POPs there are also many options and the selection must be made on similar grounds to the decontamination requirements.

Following the rationalisation process the technology selection is applied. The summary section of the rationalisation part will determine which of the various technologies are appropriate and will be most efficient to use. There are decisions to be made regarding appropriateness of the technology, environmentally sound management principles, economics and ability of the technology to be applied.

Several technologies are described here and there are many more that are not. We have attempted to provide descriptions of the most commonly used technologies but also include emerging technologies.

<table>
<thead>
<tr>
<th>Technology Types</th>
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<tr>
<td><strong>Established</strong></td>
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<tr>
<td>- Incineration (HTI)</td>
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<tr>
<td>- Thermal desorption</td>
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<tr>
<td>- Dechlorination</td>
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<td>- Solvent Extraction</td>
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<td><strong>Emerging</strong></td>
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<tr>
<td>- Solidification</td>
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<td>- Stabilisation</td>
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<td>- Bioremediation</td>
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<tr>
<td>- Vitrification</td>
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<td>- Ball Milling</td>
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Step 6 Technology selection

<table>
<thead>
<tr>
<th>Technology Type</th>
<th>DESTRUCTION</th>
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<tr>
<td></td>
<td>HIGH TEMPERATURE INCINERATION</td>
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Description of process

Hazardous waste incinerators have a main chamber (also called the primary chamber) for burning PCBs and POPs such as unwanted and obsolete pesticides and a secondary chamber. The secondary chamber is used for extending the residence time for maximum destruction of the material and its thermal oxidation into gases and unburnable solids. Well managed incineration can destroy POPs with a destruction and removal efficiency greater than 99.99 per cent. Removal efficiencies at this level (and higher levels of 99.99995 percent) require carefully controlled conditional and management of the incinerator to achieve these efficiencies. The effectiveness depends on the type of waste, turbulence, temperature and the residence time being maintained.

Downstream of the secondary chamber is the gas treatment system. This often comprises a quench system (to reduce dioxin formation) packed tower absorbers, precipitators and other reactive absorbers. The chemistry of incineration is the controlled high temperature oxidation of primarily organic compounds to produce carbon dioxide and water. Inorganic substances such as salts, acids and metallic compounds may also be produced from these wastes. Incineration processes for management of hazardous wastes are highly complex and require control of the kinetics of chemical reactions under non steady state conditions.

Sustainability factors

Inappropriate use of incinerators and poor management procedures can cause incineration to produce hazardous by-products that pose severe threats to the environment and to human and animal health. Sometimes the by-product can be more toxic than the original incinerated product. Of major concern are the formation during the incineration process of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (dioxins and furans). Dioxins and furans are

Benefits

Total destruction in proven system. Generally accepted technology by many nations. Long history of experience with management of HTI. Problem of hazardous chemicals with attendant liability problems is ended. No ongoing storage or contamination problems.

Disadvantages

Dangerous air emissions if incinerator operation or design inadequate. Transboundary movement across oceans. Overall high cost.

Key Points

- large capacity
- located in developed countries
- total destruction
- high DRE
- medium cost
extremely ecotoxic and persist in the environment for long periods of time. Dioxins and furans are formed during the cooling of the gasses after the secondary chamber. It is a formation reaction that is effected by the gas temperature, the occurrence of chlorine or other halogenated compounds and the presence of a catalyst. Modern HTI are now built with rapid quenching systems that quickly cool the gas to safe temperatures at which reformation does not occur and the use of wet scrubbers. In addition incinerators are now being fitted with dioxin removal facilities such as catalytic reduction. From a sustainability point of view there are many who say that high temperature incineration is unsustainable in that the pollution to the air is unacceptable due to the emissions of dioxins and furans as well as greenhouse gases such as CO2. In the past this view was correct. However modern incinerators that are designed for high temperature and are equipped with reformation prevention and dedicated dioxin removal facility have removed the problem of dangerous emissions. Dioxins and furans is one of the most controversial issues surrounding HTI. Dioxins are a family of organic chemical compounds known as polychlorinated dibenzodioxins (PCDDs) with 75 different forms that are characterised by the placement of 1-8 chlorine atoms and their aromatic rings. Tetrachlorodibenzo-p-dioxin (TCDD) is the most widely known and is found as an unwanted contaminant in pesticides. Furans (polychlorinated dibenzofurans or PCDFs) are a family of 135 organic compounds. Of the 210 compounds, seventeen are considered to be harmful to the environment. Dioxin is a natural by product of most combustion processes and is created by forest fires, woodstoves, automobiles, power plants and smelters. Although incineration has been often been cited as the major cause of dioxins, recent USEPA data suggests that hazardous waste incinerators produce less than 0.2% of the dioxin that is produced by wood stoves and indeed are not a major cause of dioxin in the environment.

Cost effectiveness factors

It is not possible to simply consider the cost of the incineration process in isolation when comparing with other technologies. Given that it is likely that an incineration process will be unavailable in a developed country the costs of packaging, containerisation and shipping of the waste must also be considered. The cost of the incineration (which is anywhere between US$200 to US$5000 per tonne) is often the lower component of the costs compared to the recovery, stabilisation, repackaging, separation and transport of the waste. As rule of thumb for the on shore activity and the transboundary movement of the waste, this cost will be up to five times the cost of incineration.

Selection of pesticides for destruction by incineration

Selection of incineration depends on the type of pesticide, the type of incinerator and its associated gas treatment system. Inorganic pesticides cannot be incinerated. Organic pesticides must be burned in HTI at over 1100 degrees centigrade for more than 2 seconds. Organic products with heavy metals content can only be incinerated in special facilities.
### PCBs and POPs HTI in Europe

<table>
<thead>
<tr>
<th>Country</th>
<th>Facility Operator</th>
<th>Contact</th>
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<tbody>
<tr>
<td>Denmark</td>
<td>Kommunekeimi a/s</td>
<td>Fax 45 65 30 27 63</td>
</tr>
<tr>
<td>Finland</td>
<td>Ekochem Oy Ab</td>
<td>Fax 35 8 19 715 300</td>
</tr>
<tr>
<td>France</td>
<td>Tredi</td>
<td>Fax 00 33 4 74 61 52 44</td>
</tr>
<tr>
<td>Germany</td>
<td>Entsorgungsbetrieb (GSB)</td>
<td>Fax 49 8453 91-151</td>
</tr>
<tr>
<td>Germany</td>
<td>Bayer</td>
<td>Fax 49 2133 515893</td>
</tr>
<tr>
<td>Netherlands</td>
<td>AVR-Chemie</td>
<td>Fax 31 181 242 502</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Akzo Nobel Chemicals</td>
<td>Fax 31 10 4389295</td>
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<tr>
<td>Norway</td>
<td>Norcem AS</td>
<td>Fax 47 35 57 1400</td>
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<tr>
<td>Sweden</td>
<td>SAKAB</td>
<td>Fax 46 19 577027</td>
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<tr>
<td>Switzerland</td>
<td>ETI</td>
<td>Tel 41 81 253 54 54</td>
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<tr>
<td>Switzerland</td>
<td>EMS-Dottikon AG</td>
<td>Fax 41 56 616 8120</td>
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<tr>
<td>Switzerland</td>
<td>Novartis Services AG</td>
<td>Fax 41 61 468 3348</td>
</tr>
<tr>
<td>UK</td>
<td>Cleanaway Ltd</td>
<td>Fax 44 151 357 3313</td>
</tr>
<tr>
<td>UK</td>
<td>Reychem International</td>
<td>Fax 44 1495 759 019</td>
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Not all of these operators will import PCB or POPs

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**Incinerator types**

**Rotary kiln incinerators**

Rotary kilns consist of an inclined rotating tube so that the waste moves horizontally as well as radially through the cylinder. Rotation speeds are low at 0.5 to 2 rpm in order to encourage turbulence. Waste is fed into the high end and ash is discharged at the low end. Combustion gases pass from the kiln into the secondary combustion chamber.

**Liquid injection incinerators**

Liquid injection incinerators are refractory lined cylinders, either horizontal or vertical and are equipped with a primary burner for waste and additional fuel to atomise the waste into the combustion chamber. Mainly used for highly mobile liquid waste.

**Static kiln incinerators**

Static kilns use a two stage combustion process on a horizontal grate in the primary chamber. In large units a ram constantly charges the unit and removes the ash at the same time.

**Fluidised bed incinerators**

Fluidised bed incinerators employ a bed of sand held in suspension by air in which the waste is injected.

**Cement kilns**

Wastes with a suitable calorific value is used as fuel and solid materials can be fed in part way down the kiln. For chlorinated wastes the residues are contained within the clinker.
Step 6 - Technology selection

<table>
<thead>
<tr>
<th>Technology Type</th>
<th>DECONTAMINATION</th>
<th>PCBS</th>
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<tbody>
<tr>
<td>AUTOCLAVE</td>
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Description of process

Autoclaving is a technology that has been around for many years now and is well proven. In general for PCBs, only the oil and transformer components such as ceramics, cardboard and wood are incinerated. The rest of the transformer is autoclaved and after decontamination the various metals such as copper, steel and aluminium are sent to the metals recycling industry. Autoclaving is a solvent decontamination process that extracts PCBs from contaminated material. The process can only be used for PCBs not for any of the other POPs. It is most often used in projects in conjunction with HTI. For capacitors the process involves shredding and placing all the material into the autoclaving chamber and by vacuum extraction with solvent remove the PCB. The resulting decontaminated capacitor materials can then be landfilled with the extracted oil and PCBs being sent for HTI incineration. Transformers on the other hand are drained, completely disassembled including the core and windings and the casing and all components are placed in the autoclave chamber and decontaminated.

Autoclaves may either be fixed or mobile. If sufficient quantities exist in the country then a mobile autoclave can be considered. Obviously the unit can be moved about according to location of PCB stock. It is also possible to build a fixed autoclave plant in the origin country. When looking at Autoclaving as a fixed plant in origin country consideration must be given to utility supplies such as energy, Compressed air, water, trade waste etc.

Sustainability factors

Autoclaving is a very good option when quantities of transformers and capacitors are large. Only the oil is sent overseas for destruction thus reducing the amount of material, weight, space and

Benefits

Excellent decontamination standard (to NDT) and recovery of metals often contributes to reducing the overall cost of autoclaving. In some cases the recycling revenue exceeds the autoclaving costs. If done onshore vast cost reduction to disposal costs for PCBs. Low emissions.

Disadvantages

Complex plant requiring expertise to run in origin country. Need large amounts of waste to justify location in origin country (in excess of 2000 tonnes). Large amounts of solvent used initially although solvent is recovered during the process.

Key Points

- Transformers and capacitors decontaminated
- Need large quantities for origin country installation
- Expertise of operators
- Mobility of plant
- Utilities availability
danger in the shipment. The copper, steel and aluminium is recycled in origin country. For PCBs and PCB contaminated equipment decontamination of the equipment is to be preferred over complete incineration. It is unsustainable to incinerate transformer coils, windings and tanks.

**Cost effectiveness factors**

Autoclaving is very cost effective given the correct circumstances. For large onshore origin country stocks of contaminated equipment then mobile or fixed autoclave plant can offer excellent opportunities for cost reduction compared to sending all the material offshore. The costs are comparable with incineration but has none of the attendant cost of packaging and transportation. Indeed the recycling of the materials will often produce a positive cost result.
Step 6 - Technology selection

<table>
<thead>
<tr>
<th>Technology Type</th>
<th>PCBs</th>
<th>POPs</th>
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<tr>
<td>DESTRUCTION</td>
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<tr>
<td>PLASMA ARC</td>
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</table>

Description of process

Plasma systems technology use a plasma arc device (often called a plasma torch) to create extremely high temperatures up to 10,000 degrees centigrade for destruction of highly toxic wastes such as PCBs and POPs. Plasma arc destruction has only recently moved from the pilot stage to full scale production stage for hazardous wastes but shows promise for liquid PCB and POPs. Emissions are gaseous and slag and are treated in a gas treatment system similar to that of HTI but on a much reduced scale. The most common form of plasma arc generation is via an electrical discharge via a gas. In passing through the gas, electrical energy is converted to thermal energy and is absorbed by gas molecules which are activated into ionised states. Plasma Arc is a pyrolysis process. It does not need energy to heat excess air like conventional incinerators. Because of this the downstream gas treatment systems are very small as there is no excess air. Plasma Arc systems use electrical energy as their energy source and as such is expensive. Plasma arc installations are easily set up in origin countries and occupy a small footprint.

Sustainability factor

For significant quantities of liquids in country of origin Plasma Arc technology represents a good option from a sustainability point of view. There is no shipping offshore for PCB oil or pesticide liquids. This means that coupled with autoclaving this technology can be very effective providing the quantities are adequate.

Benefits

- Very small footprint.
- Low emission simple gas treatment systems.
- Portable and mobile easily set up in origin country.

Disadvantages

- Generally restricted to liquids and for PCBs must be located with autoclave or solvent washing plant.
- Expensive in comparison to incineration.

Key Points

- Portability
- Small footprint
- Liquids
- Expensive
- Simple operation
- High DRE
- Best in origin
Cost Effectiveness factor

This type of technology is best used in the country of origin and should involve significant amounts of liquid PCBs or POPs. Cost is about $US1200 per tonne with set up costs of up to $US 1 million.
Step 6 - Technology Selection

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<thead>
<tr>
<th>Technology Type</th>
<th>DECONTAMINATION</th>
<th>PCBs</th>
<th>DECHLORINATION</th>
<th>POPs</th>
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</table>

**Description of process**

Chemical Dechlorination is based on reactions with either an organically bound alkali metal or an alkali metal oxide or hydroxide.

Dechlorination processes are well developed for the treatment of liquid PCBs and PCB contaminated oil. The chlorine content is converted to inorganic salts, which can be removed from the organic fraction by filtration. Reactions take place under inert atmosphere and can be used on an operating transformer in the field.

The Base Catalysed Dechlorination process (BCD) is a batch process operated in a series of stages and can treat wastes up to 10 % PCB. The key to the BCD process is the hydrogen donor with oxidation potential low enough to produce nucleophilic hydrogen in the presence of base NAOH at low temperatures. Capacitors cannot be treated with this process and solvent washing is required for the transformer components. The Base Catalysed Dechlorination (BCD) process was developed to treat halogenated organic compounds. The process was developed from work by the USEPA on earlier forms of dechlorination (in particular the "KPEG" process). This work was undertaken at the Cincinnati Risk Reduction Research Laboratory. The proponents claim BCD is suitable for treatment of wastes which contain up to 100000 mg/kg of halogenated aliphatic or aromatic organic compounds such as PCBs. In practice, the formation of salt within the treated mixture can limit the concentration of halogenated material able to be treated. Reduction of chlorinated organics to less than 2 mg/kg is achievable.

The BCD process can involve direct dehalogenation or decomposition of the waste material, or can be linked with a pre-treatment step such as thermal desorption which yields a relatively small

**BCD Process Performance**

The process has been shown to reduce contaminated soils from 10,000 ppm to below detectable with two hours.

For PCBs and contaminated transformer oils the BCD treatment process will typically reduce the contamination to below detection.

Direct treatment of capacitors by the BCD process is not possible and solvent extraction is required. Although some facilities shred the capacitors and treat the material with sodium hydroxide. The shredded material can then be treated with the BCD process.

**Benefits**

- PCB and POPs destroyed in one step.
- Simple process with very small emissions
- Proven technology
- Small facility foot print.

**Disadvantages**

Must use solvent extraction with transformers and capacitors or other pre-treatment
quantity of a condensed volatile phase for separate treatment by the BCD process. The BCD process involves the addition of an alkali or alkaline earth metal carbonate, bicarbonate or hydroxide to the contaminated medium containing one or more halogenated or non-halogenated organic contaminant compounds. Alkali is added to the contaminated medium in proportions ranging from 1 to about 20 percent by weight. The amount of alkali required is dependent on the concentration of the halogenated or non-halogenated organic contaminant contained in the medium.

A hydrogen donor compound is added to the mixture to provide hydrogen ions for reaction with the halogenated and non-halogenated contaminants, if these ions are not already present in the contaminated material. The hydrogen donor compound may comprise the high boiling point solvent in which the alkali or alkaline earth metal compound is added, or it may include fatty acids, aliphatic alcohols or hydrocarbons, amines or other similar compounds. In order to activate these compounds to produce hydrogen ions a source of carbon must be added, either in solution or in suspension. An inexpensive carbon source which is water soluble and suitable for use, is a carbohydrate such as sucrose.

The mixture is heated at a temperature and for a time sufficient to totally dehydrate the medium. This may be performed at atmospheric or at reduced or elevated pressure. The water which is included in the aqueous solution allows homogeneous distribution of the alkali throughout the mixture and acts as a wetting agent and penetrant. When the water is removed from the medium during the dehydration step, the alkali is concentrated to a reactive state.

After dehydration, the medium is further heated at a temperature between 200oC and 400oC for a time sufficient to effect reductive decomposition of the halogenated and non-halogenated organic contaminant compounds, typically 0.5 to 2 hours. At this temperature the carbon source (eg the carbohydrate) acts as a catalyst for the formation of a reactive hydrogen ion from the hydrogen donor compound. Finally, the mixture is neutralised by the addition of an acid, preferably to a pH of 7 to 9. Depending on the nature of the feed material, the reagent additions and the site use, it may be possible for the treated material to be returned to the site if desired, although this may not be possible if the treated material is oily or has a high salt content.

- **Cost Effectiveness**
  - Up to USD1000 per tonne PCB contaminated oils and up to USD 250 for contaminated soils

- **Safety and Environmental Considerations**
  - Potential to form dioxins and furans is very small and if formed then the BCD process will Dechlorinate. Emissions low. Low operating temperatures.
**Eco Logic Process**

A gas reduction process uses high temperature hydrogen as a reducing agent to destroy chlorinated organic compounds. Eco Logic International Inc. (Eco Logic), Canada has developed a hydrogenation process known as Gas-Phase Chemical reduction (GPCR). The process is based on gas-phase thermo-chemical reaction of hydrogen with organic compounds. At 850°C or higher, hydrogen combines with organic compounds in a reaction known as reduction to form smaller, lighter hydrocarbons, primarily methane. For chlorinated organic compounds, such as PCBs, the reduction products include methane and hydrogen chloride. This reaction is enhanced by the presence of water, which acts as a reducing agent and a hydrogen source.

Organics such as PCBs, PAHs, chlorophenols, dioxins, chlorobenzenes, pesticides, herbicides and insecticides are quantitatively converted to methane. Approximately 40% of the methane produced can be subsequently converted to hydrogen via the water shift reaction and the remaining methane converted to hydrogen in the catalytic steam reformer. Thus, the process can operate without an external supply of hydrogen.

The mixture of gases and vaporised liquids are heated as they pass electric heating elements situated around the central ceramic-coated steel tube of the reactor. Gases and any entrained fine particulates proceed up the central tube providing in excess of 2 seconds retention time at 900°C. The reactions come to completion before the gases reach the scrubber where the water, heat, acid and carbon dioxide are removed. A caustic scrubbing agent is added, if required, to maintain the scrubber water pH at between 6 and 9. The temperature of the exit gas is maintained near 35°C by cooling the scrubber water using dual plate heat exchangers and cold water from an evaporative cooler.

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**Eco Logic Process Performance**

As the Process is a hydrogenation process and thus will add hydrogen molecules to any incomplete hydrogenated organic molecule the process will Dechlorination molecules and break down chlorine rings and will therefore treat PCP, PCP and other POPs and dioxins in a similar manner and achieve very high destruction rates.

**Benefits**
- low emissions
- treats all chlorinated molecules
- complete destruction
- converts chlorinated compounds into fuel

**Disadvantages**
- large fixed plant (Mobile and portable units available)
- use of hydrogen
Contaminated equipment processed in the pretreatment desorber unit (TRBP) constitutes a relatively small organic load to the reactor and high strength organic wastes such as Askarel fluids can be processed simultaneously. The TRBP is also suitable for processing high-strength organic wastes such as obsolete pesticides which are sufficiently volatile to evaporate directly from drums. The advantages of this approach are that handling is reduced, drums are cleaned in place and inorganic solids remain behind in the drums. Fugitive emissions are minimised due to the reduced handling requirements and the elimination of transfer operations.

Cost Effectiveness Eco Logic
Up to USD2500 per tonne PCB and USD5000 for capacitors. Contaminated soils etc. USD3000 per tonne (If treated using TRBP). Relatively expensive option. If contaminated soils are treated using the TORBED system then costs reduce to US$200-700 per tonne depending on soil characteristics, volumes etc.

PCB Gone
In service treatment of transformers is possible using dechlorination processes. A process developed by S D Myers called PCB Gone involves circulating the transformer fluid through a filtration system until the PCB concentrations are below the recategorisation level. The PCB Gone process is very specific in the scheduled wastes it is able to treat, as it is designed to treat PCB contaminated transformer oils without the need to remove the transformer or take the transformer out of service. The fluid is recirculated through the treatment system until the residual PCB concentrations are below those required (< 2 ppm in the USA). The continued recirculation of the fluid through the transformer largely flushes the PCBs from the transformer windings and other internal components. The treated oil is then suitable for continued use.

PCB Gone Process performance
With concentrations within transformer below 50,000 ppm the PCB gone process is quite effective and will reduce the PCB concentration to below 5ppm. Leaching can occur and the transformer may continue to require polishing for some time. Easy to set up and operate.

Benefits
• For low contamination cost effective
• Portable process
• minimal air emissions
• low temperature system
• treats in service transformers

Disadvantages
• gaining approval for portable systems
• not appropriate for pure PCB transformers
• not applicable for capacitors
• collected PCB must still be destroyed.
In addition to removing PCBs, the PCB Gone treatment system also regenerates the used fluid by filtration through Fullers Earth as with other conventional transformer fluid reclamation systems. This treatment removes acids, sludges and other oxidation by-products by a mechanical filtration process, that in effect reclaims the contaminated transformer fluid. As the treated oil is reused and the transformer decontaminated without the need to remove it from service, significant cost savings could be expected from this treatment approach. The process uses a proprietary Dechlorination reagent that provides for safe operation and is non-destructive to the transformer oil's dielectric properties.

PPM Process

The process operates at ambient temperature and does not use flammable solvents. The process uses a complex organo-sodium reagent. The reagent is air and water sensitive and during reduction the process must be blanketed with nitrogen. When introduced to the reaction tank, the reagent reacts immediately with the PCBs and chlorinated hydrocarbons to form sodium chloride and a polyphenylene polymer. The reagent reacts with inhibitors, acids, thiols, and chlorides to form the appropriate sodium salts, which are then present in the oil as an insoluble sludge. After decontamination small quantities of water are added to destroy and excess reagent.

The process consists of three parts. Pre-treatment, decontamination and Clarification. In the pre-treatment part water is reduced to acceptable levels by draining the water and other impurities off the bottom of the reception tank holding the contaminated transformer oil.

After pre-treatment the oil is decontaminated The sodium reagent is added directly to the oil after
the application of a nitrogen blanket. The amount of reagent added is determined before the cleanup to determine the PCB, chlorinated hydrocarbon, sulphur and other impurity levels. As the PCBs react to the sodium they are monitored on site with a gas chromatograph.

After decontamination the oil is cleaned of salts and solids through filtration. During this stage, small amounts of water are introduced to destroy excess amounts of reagent. The solids, salts and small amounts of water solution of sodium hydroxide are removed at this stage. All wastes removed at this stage is small and non PCB. The process consists of three parts. Pre-treatment, decontamination and Clarification. In the pre-treatment part water is reduced to acceptable levels by draining the water and other impurities off the bottom of the reception tank holding the contaminated transformer oil.
Step 6 - Technology selection

<table>
<thead>
<tr>
<th>Technology Type</th>
<th>DECONTAMINATION</th>
<th>DESORPTION</th>
<th>PCBs</th>
<th>POPs</th>
</tr>
</thead>
</table>

### Description of process

Thermal desorbers are used to vaporise hazardous organic contaminants so that they can be separated from the solid materials to which they adhere or are adsorbed. Other systems are then required to treat the desorbed organics. Elements of a desorber unit are waste handling and feed systems, thermal Desorption chamber, off gas condensation and separation and treatment systems for the separated organic compounds. Thermal desorption separates contaminants from soil. Soil is heated in a chamber where water, organic contaminants and certain metals are vaporised. A gas or vacuum system transports vaporised water and contaminants to an off-gas (i.e., air emission) treatment system. The design of a system aims to volatize contaminants, while attempting not to oxidise them. Based on the operating temperature of the desorber, thermal desorption processes can be categorised into two groups: high temperature thermal desorption (HTTD) and low temperature thermal desorption (LTTD). It is important to note that thermal desorption does not to destroy organics.

**High Temperature Thermal Desorption (HTTD).** In HTTD, wastes are heated to 320 to 560 °C (600 to 1,000 °F). HTTD is frequently used in combination with incineration, solidification/stabilisation, or dechlorination, depending upon site-specific conditions. Low Temperature Thermal Desorption (LTTD). In LTTD, wastes are heated to between 90 and 320 °C (200 to 600 °F). LTTD is most often used for remediating fuels in soil.

### Thermal Desorption Performance

Generally low emissions and the process needs careful control to be effective. DRE's for PCB contaminated soils and dioxins is 6 nines. Does not use large amounts of excess air and operates under reduced pressure.

### Benefits

- **Indirect heating**
- For soils very effective can handle full range of chlorinated hydrocarbons, PCBs, POPs etc.

### Disadvantages

- **Fixed large plant**
- Metal hydroxides from plant may need disposal.
- Off gas requires treatment
Unless being heated to the higher end of the LTTD temperature range, organic components in the soil are not damaged, which enables treated soil to retain the ability to support future biological activity.

Treatment of the off-gas must remove particulates and contaminants. Particulates are removed by conventional particulate removal equipment, such as fabric filters. Contaminants are removed through condensation followed by carbon adsorption, or they are destroyed in a secondary combustion chamber or a catalytic oxidiser.

Treatment and control of air emissions from thermal desorption operations is an extremely important consideration. It is important that there are no emissions problems concerning metals, certain PAHs and dioxins/furans. Mercury emissions are very difficult to control, and using an afterburner is unacceptable.

Thermal desorption systems are somewhat effective in removing VOCs, SVOCs, fuels, pesticides and some metals from soil. High temperature units are more effective removing volatile metals and SVOCs.

**Cost Effectiveness**

Cost vary across different facility operators but generally for contaminated soils about USD250 per tonne.
In situ Vitrification (ISV) is a commercially available technology used for contaminated site remediation and waste treatment. It is a mobile, thermal treatment process that uses electricity to heat and melt contaminated soils, sludges and other earthen materials. The treatment results in the permanent destruction of organic contaminants and the permanent immobilisation of inorganic contaminants within the high integrity vitreous product.

ISV has been demonstrated to be effective in the treatment of all classes of contaminants including organics, heavy metals, radioactive material, and explosive compounds. The ISV process has been successfully used at full scale to treat a wide range of soils and wastes including contaminants such as pesticides, herbicides, dioxin, PCB’s, arsenic, mercury, lead etc.

The ISV process is distinguished by its ability to accommodate a wide range of wastes and debris. This eliminates the need for handling, sorting and size reduction activities. Virtually all types of debris can be accommodated by the process including drums, scrap metal, concrete, boulders wood and plastic. Using the process a destruction efficiency of 99.9999% can be achieved.

In Situ vitrification involves the electric melting of earthen materials at high temperature for purposes of destroying organic contaminants and permanently immobilising non-volatile inorganic contaminants in a glassy, rock-like vitrified product, thereby rendering the treated product non-hazardous. The process employs joule heating and typically operates in the range of 1,600 to 2,000 degrees C for most earthen materials.

In Situ Vitrification (ISV) is a commercially available mobile, thermal treatment process that involves the electric melting of contaminated soils, sludges, or other earthen materials, wastes and debris for the purposes of permanently destroying, removing, and/or immobilising hazardous and radioactive contaminants. The process is widely applicable to all soil types and all classes of contaminants including organics, heavy metals and radionuclides. The ISV process is a batch process that involves forming a pool of molten soil at the surface of a treatment zone between an array of four electrodes. The molten soil serves as the heating element of the process wherein electrical energy is converted to heat.
via joule heating as it passes through the molten soil. ISV melt temperatures typically range between 1,500-2,000°C. Continued application of energy results in the melt pool growing deeper and wider until the desired volume has been treated. When electrical power is shut off, the molten mass solidifies into a vitreous monolith with unequaled physical, chemical, and weathering properties compared to alternative solidification/stabilisation technologies.

Extrapolating established US costs results in a cost of $500 to $750 per tonne for contaminated soil.

**PROS**

- The process is widely applicable to all soil types and all classes of contaminants including organics, heavy metals and radionuclides.
- The process is operated on an around the clock basis and can achieve treatment rates of up to 150 tonnes per day.
- High concentrations of organic contaminants, 10-20 wt%, can be treated by the process with existing equipment. Organic concentrations in excess of 20 wt% can be treated with modified equipment.
- The ISV process equipment is all trailer mounted except for the off-gas hood, which is transported to the site and then assembled. Only two personnel are required to operate the equipment.
- ISV is relatively safe and represents a low risk to the environment as demonstrated by successful commercial operations in the US and in Japan.
- A very high percentage of organic contaminants are destroyed in the ground (typically >99.9%);
- Most heavy metals and all radionuclides are largely retained in the melt so the emissions of these species from the melt to the off-gas treatment system are minimal;
- The treatment process is relatively slow; the melt grows at a rate of only a few cm per hour resulting in only a small fraction of the waste material being treated at any one time;
- The off-gas treatment system is robust and has been demonstrated to be effective on a wide range of contaminant types; provision of a back up system in case of primary system failure covers the contingency of breakdown and discharge of untreated waste gases.
- For the in situ mode of treatment, the process does not require excavation and handling of contaminated soils so the risk to workers, the public, and the environment are minimised;
- Since the process treats wastes on-site, there is no requirement for, or risk from, the off-site transport of wastes;
- No organic contaminants remain in the vitrified product;
- The vitrified product is extremely effective at immobilising heavy metals and radionuclides and the product far surpasses TCLP requirements;
- The process equipment includes back-up safety systems and an alternate power supply in case of equipment or power failure.
- Liquids and non-soil wastes would be mixed with soil. Treatment costs for liquid and non-soil wastes would depend on the soil mixture ratios.

**CONS**

- Off-gas treatment required to treat volatile organics.
• Other major components include the process control station, a back-up off-gas treatment system and a diesel powered generator.
• 11 kV three phase electrical power which can be supplied either from the utility grid or from diesel powered generators.
• The thermal oxidiser, if used, typically requires 3 Mbtu/hr of fuel.
• A source of potable water is also required to support process operations.
• For the in situ mode of treatment, sites must be characterised to ensure that there are no high integrity sealed containers, such as drums, and that there are no other structures present where liquids can accumulate and become trapped. Sealed containers and other trapped liquids become pressurised upon heating and can result in sudden gas releases through the melt.
• Establishment costs are expected to be significant for the ISV process and therefore it is likely to be relatively expensive for smaller projects.
• ISV requires either soil or some other earthen material to serve as the treatment media (melt).

The process works by melting soil in place using electricity applied between pairs of graphite electrodes. A highly conductive starter path is placed between the electrodes to allow initiation of melting. As electricity flows through the starter path, the path heats up and causes the surrounding media to melt. Once the media is molten, it too becomes electrically conductive. Continued application of electricity results in joule heating within the molten media between the electrodes. After the melt is fully established, the melt zone grows steadily downward and outward through the contaminated volume.

The media being treated must be capable of forming a melt with adequate electrical conductivity. Most natural soils and other earthen materials meet this criterion and can be processed without modification. If necessary, additives can be used to allow treatment of otherwise unacceptable media.

Organic constituents are thermally desorbed and then destroyed by thermal decomposition (pyrolysis) within the oxygen-depleted media being treated. Non-volatile inorganics are typically incorporated into the melt and the resulting vitrified product. Such incorporation occurs within the framework of the glassy product itself, as opposed to simple encapsulation (being surrounded) by the glass. A large volume reduction (25-50% for soils) occurs due to elimination of void volume and vaporisable materials during processing.
Step 6 - Technology selection

<table>
<thead>
<tr>
<th>Technology Type</th>
<th>DECONTAMINATION &amp; DESTRUCTION</th>
<th>PCBs</th>
<th>EMERGING</th>
<th>POPs</th>
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</table>

**BIOREMEDIATION**

Bioremediation refers to the use of micro-organisms to break down organic chemical compounds that contaminate soil. The key to the process is the identification of an appropriate organism to perform the bioremediation process. The effects of moisture content, temperature, oxygen levels, food sources are required to be understood so that successful application can be achieved. In situ bioremediation treats the soil in place and eliminates the need to transfer the soil elsewhere for treatment. In situ remediation usually uses the indigenous bacteria and supplements with nutrient water to increase microbial rates. Ex situ technologies treat excavated soils under controlled conditions where temperature and moisture is managed. For sites without owners that have low levels of contamination this process can be very cost effective and after time very effective in cleaning contaminated sites. Generally unsuitable for heavily contaminated pesticide sites but will work on low levels of POPs and PCBs.

**SOLIDIFICATION AND STABILISATION**

These technologies rely on limiting the solubility or mobility of the toxic component in hazardous waste generally by physical containment. Five containment methods are used. Solidification by pozzolan reactions, possolan-portland cement reactions, thermoplastic micro encapsulation, and macro encapsulation. The sorption process requires additional solid materials to take up free liquids.

**SOIL WASHING**

PCB and POPs and other particles that are adsorbed into the surface of particles can be leached from soil by caustic agents such as sodium hydroxide.

**SUPERCritical WATER OXIDATION**

This technology is a high temperature and pressure system that uses the properties of supercritical water in the destruction of organic compounds. The process is applicable to the treatment of a range of contaminants including acrolonitrile wastewater, pesticide waste water, PCBs, halogenated aliphatics and aromatics. The process is established with a totally enclosed in a reactor. The oxidant is injected as required on a heat based transfer, thermal and kinetic considerations. The process results in the formation of disposable ash and releasable gases.

**GASIFICATION**

This process uses a low pressure steam at high temperatures and a thermochemical reaction to vaporise and separate waste into their elemental components. A reduction process takes place in a reaction vessel which is directly heated. A reductive process rather than combustion takes place. There is no reactor stack gas.
CHEMICAL OXIDATION

Hydrogen peroxide, potassium permanganate, Oxone (DuPont chemical), peroxydisulfate, ultraviolet activated hydrogen peroxide and ozone oxidation are all viable oxidants for the treatment of nonstockpile neutralents. Under appropriate operating conditions and with sufficient reagent, the organic compounds present in the neutralents can be expected to be mineralized with any of these oxidants.

For chemical oxidation not activated by UV light, conventional process equipment and procedures are used. The reactions are carried out at 80-100°C at Atmospheric pressure in aqueous solutions.

When an organic phase is present, vigorous agitation is necessary to suspend and disperse the organic materials in the aqueous phase.

PROS

• Relatively mild conditions (low temp and press)
• Only gas evolved is CO2.
• Inorganic salts precipitate when water is evaporated and are sent to landfill.
• Dioxins and furans are not formed
• Low cost
• Robust
• Good pollution prevention
• No large gas streams

CONS

• Reagent cost high.
• May not fully mineralize the compounds in the neutralents, or reaction may be prohibitively slow.
• Technology not yet mature.
• Capital and operating costs are expected to be moderate.
• Large equipment
ELECTROCHEMICAL OXIDATION

At low temperature and atmospheric pressure, electrochemically-generated oxidants react with organochlorines to form carbon dioxide, water and inorganic ions. High destruction efficiencies. All emissions and residues can be captured for assay and reprocessing, if needed. An electrochemical cell is used to generate oxidizing species at the anode in an acid solution, typically nitric acid. These oxidizers and the acid then attack any organic compounds, converting most of them to carbon dioxide, water and inorganic ions at low temperature (< 80 °C) and atmospheric pressure.

PROS

• The organic content of the feed, which can be soluble or insoluble organic liquids or solids, can vary between 5 and 100 percent without affecting the process unduly.
• Likewise, the water content of the waste can vary over a wide range.
• overall costs are estimated to be some 30 percent of the current estimate of demilitarization through incineration
• Materials can be fed by gravity or by pumping, and can be solid (such as PCB-laced wooden pallets) or liquid.
• The SILVER II TM process operates at relatively low temperature and pressure (up to 90 o C and nominally atmospheric pressure).
• AEA reports that there are low volumes of by-product streams (gaseous, liquid, and solid), and that dioxins and dibenzofurans are not produced by the process.
• when organics react with SILVER II TM , they are completely mineralized
• Positive characteristics include low temperature, low off-gas, and an apparent ability to treat diverse waste streams.

CONS

• off gases passed through a scrubber and potentially through an activated carbon filter before being discharged to the atmosphere
• By-products of the process include salts (referred to on Figure 2.1.1 as miscellaneous inert solids), nitric acid, spent scrubbing solutions, and off gases.
• AEA indicated that a key factor affecting cost is electrochemical efficiency
• reactions are strongly surface area dependent, solids and some liquids require significant size reduction and/or mixing for adequate oxidation to occur, whereas soluble organics are more easily oxidized
• Because the reactions take place at low temperature and in a liquid state, the times required for the reactions are much longer than for thermal systems, and typically, more secondary waste is generated by the oxidizing agents.
ELECTROCHEMICAL OXIDATION - CERIUM

The CerOx process is similar to the Ag(II) process except that it uses 0.8M Ce(IV) solution in 3M nitric acid at 100C to oxidize and destroy organic compounds. Unlike Ag(II), Ce(IV) is stable. The Ce is produced and regenerated by the electrolysis of Ce (III) in a bipolar electrochemical cell (T-cell). Carbon is converted to CO2; chlorine compounds are converted to elemental chlorine, which is scrubbed and converted to hypochlorite. CerOx uses few reactants, principally nitrate (recycled), nitric acid, and sodium hydroxide to treat off-gases. Biggest cost is for electricity to operate the electrolysis T-cells.

PROS
- Cerium is much cheaper than Ag and much less toxic
- Low temperature and low pressure.

CONS
- High chlorine content in feed would result in lots of chlorine gas which would have to be treated.
- Uses large quantities of nitric acid
- Inorganic salt concentration builds up in anolyte solution and solution must be replaced periodically.
- Less developed than Ag(II) technology
STEAM REFORMING

The Steam Detoxification process involves very high temperature steam reforming (i.e. 1100 to 1500°C) to destroy hazardous wastes. Vent gases are carbon dioxide and water. Steam Detoxification consists of a two step process, and is carried out in a Pyrolysis Detoxifier. The hydrocarbon component of the waste is first evaporated in a first-stage waste feed evaporator unit and the vapourised gases are then mixed with superheated steam and fed into a "pyrolysis reactor" where they are further electrically heated under a slight vacuum. A carbon monoxide converter oxidises the detoxified gases and an activated carbon adsorber removes the last of the trace organics and metals.

PROS

• As the reactor is heated electrically the gases are free of the fuel combustion particulates common to incinerator systems.
• is small enough to readily fit into existing buildings;
  provide acceptable installation costs;
  destroy liquid solvents and their contaminants;
destroy organic contaminants adsorbed onto activated carbon;
  destroy organics in the vapour phase;
  process continuous liquid feed streams;
  process drummed wastes without removal of drums;
  operate with a high temperature waste feed evaporator for solid organics;
  serve as part of a process to purify ground water; and reactivate vapour and liquid phase activated carbon canisters.
• Costs are estimated by the proponent at approximately half the average cost of incineration or landfill in the US.
• Most promising technology according to DOE (DOE/SEAB)

CONS

• The process requires potentially elaborate gas treatment systems, and the overall system can be expected to be of similar complexity to the Eco Logic system
• Some pretreatment required for solid wastes (shredding, grinding, desorption).
• Some of the solid residues left over after the evaporation stage may require solidification and fixation before landfill disposal.
• The high temperatures used in the process require specialised equipment and reactor materials. The process requires containment of potentially hazardous gases at high temperatures and therefore will require careful design and operation.
• Mainly suitable to liquid and aqueous wastes.
**WET AIR OXIDATION**

The WAO process oxidizes and hydrolyzes organic contaminants in water at temperatures of 150-315°C and pressures of 150 to 3150psi, below the critical temperature of water and pressure (374°C and 3,204psia). If pure oxygen is used instead of air as the oxidizing agent, the gas volumes that must be managed are greatly reduced.

Organic compounds containing carbon, hydrogen and oxygen are converted to CO2, H2O and short chain biodegradable compounds such as acetic acid and formaldehyde. Depending on reaction conditions, further biotreatment of residues may be necessary. Toxic heavy metals in the neutralent would have to be precipitated and filtered out prior to biotreatment. Sulphur containing organics are mineralized to sulfate ions in solution, Phosphorous to phosphate ions, chlorine to chloride ions, nitrogen to ammonium and nitrate ions and nitrogen and nitrous oxide gas, cyanides are converted to CO2 and ammonium ions.

**PROS**

- Mature technology, Zimpro has installed more than 300 units worldwide
- Requires only the addition of air/oxygen and water
- No dioxins formed, proponent claims they are destroyed.
- Titanium liner prevents corrosion
- Costs lower than for incineration.

**CONS**

- Most effective on dilute aqueous solutions
- May not be effective against PCBs and HCB.
- Effluent needs to be treated biologically.
BALL MILLING

The Ball Milling process is a mechano/chemical process, relying on the energy released at the point of collision between balls in a ball mill to activate a reaction between the waste and CaO (lime), breaking down the organochlorine compounds. By-products of the destruction of organochlorine compounds using CaO are generally of low toxicity and may include graphite, calcium chloride and calcium hydroxide. The process may be applied to concentrated forms of halogenated hydrocarbons such as PCBs and DDT. In the case of contaminated electrical components, the possibility exists to destroy the encapsulating container in the same process. Disperse wastes (e.g., contaminated soil) would preferably be concentrated by solvent extraction or a similar process prior to destruction within the ball mill treatment system.

PROS

- treated materials are expected to be suitable for disposal to landfill in the case of solid wastes, or other normal disposal methods in the case of liquid wastes
- In the case of contaminated electrical components, the possibility exists to destroy the encapsulating container in the same process.
- the low energy potential of the system in relation to the surrounding environment means that the potential for release of contaminants is reduced. Also, the process can be readily shutdown in a short period of time, further reducing the potential for release in case of an emergency or power failure;
- the process operates at low temperatures increasing safety, reducing energy consumption and reducing the potential for formation of dioxins;
- items of electrical equipment, contaminated with PCB or damaged or corroded waste containers may be fed directly into the ball mill system for destruction;
- the process largely uses well established mineral processing equipment and principles;
- the process by its nature will result in a high degree of mixing of wastes and would tend to break up agglomerated material;
- no gaseous emissions are produced;
- the process is likely to readily treat wastes containing a range of organic contaminants, or mixtures of organic contaminants in one step, reducing waste handling and the associated risk.

CONS

- Disperse wastes (e.g., contaminated soil) would preferably be concentrated by solvent extraction or a similar process prior to destruction within the ball mill treatment system.
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