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The Scientific and Technical Advisory Panel of the GEF
United Nations Environment Programme

REVIEW OF EMERGING, INNOVATIVE TECHNOLOGIES FOR THE DESTRUCTION AND DECONTAMINATION OF POPS AND THE IDENTIFICATION OF PROMISING TECHNOLOGIES FOR USE IN DEVELOPING COUNTRIES

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FOREWORD

This document originated as the background document for The Scientific and Technical Advisory Panel (STAP) of the Global Environmental facility (GEF) United Nations Environment Programme workshop held in Washington DC, USA on the 3-7 October 2003. Subsequent to the workshop, which was attended by over 30 experts from around the world the background, document has evolved into this final report, which includes conclusions, and recommendations.

The original background document and associated critical review research was done at the International Centre for Sustainability Engineering and Science, Faculty of Engineering, University of Auckland New Zealand. We thank Ian Rae (University of Melbourne), Trevor Bridle (Environmental Solutions International Ltd), Zoltan Csizer (Director, Cleaner Production and Environmental Management Branch, UNIDO) and John Vijgen (Director IHPA) for their editorial contributions to the document.

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15 January, 2004

EXECUTIVE SUMMARY

The purpose of this work was to review all existing technologies that were non-combustion in character and identify those technologies that are innovative and emerging and hold promise for the destruction of the POPs stockpiles.

The definition of non-combustion technologies used in this report are processes which operate in a starved or ambient oxygen atmosphere. Such technologies may produce dioxins or furans but require less technology to remove those chemicals than an oxidised process such as a high temperature rotary kiln.

Approximately 50 technologies were reviewed and placed into one of four categories:

A Commercialised technologies with considerable experience
- Gas Phase Chemical Reduction (GPCR)
- Base Catalysed Decomposition (BCD)
- Sodium Reduction
- Super-Critical Water Oxidation (SCWO)
- Plasma Arc (PLASCON)
- Pyrolysis/gasifiers

B Technologies near or at the start of commercialization
- Molten Salt Oxidation
- Solvated Electron Technology

C Promising technologies
- Ball Milling
- GeoMelt™ Process
- Mediated Electrochemical Oxidation (CerOx)
- Mediated Electrochemical Oxidation (AEA Silver II Process)
- Catalytic Hydrogenation

D Technologies which require significant research

No technologies were found which were suitable for this category although preliminary research had been undertaken on some technologies. These are placed in Annexure 1.

E Technologies which are unlikely to be applicable for destruction of POPs stockpiles
- $MnO_x/TiO_2–Al_2O_3$ Catalyst Degradation
- TiO_2-based V_2O_5/WO_3 Catalysis
- Fe(III) Photocatalyst Degradation
- Ozonation/Electrical Discharge Destruction
- Molten Metal
- Molten Slag Process
- All bio- and phytoremediation including:
  - Photochemically Enhanced Microbial Degradation
  - Biodegradation/Fenton's Reaction
  - White Rot Fungi Biodegradation
  - Enzyme Degradation
  - In situ Bioremediation of Soils
  - DARAMEND Bioremediation
  - Phytoremediation

In addition, there was considered to be insufficient information to classify one technology, Self-Propagating High Temperature Dehalogenation (SPHTG).

It is of concern that there are so few emerging technologies, especially those that may be suited for in situ destruction of POPs. To some extent this may be a reflection of the large amount of low cost high temperature incineration capacity in Europe, the ongoing POPs removal in developing countries to HTI coupled with a reluctance of research funding in this sector.

A number of technologies have been placed in Annexure 1 as technologies which have been insufficiently researched to indicate their promise. It is likely that some of these technologies should have been placed in Category D but there was insufficient information to place them in that category.

It is also possible that some technologies which were identified as unsuitable could be successfully developed as suitable technologies. However, with the direction of the research and the limited availability of information for some technologies, it was considered appropriate by the workshop to place them in Category E.

In addition, information was provided by Zoltan Csizer, Director, Cleaner Production and Environmental Management Branch, UNIDO, on technologies acceptable for use in Japan for destroying PCBs (Annexure 2). There was insufficient information provided to include them in this report although some of the technologies have been included as they are used elsewhere and data were available.

An additional goal of this work was to examine the criteria that a developing country could use to evaluate the application of a particular technology. A set of criteria was developed that has two elements. These criteria can be used as they stand for evaluative purposes but with an application of an 'Expert' system a fully integrated and interactive evaluation model cam be achieved that is dynamic in that new technologies can be added to it as they become available.

Recommendations

It is recommended that the five identified emerging and promising technologies be further evaluated for the purpose of providing funding so that the technologies may become commercialised in the near future.

It is also recommended that a decision support system be developed which will assist users in deciding which technologies are appropriate for treating POPs wastes and contaminated soils in their region. Such a system should be developed as soon as possible to enable users around the world to make effective decisions on POPs management.

1.0 INTRODUCTION

1.1 Background

Environmental and health concerns about the use of combustion systems for the destruction of obsolete POPs have encouraged the development of alternative destruction technologies. Emerging technologies could play an important role in the final treatment and/or destruction of large numbers of obsolete POPs stockpiles, including the soils surrounding the stockpiles, provided their further development and deployment is encouraged and supported. Non-combustion technologies, including bioremediation technologies offer an environmentally sound alternative to traditional incineration technologies.

In the case of developing countries, appropriate and adequate destruction facilities are lacking, and the costs associated with providing them may be greater than what the region can afford without technical assistance. Moreover, countries are generally reluctant to divert development funds for disposal of obsolete pesticide stockpiles. As a result, the majority of obsolete pesticides disposed of from developing countries, have been shipped to developed countries for destruction, mostly by high temperature incineration.

However, after the Stockholm Convention enters into force and Parties develop their national implementation plans pursuant to the obligations arising from the Stockholm Convention on POPs, almost all will need to develop programs to identify and destroy their POPs pesticide stockpiles. Whereas the requirements of the POPs Convention will create incentives to develop and encourage the use of technologies that are environmentally sound and that do not produce other POPs by-products, there is a need to assess the experience so far, and to identify promising technologies that could be supported.

Developing countries present a unique challenge to modern technology. Instead of following the general trend of increasing complexity, the situations in developing countries demand simplicity. Any technology used in this situation must be appropriate. It must be able to operate successfully in the face of limited infrastructure, technical knowledge and expertise.

The challenge of making technology appropriate and development sustainable has been a high priority for many years. With respect to obsolete pesticides the challenges are great. Obsolete pesticides are classified as hazardous waste requiring extensive training and expertise for safe handling and management. Present disposal technologies involve complex equipment, sophisticated controls and dangerous processes. Extensive infrastructure, such as a reliable power supply, is needed for safe operation. These factors conspire to prevent many established technologies from operating in developing countries. With obsolete pesticides the problem is compounded by the wide dispersal of obsolete stocks and their deteriorated condition.

1.2 Project Objectives

Introduce the subject of the review by outlining the potential and drawbacks of non-combustion and bio-remediation technologies, the constraints for their further development and use, the experience so far with larger scale use, and current trends.

1.2.1 Provide a comprehensive overview of existing and emerging innovative non-combustion and bio-remediation technologies for the destruction of POPs, with a focus on emerging technologies, using categories that reflect the different stages of experience and development with a technology (it is suggested that the NATO categories are used, namely: 1. direct applicable technologies with considerable experience; 2. applicable technologies on the stage of a "breaking through and/or start of commercialization"; 3. technologies that given the right financial circumstances could be full scale within approximately 5 years; 4. technologies in the stage of laboratory scale testing).

1.2.2 Summarize their performance and evaluation results as described in case studies, evaluations, commercial information or other sources, and citing the source of information.

1.2.3 Provide a global overview of sites where non-combustion and bio-remediation technologies are being used at different scales, and supplement his information where possible and relevant with available case studies.

1.2.4 Describe experiences to date with non-combustion and bio-remediation technologies in developing countries and countries with economies in transition.

1.2.5 Review non-combustion and bio-remediation technologies critically in terms of their potential use in developing countries and countries with economies in transition, using criteria of robustness, safety, sustainability, ease of operation, cost-effectiveness, conformity with the Basel Convention and Stockholm Convention, and taking into account the composition of existing stockpiles, as well as the conditions prevailing in developing countries, with the view to identify promising technologies.

1.2.6 Based on the critical review, examine the issue of selection criteria and identify good practices in technology selection.

In its conclusions on promising technologies, the review will consider if there is anything in the technology pipeline approaching the ideal of a technology that meets the criteria described above, and if there is any potential for existing systems to be modified to make them more cost-effective.

In order to ground the review in the reality of different situations, the review will be supplemented with three country case studies (two from developing countries and one from a country with an economy in transition), in which the stockpile situation will be analysed and different disposal options explored.

1.3 Overview of non–combustion technology

The definition of non-combustion has not been provided as part of the TOR. A scientific/engineering definition of a non-combustion process would be a process that operated in a reducing atmosphere. For the destruction of POPs, the issue that arises is the production of POPs such as dioxins or furans. Only a few technologies would meet either of these definitions – Base Catalysed Decomposition, Solvated Electron Transfer and Sodium Reduction.

As a result a further definition is processes which operate in a starved or ambient oxygen atmosphere. Such technologies may produce dioxins or furans but require less technology to remove those chemicals than an oxidised process such as a high temperature rotary kiln. This definition would include technologies such as pyrolysis and plasma arc ((PLASCON)) as well as a number of other technologies. This definition that has been included in preparation of this document.

2.0 REVIEW OF TECHNOLOGY

Over the past ten years, much of the research focus on hazardous waste technologies has been on the treatment of contaminated soils and wastewaters. Few new technologies have been developed which would be applicable for the destruction of stockpiles of POPs although it is feasible that some of the new technologies that have been developed could be applied to such stockpiles.

The following technology summaries provide the available information on non-combustion technologies. Only a few have been proven in the field and, of these, two companies have gone bankrupt. There are, however, a number of emerging technologies which have potential for treatment of POPs stockpiles. In addition, there are also variants of the technologies that have been included here and some are also known under different names.

Commercially demonstrated technologies include gasification, steam reforming and plasma arc which are undertaken in a starved oxygen atmosphere. It must be noted that some of the technologies require a combustion process following the main treatment process to either ensure removal of any formed POPs or to allow for heat recovery.

This summary classifies the technologies into five categories:

A Commercialised technologies with considerable experience

Technologies with operating plants which are licensed to destroy high strength POPs stockpiles.

These include:

- Gas Phase Chemical Reduction (GPCR)
- Base Catalysed Decomposition (BCD)
- Sodium Reduction
- Super-Critical Water Oxidation (SCWO)
- Plasma Arc (PLASCON)
- Pyrolysis/gasifiers

B Technologies near or at the start of commercialization

Technologies which have operating pilot plants, are starting to build operating plants and are claimed to be suitable for treating high strength POP wastes. The latter treatments would require proof of concept (99.9999% destruction and no formation of toxic daughter products) before being considered fully suitable.

These include:

- Molten Salt Oxidation
- Solvated Electron Technology

C Promising technologies

Technologies which require minimum research to prove capability to destroy high strength POPs stockpiles or which are operating successful pilot plants. Processes which have demonstrated in the laboratory the ability to treat moderate to high strength POPs with a high efficacy and no formation of toxic daughter products are included.

These include:

- Ball Milling
- GeoMelt™ Process

Mediated Electrochemical Oxidation (CerOx)
Mediated Electrochemical Oxidation (AEA Silver II Process)
Catalytic Hydrogenation

D Technologies which require significant research

Emerging technologies which require significant research to determine their potential to destroy POPs. These include technologies which have been proven to treat low levels of POPs but have not been developed to treat high strength wastes or technologies for which there is limited data. No technologies were found which were suitable for this category although preliminary research had been undertaken on some technologies. These are placed in Annexure 1.

E Technologies which are unlikely to be applicable for destruction of POPs stockpiles

Technologies which have inherent flaws which will make them unlikely to be successful in treating high strength POPs. It must be recognised, however, that it is likely that some information on these and other technologies has not been published and therefore some data may not be available which could show that these technologies may be feasible.

These include:

$MnO_x/TiO_2–Al_2O_3$ Catalyst Degradation
TiO_2-based V_2O_5/WO_3 Catalysis
Fe(III) Photocatalyst Degradation
Ozonation/Electrical Discharge Destruction
Molten Metal
Molten Slag Process
All bio- and phytoremediation including:
- Photochemically Enhanced Microbial Degradation
- Biodegradation/Fenton's Reaction
- White Rot Fungi Biodegradation
- Enzyme Degradation
- In situ Bioremediation of Soils
- DARAMEND Bioremediation
- Phytoremediation

Not Classifiable

Self-Propagating High Temperature Dehalogenation (SPHTG)

Annexure 1 – Research Initiatives

A number of research initiatives were identified in the literature search which had examined some aspects of POPs destruction but were insufficiently advanced to be included in this study. They have been included in Annexure 1 and include:

Microemulsion Electrolysis
Ultrasonic Irradiation
Photocatalytic Degradation using TiO_2
Electron Beam Injection
Ozonation

Annexure 2 - Japanese Technologies for the Destruction of PCBs

Annexure 2 contains information provided by Zoltan Csizer, Director, Cleaner Production and Environmental Management Branch, UNIDO on technologies acceptable for use in Japan for

destroying PCBs. There was insufficient information provided to include them in this report although some of the technologies have been included as they are used elsewhere and data were available.

2.1 Category A

Direct applicable technologies with considerable experience

2.1.1 Gas Phase Chemical Reduction (GPCR) – GPCR Process

Process: Hydrogen reacts with chlorinated organic compounds, such as PCBs, at high temperatures (≥850°C) and low pressure yielding primarily methane and hydrogen chloride and "minor" amounts of other low MW hydrocarbons, including benzene.

Pre-Treatment: Bulk solids, including those in drums, are thermally desorbed in a Thermal Reduction Batch Processor (TRPB), and swept into the reactor using recirculated (hydrogen-rich) reactor gas. Contaminated soils/sediments are passed through a TORBED Reactor System, which allows higher throughput. Liquids are preheated (Liquid Waste Pre-heater System, LWPS) and injected directly. The TBRP has recently been adapted to also process liquid wastes.

Configurations: Modular; transportable and fixed – but probably not easily transported because the ancillary units (steam reformer, boiler, scrubber, compressed gas storage etc.) are significant. A (so-called) semi-mobile unit is available as one truck-trailer unit plus another additional trailer unit for each TRBP. The throughput of this combination (2 TRBPs) is only 75 tonnes per month. A semi-mobile unit equipped with a single TORBED reactor is expected to achieve 300 to 600 tonnes/month. A portable scale (single container) plant is also available but the throughput has not been not specified.

Capacity/throughput: the TBRP has the capacity to treat 70 to 90 tonnes of solids per month or 2 to 4 litres/min of liquids (86-172 m^3/month). Two TBRPs can be used in parallel to double capacity, but the combined throughput is still not suitable for commercial processing of large volumes of contaminated soil or sediment. The TORBED reactor involves pre-treatment at 600^oC to achieve higher throughput, but is still in the developmental phase. Expected throughput is 1000 to 3000 tonnes/month.

The LWPS has a capacity of 3 litres/min and is suitable for homogeneous liquids with up to 0.5% solids. It is intended to use the LWPS as a preheater and mixing vessel in future configurations of the GPCR (i.e. coupled with the TBRP or TORBED systems).

Efficacy: Demonstrated high destruction efficiencies (DE = 99.9999%) for PCBs, dioxins/furans, HCB, DDT.

Applicability: All POPs – including PCB transformers, capacitors, and oils. Capable of treating high strength POPs wastes.

Emissions: All emissions and residues may be captured for assay and reprocessing if needed. Dioxins/furans have not been detected in the product gas from the process, but have been detected at low levels from natural gas burner used to heat reaction vessel. Process gases are treated in a caustic scrubber. Recent modifications to the plant have given DREs of >99.999994% for 30% DDT input and >99.999999% for 90% PCB destruction (Bridle and Campbell, 1996).

Byproducts: Solid residues will be generated from solid waste inputs, but these should be suitable for disposal in a landfill, although UNEP (2003) indicates that traces of POPs may remain.

Practical issues: Use of hydrogen gas, although company has good environmental/regulatory track record. Fate of arsenic/mercury if present in wastes. Optional use of afterburner for burning product gas (methane). Supplies of sodium hydroxide or similar will be needed for

the caustic scrubber, and the used liquor will need to be treated and disposed. Possible need for supplies of hydrogen gas, at least during start-up (process gases are passed through a catalytic steam reformer for hydrogen generation during normal operation). Also propane for the boiler (off-gases are used as supplementary fuel, and may meet total fuel requirements when processing high-organic wastes).

A demonstration project has been initiated for 1000 tonnes of PCB-contaminated material in Canada and the Perth facility has been used for DDT pesticide residuals, PCB wastes, HCB and chlorobenzene. The GPCR technology has been selected for the treatment of PCB-contaminated material at an industrial site in the Slovak Republic, under a pilot project with the United Nations Industrial Development Organisation (UNIDO). The GPCR plant will be used to treat PCB wastes that are currently located at the industrial facility, as well as wastes that are brought in from other locations throughout the Slovak Republic. Funding for the project was approved by the Global Environment Facility (GEF) council in May, 2003.

Licensing: Commercially licensed in Australia for POPs wastes since 1996, but the Kwinana plant now shut down. Recently licensed in Japan for PCBs and dioxin wastes. Has been licensed and used for full-scale remediation project in Canada and pilot scale remediation in USA and is currently under assessment for US Army Chemical Weapons demilitarization programme (phase 3).

Vendor(s): ELI Ecologic International, 143 Dennis St., Rockwood, Ontario, Canada N0B 2K0

Phone: (519) 856-9591, Fax: (519) 856-9235. (www.eco-logic-intl.com)

Information sources: Detailed description given in UNIDO Annex 7, based on info provided by vendor. Also Vijgen, 2002 and UNEP, 2003.

Reason for category: This technology has been used for managing POPs waste for the past 8 years and probably has the best track record of any non-combustion destruction technologies.

2.1.2 Base Catalysed Decomposition (BCD)

Process: The BCD patented process is divided into 2 separate and distinct processing steps; the first makes use of modified indirectly heated thermal desorption to decontaminate media such as soil and building rubble contaminated by POPs and is a continuous process, the second is a batch process in which POPs in the form of pure chemicals, or concentrates obtained from the desorption step are destroyed by a chemical reaction in a heated stirred tank reactor.

In the first step the contaminated media is mixed with low concentrations of alkalis such as sodium bicarbonate. This addition of alkali often enhances the stripping of chlorinated hydrocarbons from difficult matrices. During the desorption step, especially in presence of alkali significant fractions of the POPs are destroyed.

In the second step, which may, in the treatment of POP stockpiles be the only step, the actual destruction takes place. A hydrogen transfer reaction takes place. A carrier oil which acts both as suspension medium and hydrogen donor is heated to above 326°C, the melting point of sodium hydroxide. Sodium hydroxide and proprietary catalysts are added followed by the POP chemicals, waste or desorption concentrate. Depending on the content of organically bonded halogens, generally chlorine, the POPs are either added in total or dosed in a controlled manner. The overall reaction is exothermic, so that chemicals with e.g. 50% bonded chlorine are dosed over a period of time. Under these conditions hydrogen splits off from the carrier/donor oil and hydrogenates the bonded chlorine. In the presence of the other reagents the reaction proceeds to produce water vapour and sodium chloride.

After the reaction is complete, confirmed by either on-site or off-site analysis, the oil and the reagent sludge are dumped from the reactor. In the latest designs the reactor is fist cooled to below the flash point of the carrier oil. If a low cost oil, such as No. 6 fuel oil has

been used, as is the case in the SD Meyers plant in Mexico, the oil and salt containing sludge are disposed of as fuel to a cement kiln. In other cases more reactive refined oils are used. In these cases the oil is separated from the sludge and recycled. The sludge can then be further treated to have an alkali water stream suitable as a neutralising agent in the treatment of acidic waste waters or rendered safe for land-filling as with salts from industrial off gas scrubbers.
The production of common salt, sodium hydroxide is quantitative as with all hydrogenation processes.

Pre-treatment: The first step of the BCD process, designed to treat solid matrices requires mechanical pre-treatment. Soils and other materials are sieved to remove oversize bricks and stones and metals. The oversize is then crushed and then added to the bulk of the material. A maximum particle size of 50 mm is specified. In practice materials are crushed to 35 mm or less to speed up the desorption process. The process can tolerate other inorganic or organic debris in so far as this material is smaller than 50 mm or can be shredded down to this size.
In the second reaction step liquids are pumped directly to the reactor, solids, filter dust and paste like or sticky chemicals and POP residues are suspended in carrier oil by attrition stirrers. The resulting slurries are then pumped to the reactor. Inorganic materials such as mineral dust or fillers in the chemical compositions can be tolerated in the reaction, and are generally inert.

Configuration: Modular, transportable or fixed plants have been built. The concept of transportable units has not fitted well with permitting and economic aspects. Today's units are either fixed or designed as skid mounted re-locatable units.

Capacity/ Throughput: Soil treatment units have been operated between 100 kg/h and 20 tonnes per hour. The BCD reactors are limited to the solids content in the stirred reactor and are typically 1 to 3 tonnes of POP waste per reactor batch. A reactor will process 2-4 batches per day. The batch cycle time is only marginally effected by the POP concentration.
Both systems are designed for 24 hour continuous operation.
When higher throughputs are required the number of modules is increased.

Efficiency: High destruction efficiencies (4-6 nines) have been demonstrated for DDT, PCBs, PCP, HCB, HCH, and dioxins (PCDD/F) in treatability trials and routine operations.

Applicability: All the above named chemicals as well as other pesticide formulations as pure chemicals and wastes or as contaminants in other media.

Emissions: Older plants had measurable discharges of dioxins and other POPs. Today's plants are equipped with off-gas scrubbing and filtration which has improved together with general technical developments. In line with all such batch units as well as indirectly heated desorbers not only are the emission concentrations low, but the total mass of emitted off-gas is orders of magnitude smaller than incinerators or similar directly fired units.

By-Products: Bonded chlorine is converted quantitively to salt. Either the oil- salt slurry is used as fuel in permitted facilities or separated into the components. The present development sees the use of the excess alkali in a salt solution as a neutralising agent for acidic waste waters. The remaining residue of carbon from the degradation of the POP parent organic compound may be disposed as fuel to suitable combustion processes or rendered safe for controlled landfill.

Practical Issues: Although the large soil desorption units are technically advanced, the smaller units, and the BCD reactors are characterised by their simplicity. Nitrogen blanketing is required however with low consumption rates so that even in countries with developing infrastructure these requirements should in general be obtainable. Safety risks, such as resulted in a fire in Melbourne in 1995 have now been rectified by adding cooling facilities. Emission control is at the general high standard achievable with activated carbon filtration.
The modern catalysts are of moderate cost, but consumption is extremely low.

Sodium hydroxide consumption is a major cost factor, but is directly related to the chlorine content of the POPs and may vary between 200 and 800 kg/t of POP.
Licensing: Commercially licensed in USA, Australia, Mexico, Spain, Czech Republic and neighbouring central European countries.
Vendor: Patent holder; BCD Group Inc., Cincinnati, OH 45208, USA.
Opperman_t@bcdinternational.com www.bcdinternational.com
Info Sources: BCD International literature, BCD license holders and Vijgen, 2002.
Reason for category: This technology has been demonstrated to treat both high strength POP and large throughputs of contaminated soil. Evidence of performance and emissions should be sought from vendor and license holders.

2.1.3 Sodium Reduction

Process: Reduction of PCBs with dispersed metallic sodium in mineral oil. Has been used widely for in-situ removal of PCBs from active transformers. Products of the process include non-halogenated polybiphenyls, sodium chloride, petroleum based oils and water (pH>12).
Pre-treatment: presumably minimal for transformer oil treatment. No indication of how the system is applied to the treatment of capacitors, solids, soils, etc.
Configuration: Transportable and fixed (Powertech have a mobile plant for treating 15,000 litres/day of transformer oil).
Capacity/Throughput: 15,000 litres as above. There is also a unit for treating fluorescent light ballasts with a capacity of 10,000 kg/day
Efficacy: Destruction efficiency of the process has not been reported. However the process has been demonstrated to meet regulatory criteria in EU, USA, Canada, South Africa, Australia, Japan for PCB transformer oil treatment (eg. in Canada to PCB<2 ppm for treated oil; and PCB<0.5 ppm; dioxins<1 ppb for solid residues).
Applicability: PCBs to 10 000 ppm (also claims of applicability to other POPs, but no data)
Emissions: nitrogen and hydrogen gas. No info on organic emissions.
By-products: dehalogenated organics (eg. polybiphenyls), sodium chloride and water (pH>12).
Practical Issues: Lack of information on characterisation of residues. If used for in-situ treatment of transformer oils then may not destroy all PCBs contained in porous internals of the transformer. Sodium requirements will be significant (100-500kg/tonne of PCB), and supply, storage and handling will present significant challenges in developing countries.
Licensing: Widely available worldwide
Vendor(s): many. eg. Powertech, Vancouver, Canada. (www.powertechlabs.com)
Information Sources: Powertech literature
Reason for category: This technology has been commercially used for treating PCBs for a number of years.

2.1.4 Super-Critical Water Oxidation (SCWO)

Process: SCWO destroys toxic and hazardous organic wastes in a compact totally enclosed system, using an oxidant (eg. oxygen or hydrogen peroxide) at temperatures and pressures above the critical point of water (374°C and 22.1 MPa). Under these conditions organic materials become highly soluble in water and react rapidly produce carbon dioxide, water and inorganic acids or salts. SCWO technology has been around for many years, but the earlier systems were plagued by reliability, corrosion and plugging problems. Recent developments by Foster and Wheeler and General Atomics have effectively addressed these problems through the use of special reactor designs and corrosion resistant materials. The process has now been effectively demonstrated at pilot and developmental scales and was recently

approved for full-scale development and use in the US Chemical Weapons programme. A commercial scale plant has also recently begun operating in Japan.

Pre-treatment: The system is limited to treatment of liquid wastes or solids less than 200microns in diameter, and an organic content of less than 20%. Other pre-treatment requirements have not been assessed.

Configuration: Current pilot plant systems are fixed configuration, but the units should be transportable. Recent development of an on-board unit for treatment of hazardous wastes on ships indicates the potential for transportable applications.

Capacity/Throughput: Current demonstrations units are up to 400 kg/hr, with plans for a full-scale unit of 2700kg/hr (64.8 t/day).

Efficacy: Bench scale testing has demonstrated potential for high destruction efficiency of POPs.

Applicability: Demonstrated for all POPs, but note restrictions above on liquid vs solids and organic content.

Emissions: All emissions and residues may be captured for assay and reprocessing if needed.

By-products: Limited information on by-products from the treatment of POPs.

Practical Issues: Lack of detailed analytical data on process, residues and emissions. Limited commercial operating experience until recently. Potential for dioxin formation if reaction conditions are not optimised.

Licensing: Undergoing trials for US Army chemical weapons demilitarization (Phase 3).

Vendor(s): General Atomics and Foster Wheeler (http://www.ga.com/atg/aps/scwo.html)

Info Sources: General Atomics literature and Vijgen, 2002.
Hatakeda et al., 1999; Kronholm, 2003.

Reason for category: A commercial scale system is operating in Japan.

2.1.5 Plasma Arc (PLASCON)

Process: This process involves directing an electric current through a low-pressure gas stream, creating a thermal plasma field which can reach 5000 to 15000°C. The intense high temperature zone is used to either dissociate waste into its atomic elements by injecting the waste into the plasma, or as a heat source for combustion or pyrolysis. The National Research Council (1993) described the waste streams from plasma arc destruction of wastes as *"essentially the same as those from incineration…"* such as combustion by-products and salts. Various plasma reactors have been developed for the thermal destruction of hazardous waste but only the PLASCON In Flight Plasma Arc System falls into the definition of non-combustion.

In the PLASCON system, a liquid or gaseous waste stream together with argon is injected directly into a plasma arc. Organic chemicals in the waste disassociate into elemental ions and atoms, recombining in the cooler area of the reaction. The resulting end products include gases consisting of argon, carbon dioxide and water vapour and an aqueous solution of inorganic sodium salts (including sodium chloride, sodium bicarbonate and sodium fluoride). Further treatment of the end product is not required.

The bulk of the waste treated by PLASCON originates from electrical transformers and capacitors. Once received at the plant, it is transferred to a bulk feed storage vessel. Any contaminated solids are then broken up and the remaining liquid is extracted by a thermal desorption process. The condensed vapours are added to the liquid storage. The liquid waste is then pumped directly to the PLASCON process for destruction.

PLASCON is not currently configured to treat a range of waste types (e.g. contaminated soil, capacitors, etc.) However, in conjunction with appropriate preprocessing (e.g., thermal desorption) its applicability is broadened. Bench scale tests achieved DREs ranging from 99.9999 to 99.999999 percent. Like the other plasma arc process, no data were

found describing the concentrations of undestroyed chemicals in process residues other than gaseous emissions so that the destruction efficiency of this technology remains unknown. However, dioxins were found to occur in scrubber water and stack gases in the part per trillion range.

Pre-treatment: Liquid waste streams (either organic or aqueous) of any concentration can be treated but it is most cost effective to treat concentrated wastes. Solids can be treated if in the form of a pumpable fine slurry. Contaminated soil and very viscous liquids or sludges thicker than 30 to 40 weight motor oil cannot be processed by the system without pretreatment. However, the system can be linked with thermal desorption or other pretreatment methods to treat a wide range of solids and sludges. Special wastes such as capacitors and transformers can be treated after pretreatment to remove solids.

Configuration: Transportable and fixed units are available.

Capacity/Throughput: In the order of 1 to 3 tonnes/day of waste can be treated by a 150 kW unit. The residence time of the waste in the reaction chamber is very short (approximately 20-50 milliseconds) since such high operational temperatures are utilised. This results in a small process inventory, with less than 0.5 g of waste being destroyed at any instant.

Efficacy: Test samples of PCBs made up from an Askarel type oil containing Aroclor 1260 and trichlorobenzenes in the ratio of 65:35 which were treated in a bench scale plasma arc unit showed dioxin levels in scrubber water and stack gases in the part per trillion range. The Aroclor 1260 mainly contains hexachlorinated (42%) and heptachlorinated (38%) biphenyls. DREs in the test ranged from six to eight nines confirming in-flight plasma systems can achieve very high destruction efficiencies. Dioxin formation is generally avoided in in-flight systems such as PLASCON, because the process involves pyrolysis rather than combustion.

Applicability: PLASCON has, to date, treated wastes including:

- Halon 1211;
- CFC 11, CFC 12;
- HCFC 22;
- Askarel (65% PCB, 35% trichlorobenzene);
- Nufarm waste (40% chlorophenols, 40% chloropentoxy acetates, 20% toluene).

A plant in Queensland, Australia, is used to destroy a variety of PCB wastes, containing chlorine concentrations up to approximately 60 per cent w/w. The plant operates 24 hours a day, treating waste at the rate of 40-45 kg/h. The level of PCB in the effluent discharged to the sewer from the plant complies with the 2 ppb limit specified in the Australian Government's PCB Management Plan. Recently the plant has also been configured to destroy obsolete pesticide wastes.

Emissions: Plasma arc treatment involves a much lower quantity of combustion gases than incineration, thus reducing the risk associated with the discharge of the emissions to air and the cost of air pollution control. Given the very low process inventory in the PLASCON system (i.e. less than 1 g in the reaction chamber), the risk associated with release of partially treated wastes following a process failure is very low.

By-products: Caustic scrubber solutions

Practical Issues: The capital cost of a 150kW PLASCON unit is approximately US$1million, depending on the configuration. Operating costs including labour vary depending on the work to be treated and the location of the site. These costs are estimated to be under $3000/tonne but typically range from $1500 - $2000/tonne. There is a considerable range of cost depending upon factors such as:

- waste feed - molecular structure and weight;
- electricity costs;
- argon and oxygen costs;
- geographic location and site specific issues;

- caustic costs; and
- the required emission limits.

The economics of the process are not sensitive to chlorine content of the waste.

A significant advantage of the PLASCON system is the low process inventory. The process is electrically powered and can be shut down or started up in seconds. Process control interlocks are provided to prevent the release of incompletely treated waste, in the case of power failure or similar process upset. Other safety hazards relate to the storage of hazardous materials prior to treatment and the use of high temperatures. Emissions from the treatment system are limited to an emission to air containing argon, oxygen, water vapour and carbon dioxide, and a trade waste discharge containing a sodium halide salt. Dioxin formation is avoided by the use of pyrolysing conditions.

There is a risk of explosion from internal cooling water leaks and molten metal or slag discharges.

Licensing: BCD Technologies Pty Ltd, PO Box 119, Narangba QLD 4504, telephone: +61 (0)7 3203 3400; fax: +61 (0)7 3203 3450.

Vendor(s): BCD Technologies Pty Ltd.

Info Sources: Rahuman et al. 2000; Costner, Luscombe and Simpson, 1998; CMPS&F - Environment Australia, 1997; SLR Technologies (as quoted by CMPS&F – Environment Australia, 1997).

Reason for category: This is a proven, existing technology.

2.1.6 Pyrolysis

Process: Pyrolysis is a well-known method of heating in an oxygen deficit atmosphere resulting in gasification of organic and melting of mineral components. A plasma torch (~15,000°C) is used inside a cylindrical reaction vessel containing mixed bulk gases. Plasma feed gases (air, argon, CO_2 or nitrogen) are introduced and product gases removed at the top of the chamber and waste materials (solid, liquid or gas) plus steam are fed in from the side. Inorganic portions of the waste remain in the reactor as reduced metals and a glassy slag. Off gases are polished through scrubbers and filters, and can be reused as synthesis gas. These processes are endothermic and thus require feeding significant levels of heat into the furnace, thereby increasing power in the power sources. The recuperation of energy is possible only due to combustion of obtained pyrolytic gas (syn-gas).

According to CMPS&F - Environment Australia (1997), 'the STARTECH Plasma-electric Waste Converter (PWC) was developed in the US by the Startech Environmental Corporation. The Plasma Waste Converter forces gas through an electrical field to ionise the gas into a plasma. The plasma operates at temperature in the order of 3,000 to 5,000^{o}C. The plasma chamber operates at normal atmospheric pressure. The PWC may best be described as a plasma heated pyrolysis system, where wastes are reduced to their metallic components, a slag and a gas that can be used as a fuel. In this respect the STARTECH system is more similar to the PACT technology than the PLASCON technology, although it operates in an oxygen deficient or reducing atmosphere.

Organic and inorganic wastes can be introduced into the plasma chamber as solids, liquids, gases, and sludges, where they dissociate into their elemental atomic components. Gas recovered from the top of the chamber is treated and can be reused as chemical feed stock or fuel gas. Molten solids are removed from the bottom of the chamber and can also be reused.

Solid wastes fed into the system do not ordinarily need to be pre-conditioned or shredded, and can be in bulk form. Feeding is automatic through an air locked infeed port and is normally on a continuous basis, but can be batch fed. Liquids, gases and sludges can also be fed or pumped directly into the chamber through a pipe port, and can be fed in with bulk solids at the same time if required.

The STARTECH Plasma Waste Converter is a closed-loop system in which wastes, depending on their type, may be converted into recoverable commodity products. Recovered gas, "Plasma Converted Gas", may be used for chemical feed stock to produce, for example, polymers, or fuel gas for plant heating or to produce electricity. Recovered solids include metals, and an inert silicate stone which can be used as aggregate in the building and construction industry, or as an abrasive. ‘

Pre-treatment: None needed.

Configuration: Transportable and fixed.

Capacity/Throughput: Demonstrated at 50 – 100 kg/hr and commercial unit designed for 10 tonnes/day

Efficacy:

Applicability: This treatment can process solid, liquid and gaseous pesticide wastes.

Emissions: Synthesis gas (CO, CO_2 and H_2), which can be used as a fuel

By-products: Caustic scrubber liquid, filter residues, and solid residues (slag).

Practical Issues: Moderate energy inputs and reliable electricity and cooling water supplies. Risk of explosion from internal cooling water leaks. Molten metal or slag discharges.

Licensing: Startech Environmental Corp., 15 Old Danbury Road, Wilton, CT. 06897-2525
Telephone: (203) 762-2499
Toll Free: (888) 807-9443
Fax: (203) 761-0839
Email: starmail@startech.net

Vendor(s): Startech Environmental Corp.

Information Sources: Startech Environmental Corp.

Reason for category: This is a proven, operating, commercial technology.

2.2 Category B

Technologies near or at the start of commercialization

2.2.1 Molten Salt Oxidation

Process: Molten salt oxidation is a thermal means of completely oxidizing (destroying) the organic constituents of mixed and hazardous waste. The flameless reaction takes place at 700 to 950°C in a pool of benign salts, which is usually either sodium carbonate or a eutectic of alkali carbonates.

Oxidant air is added with the waste stream into the salt bath, and the reaction takes place within the salt bath virtually eliminating the fugitive inventories found in incineration. The organic components of the waste react with oxygen to produce CO_2, N_2, and water. Inorganics like halogens, sulphur and phosphorus are converted to acid gases, which are then "scrubbed" and trapped in the salt in forms such as NaCl and Na_2SO_4. Other incombustible inorganic constituents, heavy metals and radionuclides are held captive in the salt, either as metals or oxides, and are easily separated for disposal. The materials to be processed are normally conveyed into the oxidizing chambers using pneumatic feed systems and at times, solids have to be reduced to small particle sizes for pneumatic conveying. Liquid wastes are injected using commercial oil gun systems. The reaction product gases contain nitrogen, carbon dioxide, oxygen and steam, along with reaction salts, depending on the wastes (CMPS&F–Environment Australia, 1997).

From Lawrence Livermore National Laboratory website:

As part of its ancillary demilitarization and waste reduction mission, the Laboratory has developed methods for the safe and environmentally friendly destruction of difficult waste streams. Molten Salt Oxidation (MSO) is a thermal, flameless process that has the inherent capability of completely destroying organic constituents of mixed wastes (chlorinated solvents, spent ion exchange resin), hazardous wastes (PCB-contaminated oils), and explosives. ("Mixed wastes" are those that are both hazardous—toxic, flammable, etc.—and radioactive.) MSO can treat a wide variety of solid, liquid, and gaseous waste streams while producing low levels of fugitive emissions in the off-gas. Organic materials are converted into carbon dioxide, nitrogen, and water vapor. Radionuclides, metals, and other inorganic materials in the waste stream are captured and held in the salt. Chlorine, fluorine, bromine, phosphorous, sulfur and other acid-producing components are captured in the salt as chlorides, fluorides, bromides, and sulfates, respectively. MSO is an environmentally friendly alternative to incineration for the treatment of a variety of organic wastes. The Department of Energy and the U.S. Army Defense Ammunition Center direct the technology development.

MSO is an ideal way to destroy a variety of difficult waste streams. It has been demonstrated to be a safe and effective method to destroy wastes of interest to both the Department of Defense and the Department of Energy. LLNL built an integrated MSO facility in 1997 to demonstrate the technology. Over 30 types of waste streams were demonstrated in the facility from 1997 to 1999. DOE has transferred the MSO facility to Richland, Washington in 2000 for further implementation of the technology at an industrial scale with real mixed waste streams. Moreover, a Lawrence Livermore National Laboratory (LLNL) designed unit is currently at Eglin Air Force Base, and another is under construction at LLNL for the U.S. Army to be installed in the Republic of Korea (ROK). The ROK MSO system is anticipated to be fully operational in the spring of 2001. Another MSO facility is planned for the Blue Grass Army Depot in Kentucky in 2002.

Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A

Efficacy: No detailed information about true destruction efficiencies available. High DRE has been reported for chlordane in trials. Very high efficiencies (>99.9999%) are reported for liquid PCBs, PCB-containing solids, HCB, and chlordane. The process can accommodate organics with heavy metals.
Applicability: Potentially applicable to most hazardous wastes at high strengths
Emissions: CO_2, N, H_2O vapour
By-products: Salts which may contain heavy metals and other inorganic contaminants
Practical Issues: Lack of detailed analytical data. Large volume of potentially hazardous salts generated in process requiring disposal. The operating costs are high and the system requires bag-houses for the metal/ particulate content in the off-gases. Sodium carbonate is the only preferred salt and materials like phosphorus, chlorine and sulphur are converted into inorganic salts and they are part of the salt overflow collected as waste. The process has been shown to be robust with very low risks of failure (United States Department of Energy).
Licensing: Lawrence Livermore National Laboratory, USA (http://www-cms.llnl.gov/s-t/molten.html)
Vendor(s): Lawrence Livermore National Laboratory, USA
Info Sources: UNEP, 2003.
Reason for category: Proof is required to confirm applicability to high strength wastes but the technology appears to be robust and safe.

2.2.2 Solvated Electron Technology

Process: Solvated electron solutions are produced by dissolving alkali or alkaline earth metals (sodium, lithium or calcium) in anhydrous ammonia at room temperature (but in a pressurised system. Alternatively the reagent can be prepared at sub-ambient temperatures with lower pressure control requirements). Other solvents such as amines and some glycols have also been used. The contaminated materials are placed into a treatment cell with the treatment solution, and POPs wastes are reduced to metal salts and simple hydrocarbon compounds. eg. PCBs are reduced to petroleum hydrocarbons, sodium chloride, and sodium amide. At the end of the reaction, ammonia is removed for reuse, and the treatment residues (eg. oil or soil) are removed from the cell and disposed.
Pre-treatment: Solvated electron solutions are negatively affected by water, iron compounds, oxygen and carbon dioxide. Materials with a high water content (>40% w/w) must be de-watered prior to treatment. Commodore claim to have developed a special process for neutralising these potential effects as an integral part of the treatment process. Size restrictions are currently 45cm diameter for solid materials. (Note from Basel guide. Even moderate amounts of water are undesirable because this will react with the sodium and increase requirements for this chemical. Water present in the ammonia also inhibits the solvation process. Ammonia can not penetrate concrete or wood so these materials will need to be crushed or shredded if they are to be effectively decontaminated).
Configuration: The SOLV^{TM} process has been developed as a modular transportable system, based around the central SET^{TM} treatment module. Other units would include front-end modules for water removal or contaminant extraction/pre-concentration, and back-end units for ammonia recycling (refrigeration), pH adjustment, and post treatment of the residues.
Capacity/Throughput: The system is scaleable to accommodate a range of required throughputs. Current commercial systems are available for treating up to 10 tonnes/day.
Efficacy: High destruction efficiencies have been reported for DDT, dioxins/furans and PCBs. The system has been used effectively for PCB oils up to 20,000 ppm (2%), although there is some indication of applicability to higher concentrations as well.
Applicability: All POPs – including PCB transformers, capacitors, and oils. The process has been predominantly used to date for the treatment of PCB oils and soils contaminated with a

variety of organics. It has also been used for the treatment of contaminated surfaces such as concrete and metals.

Emissions: All emissions and residues may be captured for assay and reprocessing if needed. No measurements reported for dioxin/furan levels in off-gas.

By-products: sodium salts and simple hydrocarbons.

Practical Issues: Use of anhydrous ammonia and sodium metal, potential for over-pressurisation and probable supply and handling difficulties in developing countries, and significant health & safety issues. Reliable power supplies are essential to ensure the system can be maintained at the required temperatures and pressures. Limited analysis data for off-gases and limited experience at commercial scale.

Licensing: Commercially licensed for PCB wastes in USA.

Vendor(s): Commodore Applied Technologies Inc., 150 East 58th Street, New York, NY 10155, USA. Phone (212) 308-5800, Fax (212) 753-0731. (www.commodore.com)

Other Info: Commodore Applied Technologies was de-listed from the American Stock Exchange in Feb 2003. Reasons for the delisting were (i) the Company's losses from continuing operations over the five most recent fiscal years, (ii) the Company's failure to meet specified thresholds for stockholder's equity; and (iii) and the Company's failure to hold an annual meeting of stockholders.

Info Sources: Commodore Applied Technologies literature and Vijgen, 2002.

Reason for category: This is a proven technology although some proof of applicability to high strength POP wastes is necessary and it is not operating commercially yet.

2.3 Category C

Promising Technologies

2.3.1 Ball Milling

Process: The POPs wastes are placed in a ball mill with a hydrogen donor compound in the presence of an alkali metal (magnesium, sodium, etc). Reductive dehalogenation occurs due to mechanochemical process yielding, in the case of PCBs reacting with magnesium: biphenyl and magnesium chloride.

A mobile full scale Series II MCD plant for the remediation of the Fruitgrowers Chemical Company (FCC) site at Mapua, New Zealand, has been designed and is under construction. Initial full-scale trials undertaken on the skeleton plant show that the MCD process has the capacity to reduce contamination levels from >3500mg/kg DDT to below the soil acceptance criteria of 200mg/kg DDT. Other contaminants, dieldrin, aldrin and lindane, are also destroyed. Inherent in the design of the MCD process is flexibility to adjust various parameters to regulate destruction efficiency and throughput as required. Consents to remediate the site using the MCD process have been applied for. Remediation work will begin with a 'Proof of Performance' trial in October 2003.

Pre-treatment: The system has the potential capability to process a wide range of wastes without pre-treatment, including waste containers.

Configuration: Uses conventional ball milling equipment, so should be available in a range of different configurations.

Capacity/Throughput: No commercial information available as yet.

Efficacy: Limited information. Some testing data suggests may be capable of high DE. Claimed that process can be selective and generates well-defined products.

Applicability: Process should be applicable to all POPs wastes but is currently only applicable to low strength <1%) wastes.

Emissions: Ball mill operates as closed batch system, so releases should be contained. No testing data on air releases.

By-products: Reduced organics plus metal salts.

Practical Issues: The limited information characterising the residues and releases from the process. Extremely limited commercial experience of the processing of POPs wastes.

Licensing: Only trial scale processing/development in Germany. Full-scale plant under development in New Zealand.

Vendor(s): Tribochem, Wunstorf, Germany (www.tribochem.com)

Environmental Decontamination Ltd. (EDL), Auckland, New Zealand

Info Sources: Environmental Decontamination Ltd. (EDL), Auckland, New Zealand; Vijgen, 2002.

Reason for category: A pilot plant has been built in both Germany and in Japan but, at this point, there has been no confirmation that this technology can treat full strength POP stockpiles.

2.3.2 GeoMelt™ Process

Process: The GeoMelt process works by establishing a melt between pairs of electrodes inserted into the soil-bound waste materials. Electrical energy is continuously applied to the melt until it grows to encompass the entire treatment volume. Individual melts of up to 1000 tons have been performed in surface deposits and also below ground. Organic contaminants present in the soil are decomposed at the high temperatures produced in the melt. Off-gases generated by the process are collected inside a stainless steel hood covering the treatment area and are drawn off for processing by an off-gas treatment system. This consists of filtration,

dry and wet scrubbing and thermal treatment. After treatment, the residual soil solidifies into a glassy/rock-like material.

Pre-treatment: Highly saturated soils should be dewatered before treatment, and precautions taken against groundwater recharge, where relevant.

Configuration: Fixed and transportable systems

Capacity/Throughput: To date the system has been used for treating contaminated soil in quantities of up to 7000 tons. Capacity is stated to be 90 tons/day. An in-container system is also available with a throughput of 45 tons/day.

Efficacy: Organochlorine DREs of 90 to 99.99% have been demonstrated in the melt, and overall performance levels of 4 to 6 nines have been achieved in combination with the off-gas treatment system.

Applicability: The system has been used for soil contaminated with a range of POPs pesticides and PCBs, including a 33% POP/soil mixture.

Emissions: No dioxins and PCBs detected in off-gases.

By-products: The solid residues produced show no significant leaching. Other residuals include scrubbing liquors, carbon filters. These and other solid residues are typically disposed by incorporation into the next melt. No application of this technology to destruction of POP stockpiles but could be used to treat a variety of hazardous wastes.

Practical Issues: Significant electricity requirements.

Licensing: USA and Australia

Vendor(s): AMEC Earth & Environmental Inc – Geomelt Division (www.amec.com).

Info Sources: Vijgen, 2002.

Reason for category: A pilot scale plant is operating in Japan but, at this point, there has been no confirmation that this technology can treat full strength POP stockpiles.

2.3.3 Mediated Electrochemical Oxidation (CerOx)

Process: The CerOx process uses Ce^{4+} as an oxidising agent. This reacts with POPs to produce carbon dioxide, neutral salts and dilute acid solution. The process operates at low temperature (90-95^{o}C) and near atmospheric pressure. A core component is the so-called T-CELL, which utilises similar membrane technology to that commonly used for chlorine manufacture, with the anolyte (cerium reagent) and catholyte (nitric acid) being physically separated at all times by a fluoropolymer membrane. Ce^{4+} ions are produced in the cell and then mixed with the waste stream prior to passing into a liquid phase reactor. Excess reagent is maintained in the reactor by monitoring Ce^{3+}/Ce^{4+} ratios in the effluent and adjusting the organic waste input accordingly. The liquid effluent from the reactor is returned to the cell for regeneration of the cerium reagent. Gaseous products from the liquid reactor are passed into a packed bed gas phase reactor which uses a countercurrent flow of Ce^{4+} for oxidation of the residual organics. The treated gases (mainly CO_2 and Cl_2) are then passed through a condenser (for VOC recycling) and a caustic scrubber for chlorine removal.

Pre-treatment: Solids and sludges are homogenized and pumped into the system as a liquid. As this is an aqueous process, organic wastes must be pre-treated by sonication to emulsify the mixture and increase the potential liquid/liquid contact.

Configuration: Modular system design which indicates potential for set-up as a transportable system (but only for small capacities). The CerOx system is based around a number of cellpacks plus external modules for electrolyte circulation and storage, waste injection, mixing and holding, off-gas handling and processing, electrolyte regeneration, and electronic monitoring and recording. Larger units are made up by combining several treatment modules. The UNEP (2002) report suggests that this and similar AgII process would be well suited to use in developing countries because of the ease of transportation and assembly for on-site treatment operations.

Capacity/Throughput: The base unit, consisting of 2 cellpacks, has a processing capacity of 25 gallons/day, based on a 50% organics liquid input (ca. 2kg/hr of organics). Single units based on multiple cells are available up to a capacity of 100 gallons/day. Alternatively, the company offers treatment plant packages based on a bank of 30 cells, with a capacity of 2-4000 gallons/day, with larger installations being produced from multiples of these, with up to 10 times the capacity (20-40,000 gallons/day for 50% organics. i.e. approx 2-4 tonnes/hr). The footprints for these plants are 30ft x 24ft and 200ft x 90ft (the size of a football field), respectively.
Efficacy: This technology has demonstrated high destruction efficiencies in trials (eg. >99.995% for chlorinated pesticides, including chlordane. Also tested semi-quantitatively for small-scale PCB (2 ppm) and dioxin (5 ppm) destruction.
Applicability: Theoretically, all POPs, including high strength wastes.
Emissions: The system is designed for continuous discharge but would be capable of containing all process streams. There should be no significant discharges to air because of the low temperature involved. Liquid discharges are primarily caustic solution from the chlorine scrubber.
By-products: Carbon dioxide gas, and the scrubber liquor, which will contain chloride and hypochlorite plus ionic byproducts from any other hetero-atoms present in the waste (eg sulphate, phosphate). Metals and other inorganics in the waste stream are gradually concentrated in the cerium solution. This is addressed through either periodic replacement of the cerium solution (on small units) or use of a continuous bleed system to "inorganic removal modules" (on larger plant).
Practical Issues: Only laboratory scale experience with treatment of POPs wastes. Limited operating/commercial experience. It is not clear whether the electrochemical cells could tolerate organic contaminants which could be present in the treatment solution in the event of incomplete reaction.

Company information indicates that solid wastes can be processed as a slurry. However it is hard to see the system coping with high loadings of inert solids, which would presumably remain in the liquid phase reactor unit and be cycled through the electrochemical cells.

Electricity requirements are not insignificant at 40 kWh for the smallest unit, 2400 kWh for the small package plant and 23,000 kWh for the 20-40,000 gallons/day installation. Expected life of the platinum-coated electrodes appears to be "several years".
Licensing: CerOx is operated in USA (NB. Process does not apparently require licensing under RCRA due to minimal emissions).
Vendor(s): CerOx Corporation, USA (www.cerox.com)
Info Sources: CerOx literature and Vijgen, 2002.
Reason for category: Significant research has been undertaken on this process.

2.3.4 Mediated Electrochemical Oxidation (AEA Silver II Process)

Process: The AEA Silver II process is very similar to the CerOx system but utilises oxidation of organics with Ag^{2+} ions in solution. The oxidising agent reacts with the organics to produce carbon dioxide, neutral salts and dilute acid solution. The process operates at low temperature (60-90^{o}C) and atmospheric pressure.
Pre-treatment: No information provided but the system is claimed to be applicable to both solid and liquid wastes.
Configuration: Concepts developed for production as a modular/transportable system, but not yet proven. System design is similar to CerOx but includes a hydrocyclone between the reactor and the electrochemical cells, which would reduce potential problems from solids inputs to the latter.

Capacity/Throughput: According to the vendor, the optimum treatment efficiency is achieved at an organic concentration (as carbon) of 2-10 g/litre (<1%). System currently only proven to a size of 12kW, which equates to an organic throughput of about 30 kg/day (as carbon – ca. 1-2 kg/hr total organics). A costed design has been produced for a 1 MW unit, which would have a throughput of about 1-2 tonnes/day, but the vendor believes a further 2 year's development effort would be required to fully prove this system.
Efficacy: This technology has demonstrated high destruction efficiencies in trials with a range of chemicals, including some pesticides but no POPs.
Applicability: Theoretically, all POPs but it is not clear if this technology can treat high strength wastes.
Emissions: The system is capable of containing all process streams. Discharges to air and water are similar to the CerOx system.
By-products: As for the CerOx system. The plant design includes provision for filtration of solid residues from the reactor tank prior to liquid discharge.
Practical Issues: Limited detailed information about residues and process wastes. Mainly laboratory scale experience with treatment of POPs-related wastes, although a 2001 report indicated that further pesticide trials were being planned. Limited operating/commercial experience. System requires oxygen gas for nitric acid regeneration. High chlorine contents in wastes can lead to silver chloride precipitation, which would then require an auxiliary system for silver recovery (not yet developed).
Licensing: AEA Silver II process is currently undergoing trials by US Army for chemical weapons demilitarization.
Vendor(s): AEA Technologies UK, (www.accentus.co.uk)
Info Sources: AEA product literature and Vijgen, 2002.
Reason for category: Currently this is only able to treat low strength (<1%) organic wastes; further research is necessary to prove its ability to treat high strength POP wastes.

2.3.5 Catalytic Hydrogenation

Process: 'This CSIRO process is based on the mild hydrogenation of spent oil in a packed bed catalytic reactor, operating at moderate temperatures and pressures. Under process conditions hydrogen reacts with heteroatoms in the oil itself, and also with any organochlorines present.

The removal of halogen atoms from organic structures by hydrogenation over noble metal catalysts has been known for many years, and its potential application to the destruction of chlorinated wastes recognised. These reactions can be accomplished at very mild pressures and temperatures, but unfortunately the catalysts are very susceptible to poisoning by a wide range of elements commonly found in "real world" situations. Prominent among these poisons are the sulfur compounds found in petroleum products such as transformer oils. Fortunately, there is a group of hydrogenation catalysts based on metal sulfides which are extremely robust and tolerant of most catalyst poisons. They are considerably less active than noble metal catalysts, so that at the conditions required for hydrodechlorination, the hydrogen chloride formed causes extensive cracking and rearrangement of hydrocarbons. This results in excessive hydrogen consumption and unacceptable changes in transformer oil composition.

We have overcome this problem by using a proprietary additive which scavenges the hydrogen chloride and ensures that the hydrochloric acid produced does not lead to degradation of the catalyst and which reduce hydrocarbon cracking reactions on the surface of the catalyst. After a program of catalyst and process optimisation, it was possible to keep the hydrocarbon structure of transformer oil essentially unchanged, while achieving better than 99.999% destruction of PCB. With transformer oils oxygen present in compounds resulting

from aging of the oil in service is converted to water, while any chlorinated species present are converted to hydrogen chloride and light hydrocarbons (Figure 1).

Downstream processing involves separation of the gases and light hydrocarbons from the regenerated oil, and washing stages for the product oil to remove chlorides formed as a reaction product of organochlorine destruction. In the prototype most of the gases leaving the reactor are recycled, with a small purge gas stream passing to a catalytic combustor.' (Duffy and Fookes, 1997).

Pre-treatment: N/A

Configuration: Pilot scale – used for a commercial treatment of 3000 litres of PCB oil with concentration < 1000 ppm. Has also been tested on a wide range of POPs.

Capacity/Throughput: N/A

Efficacy:

Table 2.3 Destruction Efficiencies of Catalytic Hydrogenation. From Duffy and Fookes (1997)

Compound	Feed Concentration (mg/kg)	Product Concentration (mg/kg)	Destruction Efficiency (%)
PCB	40,000	<0.027	>99.99993
DDT	40,000	<0.004	>99.99999
PCP	30,000	<0.003	>99.99999
HCB	1,340	<0.005	>99.9996
1,2,3,4-TCDD	46	<0.000004	>99.99999

Applicability: Potentially all POPs in liquid form.

Emissions: Purge gases are subjected to two stages of caustic scrubbing to remove acid gases such as H_2S and HCl. The purge gas is then passed through a catalytic combustor to burn residual hydrogen and any non-condensable hydrocarbons (methane, ethane) formed in the process (Duffy and Fookes, 1997).

By-products: HCl, light hydrocarbons

Practical Issues: A 1/10 scale prototype pilot plant for transformer oil regeneration with a throughput of 1000 l/day has been operating at CSIRO Lucas Heights laboratories since 1997.

Licensing: Commonwealth Industrial Research Organisation (CSIRO), Australia

Vendor(s): Commonwealth Industrial Research Organisation (CSIRO), Australia

Info Sources: Costner, Luscombe and Simpson, 1998

Reason for category: Although a pilot plant has been developed, it is still only applicable to low level wastes; significant research is necessary to establish its applicability to POPs at high strengths.

2.4 Category D

Technologies which require significant research

No technologies appear to be currently at the laboratory scale of testing for destruction of POPs stockpiles. Annexure 1 lists some technologies which have undergone some preliminary research but there have been little published data on their potential.

2.5 Category E

Technologies which are unlikely to be applicable to destruction of POP stockpiles

2.5.1 $MnO_x/TiO_2–Al_2O_3$ Catalyst Degradation

Process: From Liu et al. 2001:
'A highly active catalyst, $M_nO_x/TiO_2–Al_2O_3$, was prepared by impregnating M_nO_x species on TiO-modified Al_2O_3. The TiO species in $TiO_2–Al_2O_3$ support is in a monolayer dispersion, and the M_nO_x species is again highly dispersed on $TiO_2–Al_2O_3$ support. The total oxidation of chlorobenzene and *o*-dichlorobenzene on $M_nO_x/TiO_2–Al_2O_3$ catalyst can be achieved at 300°C and 250°C respectively, at the space velocity of 8000 h^{-1}. The activity of $MnO_x/ TiO_2 –Al_2O_3$ catalyst (Min loading 11.2 wt%) is gradually increased in the first 10–20 h and then keeps stable at least for the measured 52 h at 16,000 h^{-1}. Furthermore, no chlorinated organic byproducts are detected in the effluent during the oxidative destruction of chlorobenzene and o-dichlorobenzene. It is proposed that the partially chlorinated and highly dispersed manganese oxide on a monolayer TiO_2-modified Al_2O_3 is responsible for the high and stable activity for the total oxidation of chlorinated aromatics.'
Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: 100% degradation
Applicability: 1300ppmv chlorinated benzene gas; potentially all POPs
Emissions: N/A
By-products: HCl, H_2O, carbon oxides
Practical Issues: This technology requires assessment for destruction of POPs
Licensing: N/A
Vendor(s): N/A
Info Sources: Liu et al., 2001.
Reason for category: This has only been tested at laboratory level for treating low level POPs; significant research is needed to determine its suitability for treating high strength POP wastes.

2.5.2 TiO_2-based V_2O_5/WO_3 Catalysis

Process: From Weber and Sakurai, 2001:
'In this study, PCB were destroyed on a V_2O_5/WO_3 supported titanium catalyst at low temperature in the range of 150–300°C. At a space velocity of 5000 h 1 more than 98% could be removed. Below 250°C, the higher chlorinated PCB remained partly unchanged on the catalyst for several minutes. In contrast, the oxidation process lasted up to hours at a temperature of 150°C. At around 200°C and below a significant part of the PCB were oxidised to the more toxic polychlorinated dibenzofurans (PCDF). The PCDF remained mainly adsorbed on the catalyst. At 250°C, no significant amount of PCDF were detected and at

300^{o}C no byproducts were found.' Lomnicki et al. (2003) found that the presence of water had a significant effect on a vanadia/titania-based catalysts and that some breakdown products were produced.

Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: >99.9% removal of PCB over 30 minutes at T=300^{o}C
Applicability: PCBs, potentially all POPs, including high strength wastes.
Emissions: potential formation of dioxins and furans if temperature should drop below 250^{o}C; removal of O_2 from gas should reduce toxic daughter product formation
By-products: N/A
Practical Issues: This was designed to mimic operation within a MSW incinerator but research is needed into its potential for destruction of POPs and other hazardous organic wastes.
Licensing: Catalyst currently used in commercial operations for NOx removal
Vendor(s):
Info Sources: Weber and Sakurai, 2001; Lomnicki et al., 2003.
Reason for category:

2.5.3 Fe(III) Photocatalyst Degradation

Process: Degradation of pesticides in water at solubility levels using Fe(III)/H_2O_2/UV. Most 100% degraded but some were lower with concerns re toxic daughter products.
From Huston and Pignatello, 1999:
'The destruction of pesticide active ingredients (AI) and commercial formulations in acidic aqueous solution with the catalytic photo-Fenton, Fe(III)/H_2O_2/UV, advanced oxidation process has been studied. The AI are alachlor, aldicarb, atrazine, azinphos-methyl, captan, carbofuran, dicamba, disulfoton, glyphosate, malathion, ethoxylchlor, metolachlor, picloram and simazine. Complete loss of pure AI occurred in most cases in <30 min under the following conditions: 5.0X10^{5}M Fe(III), 1.0X10^{-2}M H_2O_2 , T =25.0^{o}C, pH 2.8 and 1.2X10^{-19} quanta $l^{-1}s^{-1}$ with fluorescent blacklight UV irradiation (300±400 nm). Considerable mineralization over 120 min occurred in most cases as evidenced by the appearance of inorganic ions and the decline in total organic carbon (TOC) of the solution. Intermediate products such as formate, acetate and oxalate appeared in early stages of degradation in some cases. Observed rate constants calculated from initial rates varied by a factor of <03. The commercial products, Furadan (AI, carbofuran), Lasso 4EC (AI, alachlor) and Lasso Microtech (AI, alachlor) were also tested. The "inert ingredients" (adjuvants) present in these products had no effect (Furadan), a slight effect (Lasso 4EC), or a strong effect (Lasso Microtech) on the rate of degradation of the AI. Lasso Microtech, in which the AI is micro-encapsulated in a polymeric shell wall micro-sphere, required slightly elevated temperatures to effect removal of alachlor in a timely manner. The results show that many pesticides and their commercial formulations in dilute aqueous solution are
amenable to photo-Fenton treatment.'

Reactions were carried out in a cylindrical 300-ml borosilicate double-walled reaction vessel with water circulated through the walls to maintain constant temperature. The photochemical reactor chamber (Rayonet RPR-200) contained sixteen 14-W fluorescent black lamps which emit in the range 300-400 nm. Ferrioxalate actinometry indicated that the total light intensity was 1.2x10^{19}photons $l^{-1}s^{-1}$. The lamps were warmed up for 10 min to reach constant output. The pesticide, iron(III) perchlorate, and sodium perchlorate, as needed, were added to the reaction vessel and the temperature was equilibrated to 25.0^{o}C. The pH was then

adjusted to 2.8 with $HClO_4$. The reaction was initiated by adding H_2O_2 (30%), followed by inserting the vessel into the chamber.
Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: 79.4% methoxychlor; 94.3% malathion; 98.8-100% other POPs
Applicability: low level aqueous solutions
Emissions: N/A
By-products: Cl^-
Practical Issues: Current applicable and efficiency levels are too low to be of practical use for destruction of POPs. Further research is required.
Licensing: N/A
Vendor(s): N/A
Info Sources: Huston and Pignatello, 1999; Catastini, Sarakha, Mailhot and Bolte, 2002.
Reason for category: This technology is currently only feasible for treating low strength wastes and it is unlikely that it would ever be feasible for higher strength wastes.

2.5.4 Ozonation/Electrical Discharge Destruction

Process: An electrical discharge is used to either directly treat a VOC and PCDD/F containing gas stream or to produce ozone to indirectly treat the gas stream
From Sun et al., 1998:
'A systematic study with the aim to reduce NO/NO_2, SO_2 and to destroy VOCs and PCDD/F in flue gas by electrical discharge both in laboratory and at a pilot plant has been performed. Results show that 1) both indirect and direct treatment by electrical discharge can reduce NO/NO_2 and SO_2 and can destroy PCDD/F in flue gas; 2) Indirect treatment destroys about 90% of PCDD/F in real industrial flue gas; and 3) It is possible to destroy NO/NO_2, SO_2 and PCDD/F in one step.'
Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: 88% for indirect treatment of VOCs and dioxins/furans
Applicability: VOCs, chlorinated organics, PCDD/PCDF
Emissions: HCl, CO_2
By-products: N/A
Practical Issues: Currently treats only low levels of dioxins/furans; significant research needed to assess potential for treating high concentrations of POPs.
Licensing: N/A
Vendor(s): N/A
Info Sources: Sun et al., 1998.
Reason for category: This technology is currently only feasible for treating low strength wastes and it is unlikely to be successful for higher strength wastes.

2.5.5 Molten Metal

Process: Molten Metal Technology developed the Catalytic Extraction Process in which molten metal acts as both solvent and catalyst. This process uses a heated bath of molten metal to catalytically disrupt molecular bonds of contaminants and convert hazardous wastes into products of commercial value. The liquid metal acts as a catalyst and solvent in the dissociation of waste feed and synthesis of innocuous products. The molten metal causes the chemical compounds to break into their elements, which dissolve in the liquid metal solution.

By adding selected co-reactants and controlling the reaction conditions, some of the dissolved elemental intermediates can be reacted to form desired products of commercial value.

Normally, the gaseous streams contain synthesis gas, a mixture of carbon monoxide and hydrogen. This gaseous stream can be used as low NO_x fuel, or further separated to generate pure hydrogen, synthesis gas etc. The other by-product is a ceramic slag containing alumina, silica and other non-reducible metals. The slag can be usefully converted into industrial abrasives, construction materials or refractory base. Some low volatile metals are also released along with the gaseous emissions. These are trapped and recovered using a cold trap or high efficiency filter.

The process operates under reducing conditions and as such is not conducive to formation of dioxins. Iron and nickel have been used as the metals for the metal baths.

Pre-treatment: N/A

Configuration: N/A

Capacity/Throughput: N/A

Efficacy: DREs greater than 99.9999 percent were achieved with specific chemicals of concern. It is important to note that the developer of CEP has not yet presented data describing the concentrations of undestroyed chemicals found in the end products, other than gases, and other process residues; i.e., the destruction efficiencies achieved by this technology are as yet unknown.

Applicability: Specific waste streams processed using CEP include chlorotoluene, polyvinyl chloride (PVC), surplus metal and weapons components, and heavy residuals from ethylene dichloride and vinyl chloride production. Would also likely be applicable to POPs.

Emissions: Gases, primarily comprised of hydrogen, carbon monoxide and up to 1 percent ethylene, with smaller amounts of other light hydrocarbons

By-products: Ceramic slag phase consisting of silica, alumina and calcium chloride, metal by-products.

Practical Issues: From Costner, Luscombe and Simpson, 1998:

'The National Research Council has observed as follows (National Research Council, 1993)

"The metal furnace does not eliminate the need for a combustion process; the product gases would be oxidized in a separate unit. These gases would likely be very dirty, containing soot from the metal pyrolysis and possibly some slag particulate matter. Gas cleanup will be required before the gas
is released."

In their evaluation of this technology, DOE cautions that, with induction heating of the metal bath, the method apparently used by MMT, the process must be carefully controlled to prevent equipment damage and possible explosion. Other issues raised are as follows (Shwinkendorf et al., 1995):

*...[T]he potential for over-pressure due to rapid gas evolution of volatile bulk materials; ... and development of instrumentation, control, and monitoring systems, including on-line feedback of metal and slag compositions and offgas component*s.

Recently, USEPA recognized MMT's process as achieving the Best Demonstrated Available Technology (BDAT) for processing wastes for which incineration was previously the only approved processing method (Molten Metal Technology, 1996). DOE estimated capital costs for a typical MMT facility to range from $US15 to $US50 million, depending on the volume and composition of the waste stream. For example, the MMT unit at Clean Harbors, which has a capacity of 30,000 tons of waste per year, is estimated to cost between $25 and $35 million. MMT is currently designing facilities for four commercial customers: Hoechst-Celanese (chlorinated plant waste), Clean Harbors (hazardous waste), SEG (ion-exchange resin), and Martin Marietta. MMT and Martin Marietta have formed a new business,

M4 Environmental, L.P., to commercialize CEP for applications for the U.S. Department of Defense and the U.S. Department of Energy.'
Licensing: Molten Metal Technology filed for bankruptcy in 1998. No further information is known.
Vendor(s):
Info Sources: National Research Council, 1993; Molten Metal Technology, 1996; UNEP, 2003; Costner, Luscombe and Simpson, 1998.
Reason for category: Significant problems with this technology have been identified and it is unlikely to be a suitable treatment for high strength POPs.

2.5.6 Molten Slag Process

Process: A molten slag system is used for treatment of liquids, sludges and metal-bearing wastes. In this process, the waste to be treated is blended with steelworks dust and fluxing agents, extracted, dried with heat from the furnace off-gases and fed into a foaming slag layer which forms at the top of the molten iron in an electric arc furnace at a temperature of around 1500°C. The waste sinks into the slag phase, metal oxides are reduced to metals and all organic materials return to their basic elements, like in the molten metal process (CMPS&F – Environment Australia 1997).
Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: The destruction efficiency of this process is still to be confirmed especially for chlorinated organics.
Applicability: Potentially all POPs
Emissions: There is potential for volatilization of the organics if they do not dissolve in the molten slag. The formation of dioxins and other chlorinated organic materials cannot be discounted.
By-products: slag
Practical Issues: There is still insufficient information on this technology's potential to destroy chlorinated organics. Potential for dioxin and furan production poses a major concern.
Licensing: N/A
Vendor(s): Ausmelt, Australia. (www.ausmelt.com.au)
Info Sources: UNEP, 2003
Reason for category: This technology is currently only feasible for treating low strength wastes; significant research is necessary to determine its suitability for treating high strength POP wastes. Significant problems exist with emissions, formation of toxic daughter products and with disposal of the final product.

Bio- and phytoremediation technologies

2.5.7 Photochemically Enhanced Microbial Degradation

Process: From the Patent Application:
'This invention provides for a method of degrading halogenated organic compounds in a medium contaminated with said compounds comprising: (a) contacting the medium with a lignin degrading fungus resistant to ultraviolet irradiation; and (b) exposing the medium to ultraviolet light at an intensity sufficient to photochemically decay the hydrocarbons; wherein step a and step b occur simultaneously. The intensity of the ultraviolet light is not such that the fungi are killed. Preferred species of fungi are those selected from the genus *Phanerochaete*. A preferred species is *P. chrysosporium*.

The method preferably involves the step of treating the medium with an antibiotic prior to contacting with the fungus. Preferred antibiotics are fungicides such as benomyl, triforine, triadimifon, flusilazole and myclobutanil. The method optionally involves the acidification of the medium.

The medium may optionally be treated with an additional carbon source or aeration to enhance the growth rate of the fungi. The fungi are preferably attached to a solid support and more preferably in discontinuous contact with the medium.

More particularly, the method comprises: (a) treating the medium with a fungicide; (b) discontinuously contacting the medium with a strain of *P. chrysosporium*, resistant to ultraviolet irradiation; (c) adding a carbon source to the medium in an amount sufficient to maximize the growth of the *P. chrysosporium*; (d) exposing the *P. chrysosporium* and medium to ultraviolet light at an intensity sufficient to degrade the compounds; and, (e) incubating the medium to permit degradation of the compounds by the *P. chrysosporium;* wherein steps d and e occur simultaneously.

This invention further provides for a system for degrading halogenated organic compounds in a medium, said system comprising: (a) a housing having an access to the outside and defining a space wherein a portion of the space is suitable for containing the medium; (b) a solid surface support positioned within the space and having a surface permitting hyphal attachment by lignin degrading fungi; (c) a means for contacting the medium with the lignin degrading fungus; and, (d) a source of ultraviolet light able to produce sufficient energy to degrade the halogenated organic compounds and arranged to illuminate the support and a portion of the space. The system preferably comprises a plurality of rotatable discs as the solid surface support. Even more preferred is a system where the means for contacting the medium with the fungus comprises a rotatable axle to which the solid surface support is attached.

This invention also provides a strain of *P. chrysosporium* derived from the strain deposited with the ATCC of Rockville, Md. having the Accession No. 74046, deposited on Apr. 10, 1991. This strain is particularly well-suited for use in the above described method and system.'

Pre-treatment: N/A

Configuration: From the Patent Application: **'**The RBC system used was a 3 litre size plastic box (1L medium size) with 5 discs (10 cm diameter) made of polycarbonate clear plastics. The surface of the discs were scratched by filing to facilitate attaching of fungal mycelia. BU-1 was introduced to 1 litre of N-deficient medium, which is described in Table 3, and allowed to grow for 7 days with 2 hr/day irradiation of UV at 300 nm. The discs were rotated at 2 rpm using a small electric motor. Approximately 40% of the surface area of each disc was submerged into the medium. The fungus grew well to form "mylelial mats" on both sides of each disc. At the end of this preincubation period 100 mg of Aroclor 1254 (Analab Inc., lot K040) were added to the medium with enough volume of acetone-ethanol to dissolve this quantity of Aroclor 1254. The change in Aroclor concentration in the medium was monitored from time to time by taking an aliquot of the medium extracted into hexane of analyzing on gas chromatography as before. After 23 days when almost all of the initially added Aroclor has disappeared, a second 100 mg of Aroclor 1254 was added to the system and monitoring was continued up to 43 days. The results show in the accompanying figure clearly demonstrate that this system is capable of degradating Aroclor 1254. Within this time span, all of the initial 100 mg quantity was degraded, and furthermore, approximately 99% of the second batch of 100 mg added were degraded.'

Capacity/Throughput: N/A

Efficacy: 99-100%

Applicability: PCBs; other POPs potentially at high strengths

Emissions: N/A
By-products: CO_2, Cl^-, organic acids
Practical Issues: Further research is required to consider the potential for use of surfactants, the efficacy on other POPs and the limits of concentration; the formation of daughter products; the potential for use of sunlight etc.
Licensing: UNIV CALIFORNIA (US) Patent US5342779, date 1994-08-30.
Vendor(s): N/A
Info Sources: Patent application database esp@cenet
Reason for category: Further evaluation of the production of daughter products needs to be undertaken.

2.5.8 Biodegradation/Fenton's Reaction

Process: From Nam, Rodriguez and Kukor, 2001:
'Using Fe ions and a chelating agent (catechol and gallic acid) combined with H_2O_2, a Fenton reaction at neutral pH was combined with in situ soil bacteria to degrade polycyclic aromatic hydrocarbons at 250-1200 mg/kg soil by 98% for 2-3 ring and 70-85% 4-5 ring HC molecules.'
Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy0: 70-98%
Applicability: PAH contaminated soils up to 600ppm
Emissions: CO_2
By-products: N/A
Practical Issues: Requires research to determine applicability to POPs and the top level of effectiveness. Will likely require some consideration of increasing solubility and development of specialised bacteria which will successfully degrade POPs
Licensing: N/A
Vendor(s): N/A
Info Sources: Nam, Rodriguez and Kukor, 2001.
Reason for category: This technology is currently only feasible for treating low strength wastes and it is unlikely to be successful for higher strength wastes.

2.5.9 White Rot Fungi Biodegradation

Process: From Mester and Tien, 2000:
'White rot fungi are the most significant lignin degraders among the wood inhabiting microorganisms. They degrade lignin by extracellular oxidative enzymes. The ligninolytic enzymes also oxidize various environmental pollutants such as polycyclic aromatic hydrocarbons, chlorophenols, and aromatic dyes. The most ubiquitous ligninolytic enzymes produced by these fungi are lignin peroxidases (LP), manganese peroxidases (MnP), and laccases (phenol oxidases). The peroxidases are heme-containing enzymes having typical catalytic cycles, which are characteristic of other peroxidases as well. One molecule of hydrogen peroxide oxidizes the resting (ferric) enzyme withdrawing two electrons. Then the peroxidase is reduced back in two steps of one electron oxidation in the presence of appropriate reducing substrate. The range of the reducing substrates of the two peroxidases is very different due to their altered substrate binding sites. LP is able to oxidize various aromatic compounds, while MnP oxidizes almost exclusively Mn(II) to Mn(III), which then degrades phenolic compounds. Laccases are copper-containing oxidases. They reduce molecular oxygen to water and oxidize phenolic compounds. In this paper, the mechanism of

pollutant oxidation by ligninolytic enzymes is discussed giving an overview on the recent results of enzyme kinetics and structure.'

Examples of environmental pollutants oxidized by lignin-degrading fungi

Chlorinated compounds	References
2,4-Dichlorophenol, 2,4,5-trichlorophenol, pentachlorophenol,, 2,4-D, 2,4,5-T, DDT, lindane, 3,4-dichloroaniline, polychlorinated dibenzo-p-dioxines, polychlorinated biphenyls	Bumpus et al., 1985; Bollag et al., 1988 Valli and Gold, 1991; Valli et al., 1992 Field et al., 1992; Call and Mücke, 1997.

Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: 70%
Applicability: 1800 ppm PCB over 10 days; greater levels might be achieved with ongoing inoculation of fungi species but accumulation of breakdown products may pose a limit to bacterial degradation
Emissions: CO_2
By-products: N/A
Practical Issues: Research required to assess potential for POP degradation and limitations of this process, particularly for concentration
Licensing: Patents for some processes involving white rot fungi and degradation of POPs do exist but appear only to be feasible for low levels of contamination.

Patent EP1114680

Wakao Construction Co Ltd (JP); Kondo Ryuichio (JP); Bio Remediation Technorogie IN (JP).

White rot fungi capable of decomposing dioxin were screened from rotten wood to isolate the MZ-340 strain. This MZ-340 could be cultured in the Kirk liquid medium (HCLN) or PDB medium. New systems that can be used to decompose dioxins in incineration ash were constructed using this MZ-340 strain. The present invention can decompose dioxins in incineration ash effectively and efficiently in both solid phase systems and liquid phase systems. Thus, the present invention enables the prevention of environmental pollution by dioxins generated during incineration and also the clean up of dioxin pollutants.

Patent US4891320

UNIV UTAH (US) 1990-01-02

A process for degrading environmentally persistent organic pollutant compounds by reacting those pollutant compounds with fungal enzymes containing a lignin-degrading enzyme and hydrogen peroxide. This reaction preferably takes place under aerobic conditions such that the organic pollutant compounds are degraded. Using the present invention, degradation to carbon dioxide and water is possible. Alternatively, the reaction may be halted to leave desirable reaction intermediates. The enzyme and hydrogen peroxide system of the present invention is found to be ideal for degrading various types of organic pollutants. Moreover, the reaction system is nonspecific. As a result, only a single type of fungus or fungus-generated enzyme system is required in order to degrade a wide spectrum of pollutants. One embodiment of the present invention relates to a preferred process where the enzyme (peroxidase) and hydrogen peroxide are provided by a lignin-degrading fungi or fungi mixed with the pollutant organic compound. Adding the living fungus avoids the need for introducing the hydrogen peroxide and enzyme periodically into the reaction mix, since the fungus produces both the extracellular enzyme and hydrogen peroxide.

Vendor(s): N/A

Info Sources: Mester and Tien, 2000; Kubátová, 2001; Mori and Kondo, 2002; Mougin, Pericaud, Dubroca and Asther, 1997; Ruiz-Aguilar et al., 2002.
Reason for category: This technology is currently only feasible for treating low strength wastes and it is unlikely to be successful for higher strength wastes.

2.5.10 Enzyme Degradation

Process: From Köller, Möder and Czihal, 2003:
The enzyme-induced decomposition and biodegradation of PCB were investigated. 2,5-Dichlorobiphenyl (PCB 9) and 2,2′,5,5′-tetrachlorobiphenyl (PCB 52) were used as example compounds to study efficiency and mechanism of the degradation processes. It was found that the application of horseradish peroxidase (HRP) together with defined amounts of hydrogen peroxide removed 90% of the initial concentration of PCB 9 and 55% of the initial concentration of PCB 52 from an aqueous solution after a reaction period of 220 min. Dechlorination was observed as the initial step. Although the metabolites identified were mainly chlorinated hydroxybiphenyls, benzoic acids and non-substituted 1,10 -biphenyl, some higher chlorinated biphenyl isomers also appeared. The biodegradation of PCB 9 using the white rot fungus Trametes multicolor took about four weeks and reduction was about 80% of the initial concentration. The metabolites produced (dichlorobenzenes, chlorophenols and alkylated benzenes) were not quite the same as those observed upon incubation with HRP.
Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: 90% for some PCBs
Applicability: Low strength PCBs, polycyclic aromatic hydrocarbons (PAHs), phenols, organophosphorus pesticides and azo dyes
Emissions: N/A
By-products: N/A
Practical Issues: Currently only applicable to low levels (μM) of contaminant (PCB)
Licensing:
Vendor(s):
Info Sources: Köller, Möder and Czihal, 2003.
Reason for category: This technology is currently only feasible for treating low strength wastes and it is unlikely to be successful for higher strength wastes.

2.5.11 In situ Bioremediation of Soils

Process: From Guanrong et al., 1996:
'Enhancement of anaerobic DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane) biotransformation by mixed cultures was studied with application of surfactants and oxidation reduction potential reducing agents. Without amendments, DDT transformation resulted mainly in the production of DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethane) upon removal of one aliphatic chlorine. The DDT transformation rate increased with the addition of the nonionic surfactants Triton X-114 or Brij 35. The addition of either surfactant or reducing agents did not significantly extend the DDT transformation. Addition of both surfactant and reducing agents extended DDT transformation by reducing the accumulation of DDD and increasing the accumulation of less chlorinated products. It is important to minimize the accumulation of DDD because it is a regulated pesticide and is resistantS to aerobic transformation. Controlled experiments revealed that the transformation of DDT requires microbial culture, but the culture need not be biologically active. Transformation results are presented for aqueous and soil phase contamination.'
Pre-treatment: N/A

Configuration: N/A
Capacity/Throughput:
Efficacy: transformation of 90% DDT over 20 days
Applicability: 2500ppm DDT in soil
Emissions: N/A
By-products: potential for DDE product formation
Practical Issues: Unlikely to be suitable for high concentrations of POPs in soil but the use of surfactants and reducing agents may be suitable for in-vessel reactions with specialised bacteria for the destruction of stockpiles.
Licensing: N/A
Vendor(s): N/A
Info Sources: Guanrong et al., 1996.
Reason for category: This technology is currently only feasible for treating low strength wastes; significant research is necessary to determine its suitability for treating high strength POP wastes. It is unlikely that in situ treatment itself will be suitable for treatment of high level wastes but aspects of this research could be combined with other technologies to produce a successful process.

2.5.12 DARAMEND Bioremediation

Process: Patented technology that uses soil specific solid phase organic amendments to increase activity of contaminant degrading microorganisms. Anoxic conditions are created through application of Daramend and inorganic, metallic ammendments and water; subsequently air-drying and tillage are used to produce aerobic conditions to degrade the anoxic metabolites.
From the US EPA:
'Grace Dearborn's DARAMEND Bioremediation Technology was developed to treat soils/sediment contaminated with organic contaminants using solid-phase organic amendments. The amendments increase the soil's ability to supply biologically available water/nutrients to microorganisms and bind pollutants to reduce the acute toxicity of the soil's aqueous phase. Prior to technology application, soils are screened approximately to 10 cm in diameter to remove any debris. The technology can be applied either in-situ or ex-situ. Application involves the mixing of soils with amendments to a depth of 0.6m. Amended soils are then irrigated/tilled to encourage microbial growth and metabolic activity until target compounds are reduced below regulatory action levels. A soil cover may be used to control soil moisture and run-on/off. The soil cover also has the effect of maintaining elevated soil temperatures negating the usual problems experienced when applying bioremediation systems in cold climates. This technology was demonstrated at the Domtar Wood Preserving Facility, Trenton, Ontario, Canada, during an eleven-month period from October, 1993 to September 1994 using soil contaminated with polyaromatic hydrocarbons (PAH) and chlorinated phenols. The developers claimed 95% reduction in total PAHs and total chlorophenols. Demonstration soil sampling revealed that PAHs were reduced from 1,710 mg/kg to 98 mg/kg (94.3%), total chlorophenols were reduced from 352 mg/kg to 43 mg/kg (87.8%), and total recoverable petroleum hydrocarbons were reduced from 7,300 mg/kg to 932 mg/kg (87.3%). The technology also reduced soil toxicity to earthworms and plant seeds.'
Pre-treatment: Screening
Configuration: in situ
Capacity/Throughput:
Efficacy: 95% degradation of lindane over 250 days; 76% removal of HCB over 70 days; 89% degradation of DDT over 84 days

Applicability: Will biodegrade DDT, DDD, DDE, lindane, toxaphene, chlordane, dieldrin at 95ppm
Emissions: CO_2; others not known
By-products: not known
Practical Issues: Likely to be only applicable to contamination in soil at the ppm level due to toxicity of POPs; rate of reaction is very slow. Amendments could be used for in-vessel reactions.
Licensing:
Vendor(s): Grace Bioremediation Technologies, Mississauga, Canada
Info Sources: Phillips et al., 2001.
US EPA http://www.epa.gov/ORD/SITE/reports/0029a.html
Reason for category: This technology is currently only feasible for treating low strength wastes; significant research is necessary to determine its suitability for treating high strength POP wastes. It is unlikely that in situ treatment itself will be suitable for treatment of high level wastes.

2.5.13 Phytoremediation

Process: Use of phytoremediation to enhance bioremediation by improved soil aeration and release of plant enzymes and exudates, phytodegradation and phytovolatilisation; used for aldrin, dieldrin (spikerush), PCBs (plant cells, enzymes); enhanced by compost and fungi addition; large scale experience absent.
Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: N/A
Applicability: N/A
Emissions: N/A
By-products: N/A
Practical Issues: This is still at the basic research level; the potential for POPs degradation has not been explored but is unlikely to be feasible for high concentrations or stockpiles.
Licensing: N/A
Vendor(s): N/A
Info Sources: Johne, Watzke and Terytze, 2001; Rulkens, 2001.
Reason for category: This technology is suitable for long term degradation of low contamination in soils. It is unlikely to be suitable for high strength POP wastes.

Not Classifiable

There is insufficient information to classify the following technologies for their potential to destroy stockpiles.

Self-Propagating High Temperature Dehalagenation (SPHTG)

Process: This process is still at the developmental (laboratory) scale. Chlorinated organics are premixed with calcium hydride or calcium metal and placed in a sealed reaction chamber, pressurised with argon. The reaction is initiated by an applied power pulse.

From Vijgen (2002):

'The technology is based on the exploitation of self-propagating reactions to meet the current topic of treating chlorinated aromatics. The point is that the reaction of many chlorinated organic compounds with strongly reductive substrates, such as alkaline metals or their hydrides, is very exothermic and thermodynamically quite favourable. Typical reaction enthalpies are well above 1000 kJ per mole. Likewise, the adiabatic temperature of these processes can be extremely high, as high as 4000^{o}K. These features are similar to those currently met in typical processes based on self-propagating reactions where a spontaneous propagation of the reaction takes place in the form of a combustion wave. The consequence is that severe thermochemical conditions, suitable for the breakdown of hazardous organic molecules, can be reached at the self-propagating combustion front.'

Pre-treatment: no yet evaluated for real-world samples.

Configuration: only tested at lab scale to date

Capacity/Throughput: N/A

Efficacy: Test reports for hexachlorobenzene and the herbicide, Dichlorprop, indicate >99.999% destruction

Applicability: Potentially all POPs

Emissions: Not clear what would be released.

By-products: Hydrogen and methane (with CO and CO_2 in the case of 2,4-DP) were the main gaseous compounds. Traces of benzene, mono-, di- and tri-chlorobenzene, dichloroetylene, dichloro-methane, xylene and trimethylbenzene were also found.

Practical Issues: Lack of detailed information on all process streams and residues. The cost of argon could be high.

Licensing:

Vendor(s): Centro Studi sulle Reazioni Autopropaganti, Italy

Info Sources: Vijgen, 2002.

Reason for category: Limited information available on the process and its potential application but it appears to be only at the lab scale level of development.

3.0 TABLES

Table 1 List of technologies and information sources

Technology	Vendor	Information Sources
A. Commercialised technologies with considerable experience		
Phase Chemical Reduction (GPCR)	ELI Ecologic International, Canada (Beth Kummling, Director of Business Development)	www.eco-logic-intl.com, and company literature
Base Catalysed Decomposition (BCD)	BCD Group Inc., USA (Thomas Opperman, Director of Corporate Affairs)	www.bcdinternational.com and company literature
Super-Critical Water Oxidation (SCWO)	General Atomics and Foster Wheeler, USA	www.ga.com/atg/aps/scwo.html-
Sodium Reduction	Powertech, Canada	www.powertechlabs.com
Plasma Arc	BCD Group Inc., Brisbane, Australia	
Pyrolysis	Startech Environmental Corp., USA	http://www.startech.net
B. Technologies near or at the start of commercialization		
Molten Salt Oxidation	Lawrence Livermore National Laboratory, and Los Alamos National Laboratory, USA	www-cms.llnl.gov, www-emtd.lanl.gov/ASTF-NM/MSO
Solvated Electron Technology (SET)	Teledyne Commodore LLC, USA	www.commodore.com and www.teledyne.com
C. Promising technologies		
Ball Milling – 1 (also known as dehalogenation by mechanochemical reaction, DMCR)	Tribochem, Germany	www.tribochem.com
Ball Milling - 2	Environmental Decontamination Ltd, New Zealand	bryan@manco.co.nz
GeoMelt™ Process	GeoMelt, USA (licensed globally to AMEC, USA)	www.geomelt.com and www.amec.com
Mediated Electrochemical Oxidation – Ce (MEO-Ce)	CerOx Corporation, USA (G. Anthony Steward, CEO & President)	www.cerox.com and other information supplied by CerOx
Mediated Electrochemical Oxidation – Ag (MEO-Ag)	AEA Technologies, UK	www.accentus.co.uk
Catalytic Hydrogenation	Commonwealth Industrial Research Organisation (CSIRO), Australia	Costner, Luscombe and Simpson, 1998

Technology	Vendor	Information Sources
D. Technologies which require significant research (none)		
E Technologies which are unlikely to be applicable for destruction of POPs stockpiles		
$MnO_x/TiO_2–Al_2O_3$ Catalyst Degradation		Liu et al, 2001
TiO_2-based V_2O_5/WO_3 Catalysis		Weber and Sakurai, 2001
Fe(III) Photocatalyst Degradation		Huston and Pignatello, 1999; Catastini et al., 2002
Ozonation/Electrical Discharge Destruction		Sun et al., 1998
Molten Metal	Molten Metal Technologies, USA	(no longer operating)
Molten Slag Process	Ausmelt, Australia[1]	www.ausmelt.com.au
Photochemically Enhanced Microbial Degradation		UNIV CALIFORNIA (US) Patent US5342779, date 1994-08-30
Biodegradation/Fenton's Reaction		Nam, Rodriguez and Kukor, 2001
White Rot Fungi Biodegradation		Mester and Tien, 2000; Kubátová et al., 2001; Mori and Kondo, 2002; Mougin et al., 1997; Ruiz-Aguilar et al., 2002
Enzyme Degradation		Köller, Möder and Czihal, 2000; Torres, Bustos-Jaimes and Le Borgne, 2003
In situ Bioremediation of Soils		Guanrong et al., 1996
DARAMEND Bioremediation	Grace Bioremediation Technologies, Mississauga, Canada	Phillips et al., 2001 US EPA http://www.epa.gov/ORD/SITE/reports/0029a.html
Phytoremediation		Johne, Watzke, Terytze, 2001; Rulkens, 2001

Table 2 Process summaries

Technology	Process Description	Configuration	Applicability	Scale
A. Commercialised technologies with considerable experience				
GPCR	Chlorinated organic compounds are reacted with hydrogen at high temperatures (≥850C) and low pressure, yielding methane, hydrogen chloride and minor amounts of other low MW hydrocarbons.	Fixed, modular; transportable (but not easily). Thermal desorption unit required for solid wastes.	All POPs, including high strength wastes. Liquids and solids (with Thermal Desorption).	Up to 100 tonnes/day depending on waste strength and pre-treatment systems.
BCD	Batch treatment of liquid and solid wastes in the presence of a high boiling point hydrocarbon (e.g. fuel oil), sodium hydroxide and a proprietary catalyst. When heated to about 300 °C the reagent produces highly reactive atomic hydrogen, which reacts with organochlorines and other wastes.	Fixed, modular; and transportable. Thermal desorption used for some wastes	All POPs, including high strength wastes. Liquids and solids (<2 cm)	Up to 20 tonnes/hr contaminated solids, 9000 litres per batch liquids, smaller units available.
SCWO	SCWO destroys toxic and hazardous organic wastes in a compact totally enclosed system, using an oxidant (e.g. oxygen or hydrogen peroxide) at temperatures and pressures above the critical point of water (374°C and 22.1 MPa). Under these conditions organic materials become highly soluble in water and react rapidly to produce carbon dioxide, water and inorganic acids or salts.	Current pilot plant systems are fixed configuration, but the units should be transportable	All POPs, but limited to treatment of liquid wastes or solids less than 200microns in diameter, and an organic content of less than 20%	Currently up to 400 kg/hr, but planned for 2700 kg/hr
Sodium Reduction	Reduction of PCBs with dispersed metallic sodium in mineral oil. Has been used widely for in-situ removal of PCBs from active transformers. Products include polybiphenyl, sodium chloride, petroleum based oils and caustic.	Transportable and fixed	Transformer oils only	Up to 15,000 l/day

Technology	Process Description	Configuration	Applicability	Scale
Plasma Arc	Organochlorine waste is injected directly into a plasma torch, where it is pyrolysed under the extreme temperatures in the torch (>10,000 °C) and decomposed to CO, CO_2 and HCl. Acid gases are removed in a caustic scrubber and CO is oxidised in a flare prior to discharge to atmosphere.	Transportable and fixed.	Liquid and gaseous wastes, up to 100% strength. Solids pre-treated by thermal desorption.	1-3 tonnes/day (150 kW plant)
Pyrolysis	This system uses a plasma torch (~15,000 °C) inside a cylindrical reaction vessel containing mixed bulk gases. Plasma feed gases (air, argon, CO_2 or nitrogen) are introduced and product gases removed at the top of the chamber and waste materials (solid, liquid or gas) plus steam are fed in from the side. Inorganic portions of the waste remain in the reactor as reduced metals and a glassy slag. Off gases are polished through scrubbers and filters, and can be reused as synthesis gas.	Transportable and fixed	Solid, liquid and gaseous wastes	Demonstrated at 50 – 100 kg/hr and commercial unit designed for 10 tonnes/day
B. Technologies near or at the start of commercialization				
Molten Salt Oxidation	POPs wastes are injected into a bath of a molten salt (e.g. sodium carbonate) at 900-950 °C, yielding carbon dioxide, sodium chloride, water and nitrogen.	Transportable and fixed	Tested for a few pesticides	Full scale under construction

Technology	Process Description	Configuration	Applicability	Scale
SET	Solvated electron solutions are produced by dissolving sodium, lithium or calcium in anhydrous ammonia at room temperature in a pressurised system. The contaminated materials are placed into a treatment cell with the treatment solution, and POPs wastes are reduced to metal salts and simple hydrocarbon compounds. At the end of the reaction, ammonia is removed for reuse, and the treatment residues (e.g. oil or soil) are removed from the cell and disposed.	Modular transportable system	Tested for dioxins, PCBs (up to 2%) and DDT. Should work for all POPs. Liquids and solids, including packaging .	Up to 10 t/day
C. Promising technologies				
Ball Milling	POPs wastes are placed in a ball mill with a hydrogen donor compound in the presence of an alkali metal (magnesium, sodium, etc). Reductive dehalogenation occurs due to mechanochemical process.	Fixed and mobile.	All POPs at low levels; indication that high strengths can be treated	10 kg/hr to several tonnes/hr (in principle)
GeoMelt^{TM}	This process works by establishing a melt between pairs of electrodes inserted into the soil-bound waste materials. Electrical energy is continuously applied to the melt until it grows to encompass the entire treatment volume. Organic contaminants present in the soil are decomposed at the high temperatures produced in the melt. Off-gases generated by the process are collected inside a stainless steel hood covering the treatment area and are drawn off for processing by an off-gas treatment system. After treatment, the residual soil solidifies into a glassy/rock-like material.	Most wastes treated in situ but can also be set up to treat wastes inside a treatment vessel	Demonstrated for most POPs in contaminated soils; limited data for high strength wastes	Up to 1000 tonnes in situ in one treatment (also quoted as 90 t/day). 45 t/day for the in-container system.

Technology	Process Description	Configuration	Applicability	Scale
MEO– Ce	Ce^{4+} ions are produced in an electro-chemical cell and then mixed with the waste stream prior to passing into a liquid phase reactor. The Ce^{4+} acts as an oxidising agent, reacting with POPs to produceCO_2, neutral salts and dilute acid solution. The process operates at low temperature (90-95C) and near atmospheric pressure. The liquid effluent from the reactor is returned to the cell for regeneration of the cerium reagent. Gaseous products are passed into a counter-current packed bed gas/liquid reactor which uses a flow of Ce^{4+} for oxidation of the residual organics. The treated gases (mainly CO_2 and Cl_2) are then passed through a condenser (for VOC recycling) and a caustic scrubber for chlorine removal.	Modular system design which indicates potential for set-up as a transportable system (but really only applicable for small units)	Demonstrated for most POPs. Optimum performance for organic content >15%. Aqueous process with solids or sludges homogenised and pumped in as a liquid. Liquid organic wastes are pre-treated by sonication to emulsify the mixture.	The base unit (2 cell-packs) has a capacity of 25 gals/day for 50% organics liquid input (ca. 2kg/hr of organics). Multiple cell units are made for up to 100 gals/day and treatment plant packages with a capacity of 2000-40,000 gals/day
MEO– Ag	The AEA Silver II process is very similar to the CerOx system but utilises oxidation of organics with Ag^{2+} ions in solution. System design is similar to CerOx but includes a hydrocyclone between the reactor and the electrochemical cells, which may reduce potential problems from solids inputs.	Concepts developed for production as a modular/transportable system, but not yet proven	Optimum efficiency is achieved at an organic concentration of 2 -10 g/litre (<1%). Proven for some POPs, but not all	Only proven to an organic throughput of about 30 kg/day. A costed design has been produced for a throughput of about 1-2 tonnes/day
Catalytic hydrogen-ation	PCBs in transformer oils are hydrogenated by robust sulphide based catalysts, yielding hydrochloric acid and light hydrocarbons	N/A	PCBs	Laboratory
D. Technologies which require significant research				

Technology	Process Description	Configuration	Applicability	Scale
E. Technologies which are unlikely to be applicable for destruction of POPs stockpiles				
$MnO_x/TiO_2 –Al_2O_3$ Catalyst Degradation	A highly active catalyst, $MnOx/TiO_2–Al_2O_3$, with TiO species in a monolayer dispersion, and the MnOx species highly dispersed on the $TiO_2–Al_2O_3$ support. The total oxidation of chlorobenzene and o-dichlorobenzene on $MnOx/TiO_2–Al_2O_3$ catalyst can be achieved at 300^oC and 250^oC respectively, at the space velocity of 8000 h^{-1}. The activity of $MnOx/ TiO_2 –Al_2O_3$ catalyst (Min loading 11.2 wt%) is gradually increased in the first 10–20 h and then keeps stable at least for the measured 52 h at 16,000 h^{-1}.	N/A	Potentially all POPs but tested on chlorobenzene and dichlorobenzene	Laboratory
TiO_2-based V_2O_5/WO_3 Catalysis	Contaminant dissolved in toluene, heated to 300^oC and contacted with a V_2O_5/WO_3 supported titanium catalyst	Concept not developed	Potentially most POPs at high strengths; further research needed	Bench scale
Fe(III) Photo-catalyst Degradation	An advanced oxidation process combining photo-Fenton, Fe(III)/H2 O2 /UV processes. Reactions carried out in a cylindrical 300-ml borosilicate double-walled reaction vessel with water circulated through the walls to maintain constant temperature. The photochemical reactor chamber (Rayonet RPR-200) contained sixteen 14-W fluorescent black lamps which emit in the range 300-400 nm. Ferrioxalate actinometry indicated that the total light intensity was $1.2x10^{19}$photons $l^{-1}s^{-1}$. The lamps were warmed up for 10 min to reach constant output. The pesticide, iron(III) perchlorate, and sodium perchlorate, as needed,	N/A	Low strength contaminated waters: alachlor, aldicarb, atrazine, azinphos-methyl, captan, carbofuran, dicamba, disulfoton, glyphosate, malathion, ethoxylchlor, metolachlor, picloram and simazine	Laboratory scale; used for treatment of low strength wastes in the field

Technology	Process Description	Configuration	Applicability	Scale
	were added to the reaction vessel and the temperature was equilibrated to 25.020.28C. The pH was then adjusted to 2.8 with $HClO_4$. The reaction was initiated by adding 30% H_2O_2, followed by inserting the vessel into the chamber			
Ozonation/ Electrical Discharge Destruction	Gas containing the contaminant is either treated directly with an electrical discharge or with ozone produced by a discharge; the latter appears to be more effective	N/A	Dioxins/furans; other POPs in a gas form	Laboratory
Molten Metal	This process uses refractory-lined steel pressure vessels containing molten iron or nickel (1425-1650 °C). Heat is provided inductively by coils inserted in the lining. Feed material is either injected from above through lances or through the base using a system of tubes (*tuyeres*). Oxygen, methane and an inert carrier gas are also injected with the feed. The liquid metal acts as a catalyst and energy source for the reactions, and also dissolves some of the by-products.	Fixed	Liquid and gaseous wastes, plus finely divided solids.	Only proven at bench scale (5-10 kg/hr)
Molten Slag Process	Waste to be treated is blended with steelworks dust and fluxing agents, extracted, dried with heat from the furnace off-gases and fed into a foaming slag layer which forms at the top of the molten iron in an electric arc furnace at a temperature of around 1500 °C. The waste sinks into the slag phase, metal oxides are reduced to metals and all organic materials return to their basic elements, like in the molten metal process	N/A	Potentially all POPs	Laboratory

Technology	Process Description	Configuration	Applicability	Scale
Photo-chemically Enhanced Microbial Degradation	RBC system with 5 discs rotated at 2rpm and 40% submerged in an N-deficient medium innoculated with a strain of *P. chrysosporium*. The contaminant is dissolved in acetone-ethanol and added to the medium where it is treated for 23 days until fully destroyed.	N/A	PCBs; potentially all POPs but time and strength require further assessment	Bench scale
Biodegra-dation/ Fenton's Reaction	Using Fe ions and a chelating agent (catechol and gallic acid) combined with H_2O_2, a Fenton reaction at neutral pH was combined with in situ soil bacteria to degrade polycyclic aromatic hydrocarbons at 250-1200 mg/kg soil by 98% for 2-3 ring and 70-85% 4-5 ring HC molecules.		PAH contaminated soils up to 600ppm	Laboratory
White Rot Fungi Biodegra-dation	Addition of white rot fungi species to contaminated soils	N/A	Low levels of contaminants in soils, including PCBs, dioxins/ furans, polycyclic aromatic hydrocarbons, chlorophenols, and aromatic dyes	Currently used in the field only for low level contaminated soils
Enzyme Degradation	Addition of enzymes to contaminated soils	N/A	Low level of contaminants in soils and water	Currently used in the field for low level contamination
In situ Bioremediat ion of Soils	Enhancement of soil biodegradation using surfactants and reducing agents	N/A	2500ppm DDT	Laboratory

Technology	Process Description	Configuration	Applicability	Scale
DARA-MEND Bioremediation	Enhancement of soil biodegradation using specialised and metallic amendments and water, followed by drying and tilling	Field application to contaminated *in situ* soils	Will biodegrade DDT, DDD, DDE, lindane, toxaphene, chlordane, dieldrin at 95ppm	Commercial application for contaminated soils
Phyto-remediation	Use of plants to enhance bioremediation by improved soil aeration and release of plant enzymes and exudates, phytodegradation and phytovolatilisation; enhanced by compost and fungi addition	Growth of plants on contaminated soils	aldrin, dieldrin (spikerush), PCBs (plant cells, enzymes)	Laboratory

Table 3 Process performance

Technology	Performance Data	Emissions	Byproducts
A. Commercialised technologies with considerable experience			
GPCR	>99.9999% DRE for HCB, PCBs and DDT	All emissions may be captured for assay and reprocessing if needed.	Solid residues should be suitable for landfill disposal. Caustic scrubber liquid.
BCD	>99.99% DRE in trials	No significant emissions (but some dioxins measured in older plants)	Reduced organics, salts and inert solids
SCWO	>99.99% DRE	No significant releases	Unknown (for POPs)
Sodium Reduction	DRE not reported, but achieves <0.5 ppm PCB removal	Possibly hydrogen if water present	Caustic/salt solutions. Treated oil may be reused
Plasma Arc	>99.9999% DRE for PCBs	Carbon dioxide and argon	Caustic scrubber solutions
Pyrolysis	No published data	Carbon dioxide gas	Caustic scrubber liquids and solid residues (slag)
B. Technologies near or at the start of commercialization			
Molten Salt Oxidation	High DRE reported for chlordane	Carbon dioxide	Salt residues from bath need to be disposed (may be recycled).
SET	Typically >99.9% on PCB-contaminated soil	Potential ammonia releases	Sodium salts, hydrocarbons/oils, treatment residues
C. Promising technologies			
Ball Milling	>99.9% dechlorination of PCBs, at pilot scale	Closed batch system, with no expected emission (no data available)	Reduced organics, metal salts and inert finely ground solids
GeoMelt™ Process	90 to 99.99% DRE in the melt, and >99.99 overall (with scrubber)	No detectable emissions from scrubber	No leaching from solid residue (glass). Scrubber residues can be disposed in subsequent melts.
(MEO-Ce)	>99.995% DRE for chlorinated pesticides	Carbon dioxide gas	Caustic scrubber liquor. Reagent liquor will gradually accumulate metals and other contaminants
MEO– Ag	>99.9999% DRE for nerve gases. High DREs also claimed for some POPs	Carbon dioxide gas	Caustic scrubber liquor. Reagent liquor will gradual accumulate

Technology	Performance Data	Emissions	Byproducts
			metals and other contaminants. Solids removed from treatment liquor by filtration
Catalytic Hydrogenation	>99.9996% for 1300ppm PCB; >99.99999% for 40,000ppm PCB	Not known but gases are treated to remove any hydrogen and non-condensable hydrocarbons	HCl, light hydrocarbons in oil
D. Technologies which require significant research			
E. Technologies which are unlikely to be applicable for destruction of POPs stockpiles			
MnO_x/TiO_2–Al_2O_3 Catalyst Degradation	100% degradation of 1300ppmv chlorinated benzene gas	HCl, H_2O, carbon oxides	N/A
TiO_2-based V_2O_5/WO_3 Catalysis	>99.9% destruction of PCBs	HCl; water; CO_2	Reaction liquid with contaminants
Fe(III) Photocatalyst Degradation	79.4% methoxychlor; 94.3% melathion; 98.8-100% other POPs	CO_2	Cl^-; short-chain organic acids; unknown if toxic breakdown products are formed
Ozonation/ Electrical Discharge Destruction	88% for indirect ozone treatment of VOCs and dioxins/furans	CO_2	N/A
Molten Metal	No information available	Carbon monoxide and hydrogen. Reducing conditions help minimise dioxins	Trace elements will build up in treatment metal and in slag. The concept allows for adjustment of the mix to produce useful metal-based by-products
Molten Slag Process	N/A	N/A – could include dust and other contaminants	N/A

Technology	Performance Data	Emissions	Byproducts
Photochemically Enhanced Microbial Degradation	99-100% removal of PCB	N/A	Cl^-, CO_2; organic acids?
Biodegradation/ Fenton's Reaction	70-98% degradation of low level (600ppm) PAH in soils	CO_2	N/A
White Rot Fungi Biodegradation	70% PCB; 92% lindane	CO_2	N/A
Enzyme Degradation	90% for some PCBs; up to 100% of some organic contaminants	CO_2	N/A
In situ Bioremediation of Soils	90% of 2500ppm DDT in soil over 20 days	CO_2	N/A
DARAMEND Bioremediation	95% degradation of lindane over 250 days; 76% removal of HCB over 70 days; 89% degradation of DDT over 84 days	CO_2	N/A
Phytoremediation	N/A	N/A	N/A; may include runoff problems

Table 4 Practical aspects

Technology	Infrastructure Needs	Operational Needs	Practical Issues	Safety Issues
A. Commercialised technologies with considerable experience				
GPCR	Moderate amounts of propane needed for boiler unless processing high organic wastes. Hydrogen may also be needed during start up	Continuous process with batch storage.	Disposal of treated residues	Potential for hydrogen gas leaks
BCD	Nitrogen gas required for "blanketing". Also needs significant amounts of base.	Batch and continuous systems available	Disposal of treated residues	No major safety issues
SCWO	No special requirements, but note that SCWO technology has been around for many years, and the earlier systems were plagued by reliability, corrosion and plugging problems. Recent developments have effectively addressed these problems through the use of special reactor designs and corrosion resistant materials.	Continuous	None	None
Sodium Reduction	Sodium handling facilities	Continuous	Sodium supply	Sodium safety and potential hydrogen hazards
Plasma Arc	Moderate energy inputs and reliable electricity and cooling water supplies.	Continuous	Significant demand for argon. Cooling water is essential for torch.	Risk of explosion from internal cooling water leaks. Molten metal or slag discharges.
Pyrolysis	Moderate energy inputs and reliable electricity and cooling water supplies	Batch process	Support gases. Cooling water is essential for torch.	Risk of explosion from internal cooling water leaks.

Technology	Infrastructure Needs	Operational Needs	Practical Issues	Safety Issues
B. Technologies near or at the start of commercialization				
Molten Salt Oxidation	High temperature furnace/reactor	Batch or continuous	Large quantities of salt for recycling or disposal	High temperatures. Explosion hazards from wet wastes contacting molten salt
SET	Sodium and ammonia handling facilities. Stable electricity supply is essential for ammonia handling and containment	Batch process	Sodium and ammonia supplies. Wastes must be dewatered prior to treatment	Sodium, ammonia and hydrogen hazards.
C. Promising technologies				
Ball Milling	Moderate electricity demand	Batch operation	Supplies of base metal. Disposal of treated residues.	No major safety issues, but possible noise/vibration
GeoMelt™ Process	Significant electricity requirements	Batch process	Highly saturated soils need to be dewatered before treatment	No major issues
(MEO-Ce)	Significant electricity requirements	Continuous process	Not clear how solids build-up is prevented in the treatment liquor	No major issues
MEO– Ag	Significant electricity requirements	Continuous process	No major issues	No major issues
Catalytic Hydrogenation	N/A	Batch operation	Supply of sulphide catalyst	Disposal of acid; spent catalyst; further design details needed
D. Technologies which require significant research				
E. Technologies which are unlikely to be applicable for destruction of POPs stockpiles				
MnO_x/TiO_2–Al_2O_3 Catalyst Degradation	Moderate temperature requirement (300^oC)	Batch or continuous process	Supply of catalyst; disposal of spent catalyst	No major issues identified at this stage

Technology	Infrastructure Needs	Operational Needs	Practical Issues	Safety Issues
TiO_2-based V_2O_5/WO_3 Catalysis	Moderate temperature requirement (300^oC)	Batch or continuous process	Supply of catalyst; disposal of spent catalyst	No major issues identified at this stage
Fe(III) Photocatalyst Degradation	Moderate electricity/sunlight requirements	Not clear at this stage of development	Supply of iron(III) perchlorate, sodium perchlorate, hydrogen peroxide	No major issues identified at this stage of development
Ozonation/ Electrical Discharge Destruction	High electricity requirement	Batch or continuous process	Batch or continuous process	No major issues identified at this stage
Molten Metal	High temperature furnace/reactor	Batch or continuous process	Integrity ands resilience of the refractory materials. Gas supplies (oxygen, methane).	High temperatures. Explosion hazards from wet wastes contacting molten metal, and from off-gases.
Molten Slag Process	High temperature furnace/reactor	Batch or continuous process	Integrity ands resilience of the refractory materials. Gas supplies (oxygen, methane).	High temperatures. Explosion hazards from wet wastes contacting molten metal, and from off-gases.
Photo-chemically Enhanced Microbial Degradation	Moderate electricity and sunlight requirement	Batch operation	None identified at this design level	Disposal of wastewater

Technology	**Infrastructure Needs**	**Operational Needs**	**Practical Issues**	**Safety Issues**
Biodegradation/ Fenton's Reaction	Not clear at this stage of development	Not clear at this stage of development	Supply of Fe ions, a chelating agent (catechol and gallic acid) and H_2O_2	Handling of H_2O_2
White Rot Fungi Biodegradation	Not clear at this stage of development	Not clear at this stage of development	Not clear at this stage of development	No major issues identified at this stage
Enzyme Degradation	Not clear at this stage of development	Not clear at this stage of development	Not clear at this stage of development	No major issues identified at this stage
In situ Bioremediation of Soils	Not clear at this stage of development	Not clear at this stage of development	Supply of surfactants and reducing agents	No major issues identified at this stage
DARAMEND Bioremediation	Not clear at this stage of development	Not clear at this stage of development	DARAMEND, metallic amendments, water	No major issues identified at this stage
Phyto-remediation	Not clear at this stage of development	Not clear at this stage of development	Disposal of contaminated organic material	Potential long term contamination of soil

4.0 APPLICATION OF TECHNOLOGY TO DEVELOPING COUNTRIES

4.1 Background

There are several scenarios when dealing with POPs stockpiles in developing countries. Firstly there is the stockpile itself and secondly there is contaminated soil either as a result of the stockpile or from some other POPs source. Both these scenarios should be considered independently. Thirdly there is the question of whether the stockpile be treated (decontaminated or destroyed) in situ at each site or should the stockpile be recovered, identified, segregated, packed and shipped out. For contaminated soil, shipping out is almost always prohibitively expensive, although there are plenty of examples of PCB contaminated soils having being shipped out for destruction. It is generally accepted that non-combustion technology for stockpile destruction is different to the non-combustion technology required for soil decontamination.

The first requirement of an obsolete pesticide disposal technology is a destruction efficiency greater than 99.99% (Rahuman et al., 2000). Destruction efficiency (DE) is defined as the total mass of a chemical into a process, minus the mass of the chemical in all products, by-products and environmental releases, divided by the input mass (to give a percentage). This differs significantly from the other common measure, destruction and removal efficiency (DRE) which only takes into account stack emissions, with no regard for other releases and residues (Costner, Luscombe and Simpson, 1998). Only closed processes that achieve greater than 99.99% destruction efficiency can be considered. Any technology to be used in a developing country must be inherently safe. Murphy's law applies. There can be no dangerous reactants, except for the obsolete pesticides to be destroyed, of course. The process must be closed with no possibility of unplanned release of any chemicals (Rahuman et al., 2000). The process must be able to handle upsets, such as power supply failure, without danger to personnel or equipment. Handling and loading of pesticides into the process must always be safe, straightforward and controlled. Equipment and controls must be simple and robust, and will preferably make use of local resources. The operating procedure must be extremely basic and virtually foolproof. Loading and unloading, start up and shut down must all be straightforward. The process must be able to handle pesticide waste in a variety of forms i.e. solid or liquid, contaminated soil, concrete, equipment and containers. The process must be able to treat the full range of obsolete pesticides with minimum change in operating procedure and reactants (Rahuman et al., 2000).

4.1.1 In situ destruction using non-combustion technologies

In reviewing past documentation and reports regarding technology for POPs destruction there has been a noticeable preference to try find a technology that will destroy all POPs and be simple enough to transport to all sites in developing countries and deal to each stockpile in situ. This approach may be inappropriate given the complexity of the waste at the sites coupled with social and political considerations. This uncertainty about in situ destruction means that it is possible that issues associated with site, quantities, recycling,

environmentally sound management, process by-product and other matters need not form part of the evaluative criteria for developing countries.
Nevertheless we have reviewed the technologies on the basis that each site will receive a technology that can be performed in situ. In reality however we make the assertion that this approach may be unworkable in many of the undeveloped economies and therefore centralised (regional or international) facilities may be appropriate. The implications for "promising technology" is therefore significant as the issues of quantities, resources requirements, containers and mixing are no longer prevalent if the waste is to be treated ex situ.

4.1.2 Issues of complexity

In our experience, we have found that many sites where POPs wastes are stored there are substantial issues with multivariate containers, mixed non-POPs and large quantities of unidentified wastes. Many of these sites are difficult to get to and are often located far from resources such as water and electricity. Local people and politicians at many of these sites see the storage a simply dangerous waste and want it all gone.

4.1.3 Incomplete removal or destruction

We believe that it is inappropriate to leave behind a portion of the waste that is stored at a obsolete storage facility. In the African situation alone there is some 50,000 tonnes of obsolete stocks that also involve large quantities of non-POPs. Given the issues of containers, mixed waste profiles, unknown waste and distance from resources, the concept of taking a specific technology to each and every site in a developing country is, in our opinion, not acceptable (and unworkable) and that a centralised regional multi platform technology centre is more efficient, cost effective and more environmentally sound.

4.1.4 Environmentally sound management

From UNEP, 2003. Technical Guidelines on the Environmentally Sound Management of Persistent Organic Pollutants as Wastes. SBC. Rev 3(15.01.2003)

> *"Under the Basel Convention, "Environmentally sound management of hazardous wastes or other wastes" means taking all practicable steps to ensure that hazardous wastes or other wastes are managed in a manner, which will protect human health and the environment against the adverse effects, which may result from such wastes.*
> *The core performance elements of ESM are those that are applicable to all evaluation, dismantling, refurbishment, pre-treatment, treatment and disposal of wastes. According to the Stockholm Convention, recovery and recycling are, however, not applicable to POPs wastes. This requires that each destruction and/or management facility should:*
> - *have adequate regulatory infrastructure and enforcement to ensure compliance with applicable regulations;*
> - *be appropriately authorised;*

- *have waste minimisation/ recovery/ recycling procedures (Note: Recovery and recycling procedures are not applicable to POPs wastes);*
- *be appropriately certified under an applicable Environmental Management System;*
- *have an appropriate operational monitoring and reporting programme;*
- *have an operational inspection and recording programme for all input and output materials;*
- *have appropriate in-house record keeping;*
- *have an appropriate and verified emergency plan;*
- *have an appropriate and operative training programme for its personnel; and*
- *have an adequate financial guarantee for emergency situations and closure.*

In a paper presented by four UNIDO scientists at the International Centre for Science (ICS-UNIDO) (UNEP, 2003) the following basic performance criteria for POPs waste technologies were listed:

> *"The technologies used for destroying stockpiles of persistent organic pollutants (POPs) must meet the following fundamental performance criteria:*
>
> - *Destruction efficiencies of effectively almost 100 percent for the chemicals of concern: the determination of 100 percent destruction efficiency is necessarily based on findings of extremely low concentrations of the chemicals of concern, approaching zero in any and all residues, or outflow streams using the most sensitive analytical techniques available worldwide. As achieving absolute zero residues may be technically not feasible, the only possible criterion to set how low the required concentration must be, when considering toxic substances such as POPs, is the absence of any present and future harm to human health and the environment. Although expensive, complete analyses of all out flowing streams, residues, possible leaks must be carried out with a frequency sufficient to ensure compliance with this criterion during start-ups, shutdowns and routine operations.*
> - *In order to better attain the abovementioned goal, priority is recommended for technologies that imply containment of all residues and out flowing streams for screening and, if necessary, reprocessing. This is to ensure that no chemicals of concern or other harmful compounds, such as newly formed POPs or other hazardous substances, are released to the environment. Technologies, which may require uncontrolled releases (e.g. relief valve from high-pressure vessels) or environmental spreading of POPs, even at hardly detectable levels (e.g. incineration processes with high gaseous mass flow released to atmosphere), should be carefully scrutinized and possibly avoided."*

Determining the extent to which a technology meets these criteria during both preliminary tests and routine operations depends on a variety of factors including, but not limited, to:

- *scientific and engineering expertise;*

- *equipment and facilities for sampling and analysis of the materials to be destroyed and all residues of the destruction process;*
- *stringent operating guidelines; and*
- *comprehensive regulatory framework, including enforcement and monitoring requirements."*

Additional criteria for evaluating destruction technologies that have been suggested in a US Department of Energy report (UNEP, 2003) include:

- *capability of treating a variety of wastes with varying constituents with minimal pre-treatment of waste;*
- *secondary waste stream volumes that are significantly smaller than the original waste stream volumes and which contain no toxic reaction by-products;*
- *complete elimination of organic contaminants;*
- *off gas and secondary waste composition;*
- *cost; and*
- *risk.*

Considering the various technologies available or under development for handling POPs wastes, it is important to distinguish between:

(a) pre-treatment technologies that concentrate POPs in wastes so that the resulting pre-treated waste can be better subjected to a technology for sequestration or for destruction or irreversible transformation;

(b) technologies that sequestrate the waste; and

(c) technologies that actually achieve some measure of destruction or irreversible transformation.

The above ESM requirements are applicable to countries and facilities involved with POPs waste management. In the authors' experience the possibilities for application of the 3Rs (recycling, reuse, reconstitute) is greatly enhanced by a central treatment facility than by application in situ. This is especially so if the stockpile is removed from the site for processing elsewhere. Generally the opportunities for recycling some of the pesticides is greatly reduced with in situ solutions. The authors have seen many situations where a large portion of stock has been left behind for "recycling" only to find years later that the product is still there. In terms of shredding containers and recycling the plastic and steel, this is much more effective at a central facility rather than piecemeal at each of the stockpile locations.

Packaging and shipping has its risks but the authors experience clearly shows that the recovery, identification, segregation packaging and containerisation is now very sophisticated and given the vast quantities of POPs that are shipped every year to Europe for destruction, the recorded releases to the environment are minimal. Without doubt the possibilities for environmental pollution are much greater if in situ destruction is performed on hundreds of remote difficult

locations than for shipment to a central location where the quality assurance can be maintained and the operators are fully trained and spills are contained in a purpose-built facility. One of the biggest problems when applying non-combustion technologies is that most of the technologies require substantial pre-treatment, shredding or other handling and failure in this area can lead to gross environmental contamination.

4.1.5 Implications

By accepting that a 'multi platform' centre maybe more appropriate, then this has significant implications for the application of non-combustion technology for developing countries. Whereas a particular individual non-combustion technology may have been useful in situ, it is unlikely that the particular technology would be able to destroy all the waste and there may be insufficient material to be able to bring another technology on site that could destroy the balance. On the other hand if the waste in its entirety is transported to the multi platform regional centre then economies of scale apply and all waste can be treated using a battery of non-combustion technologies that overlap each other along with shredding facilities and recycling systems.

4.2 Characteristics of stockpile sites in developing countries

The annexes include a photographic record of actual obsolete pesticides and POPs stockpiles in many countries. In particular the record shows photos from Senegal, Mauritania, Cape Verde, Jamaica, Venezuela, Argentina, Taiwan Cambodia, Cameroon and others. The stockpiles are clearly mixed, non-uniform and often completely chaotic. Many of the containers are broken and leaking. Large quantities are unidentified or classified.

4.3 Logistics of application of non-combustion technology

The logistics of non-combustion technologies differ in terms of in and ex situ. The criteria below are based on the technology being in situ. The output table from the application of the criteria to the emerging and promising non-combustion technologies will deal with in situ. Of note is technology that is still at lab scale. The comparison table cannot be used for this type of technology with emerging technology as many of the criteria cannot be calibrated.

4.4 Criteria

Notwithstanding our statements above regarding a multi platform regional centre facility we have established a set of criteria built on the application of a non-combustion technology to individual sites within a developing country. We have used a simple comparative set of criteria measuring one type of non-combustion technology against the other. For instance for a technology that has a high power requirement a high rating will be assigned where the top rate of 100 would be for a technology that required 1-2 MVA of energy. For a technology that requires only 25 KW this would attract a rating of 10. Therefore in a comparative sense it is better to have a lower overall number that a high one. This means of course that a judgment is required to set

the comparative scale. In the case of energy requirement the authors have set the fatal flaw scale at 1 MVA. For many remote, difficult sites this value is probably fair enough. A one MVA energy provision at a remote location will require a substantial electrical supply network along with a well-sized distribution transformer and associated switch gear. A generator at 1 MVA would be a large truck mounted unit that would use vast quantities of diesel and we consider that also to be a fatal flaw at that size for most sites. On the other hand should the site be located in a commercial area with a large power supply system then the top scale would be reset at say 5 MVA.

It should also be noted that a fatal flaw is recognised by a score of 100. If for instance the discharge to the environment of a particular residue waste stream is scored at 100 then the fatal flaw provision is applied and the technology is discounted. The assignment of the values is an exercise in judgment and is something that engineers have to do all the time when evaluation the application of technologies.

4.4.1 Two levels of criteria

There are two distinct areas of criteria. The first is the adaptation of the non-combustion technology to the developing country and the second is the adaptation of the developing country to the non-combustion technology. Both of these sets of criteria form a matrix of mutual adaptation.

4.5 Adaptation of the non-combustion technology to the developing country

All criteria elements are scaled 0-100 points. Those elements that are marked "Not FF" means that while the points of 100 may be reached the element itself is not a fatal flaw.

4.5.1 Performance

Destruction efficiency	(Scale 0-100) Units
Capability to treat all	(Scale Binary 0-1) N/Y NotFF
Secondary waste streams volumes	(Scale binary 01-) N/Y NotFF
Off gas treatment	(Scale linear 0-100)
Containment	(Scale binary 0-1) N/Y NotFF
New POPs formation	(Scale binary 0-1) N/Y
Uncontrolled releases	(Scale binary 0-1) N/Y
Minimum pre-treatment	(Scale binary 0-1) N/Y
Toxic reaction byproducts	(Scale binary 0-1) N/Y
Complete elimination	(Scale binary 0-1) N/Y
Waste/ tonne	(Scale linear 0-24) Units hrs /tonne
Quantity per day/month	(Scale linear 0-5) Units tonne /day

4.5.2 Costs

This criterion involves all the economic considerations of the adaptation of the non-combustion technology.

Capital cost	(Scale Linear 0-250) Units US$K

Set up costs	(Scale Linear 0-250) Units US$K
Per tonne cost	(Scale Linear 0-3000)Units US$
Gas cost	(Scale Linear 0-1)Units US$K/tonne
Reagents cost	(Scale Linear 0-1)Units US$K/tonne
Patents and royalties costs	(Scale Linear 0-1)Units US$K/tonne

4.5.3 Input waste

For a non-combustion technology to be viable it will require certain minimum stockpile quantities. Some technologies will require a higher minimum than others.

Min stockpiles size	(Scale 0-50) Units tonnes
Breakeven volumes	(Scale 0-100) Units tonnes
Dewatering	(Scale binary 0-1) N/Y Not FF
Size reduction	(Scale binary 0-1) N/Y Not FF
Scalability	(Scale binary 0-1) N/Y Not FF

4.6 Adaptation of the country to the technology

4.6.1 Resource needs

This criterion involves all aspects of required resources to set up the non-combustion technology and operate the plant within a developing country. Includes the requirements for buildings, communication systems, sampling facilities etc. Reagents and gas requirements are also noted. We have set the scale requirements according to our experience. Those elements that are marked "Not FF" means that while the points of 100 may be reached the element itself is not a fatal flaw.

Power requirements	(Scale Linear 0-1MVA)
Water requirements	(Scale Linear 0-1 Cu/day)
Labour requirements	(Scale Linear 0-50)
Technician requirement	(Scale Linear 0-50)
Laboratory requirement	(Scale Binary 0-1) Not FF
Has waste personnel requirement	(Scale Linear 0-50)
Reagents volumes	(Scale Linear 0-1000kg/day)
Gas volumes (off site supply)	(Scale Linear 0-200cuf)
Weather tight buildings	(Scale Linear 0-5)
Communications systems	(Scale Binary 0-1) Not FF
In situ sampling requirements	(Scale Linear 0-250/day)
Peer sampling requirements	(Scale Linear 0-1000)

4.6.2 Costs

Installation and commissioning costs	(Scale Linear 0-250) Units US$K
Site preparation costs	(Scale Linear 0-250) Units US$K
Energy & telecom installation costs	(Scale Linear 0-100) Units US$K
Monitoring Costs	(Scale Linear 0-5) Units US$K/Day Not FF
Compliance costs	(Scale Linear 0-5) Units US$K/Day Not FF

Reporting costs	(Scale Linear 0-5) Units US$K/Day Not FF
Running cost with no waste	(Scale Linear 0-5)Units US$K/Day
Running cost with waste	(Scale Linear 0-20)Units US$K/Day
Decommissioning costs	(Scale Linear 0-100)Units US$K
Landfill costs	(Scale Linear 0-50)Units US$/tonne
Residue waste transport costs	(Scale Linear 0-500Units US$/tonne

4.6.3 Impact

All non-combustion technologies will have some impact both on and off site. This criterion looks at those impact issues and assigns values to them which are dependent on the dimension of the impact.

Discharges to air	(Scale Linear 0-100) Units $\mu gm/m^3$
Discharges to water	(Scale Linear 0-100) Units ppm
Discharges to land	(Scale Linear 0-100) Units Tonnes
Social Impact (noise etc)	(Scale Linear 0-100) Units DBa

4.6.4 Danger

Toxicity of reagents is included here along with other issues of the technology that are dangerous. For example sodium reduction has a high risk factor during operation of explosion and fire and thus would score higher than for example autoclaving technology.

Danger of reagents	(Scale binary 0-1)Units Class 3/6/8 Not FF
Danger of technology	(Scale linear 0-5) Units Danger scale
Danger of operation	(Scale linear 0-5) Units Danger scale

4.6.5 Constructability

Complexity of construction is an issue in developing countries as is the ease of shipping and transit, operations and the actual processing.

Ease of installation/constructability	(Scale Likert 0-5) Units %
Ease of shipping/transit	(Scale Likert 0-5) Units %
Ease of operativability	(Scale Likert 0-5) Units %
Ease of commissioning	(Scale Likert 0-5) Units %
Ease of processing	(Scale Likert 0-5) Units %

4.6.6 Output waste

Of great importance are the volumes and final disposition of final wastes.

Output wastes volumes	(Scale 0-100) Units % of input wastes
Final disposition	(Scale 0-100) Units % to landfill
Waste quality/properties (e.g. pH and leachable metals)	(Scale 0-5) Units TCLP

4.6 Matrices

The two sets of criteria are displayed in Figures 1 and 2. These figures are example sheets only. One of each matrix is required for each technology.

4.7 Expert system

The criteria and matrices lend themselves to the development of a decision support system which would assist in determining the appropriate technology for a specific site and pollutant. Such a system could encompass a range of technologies which would be suitable for various POPs and contamination levels. It would also identify the requirements for using any of the technologies and could also include a cost component to enable the user to both identify infrastructure requirements as well as economic issues.

The system would be based on the criteria and would initially include data for the technologies included in this report. However data for further technologies could be added as the system is expanded. In addition, as a country or region applies the system, decisions can be stored within the database to provide a clear profile of the weighting factors and decision making process.

Such a system would be valuable for communities as well as governments who are seeking to determine appropriate technologies for managing POPs. It could also be expanded to deal with a broader range of hazardous chemicals and contamination materials such as water. The initial focus of the system would, however, be on POPs stockpiles and the available commercial technologies.

MATRIX ONE : Adaptation of the Technology to the Country											
CATEGORY A : COMMERCIALISED TECHNOLOGIES WITH CONSIDERABLE EXPERIENCE TECHNOLOGY: GAS PHASE CHEMICAL REDUCTION (GPCR)											
CRITERIA: PERFORMANCE											
Destruction efficiency	Capacity treat all	Secondary Waste streams	Off gas Treatment	Containment	New POPs formation	Uncontrolled releases	Min pre treatment	Toxic by products	Complete elimination	Waste/ tonne	Qty/ day
Scale Score Weight Net											
CRITERIA: COSTS											
Capital cost	Set up costs	Per tonne costs	Gas Cost	Reagents Cost	Patents & royalties						
Scale Score Weight Net											
TOTAL Score for Category A Technology 1 =											

Figure 1 Matrix one : Adaptation of the Technology to the Country. Example page: each technology would have one page.

MATRIX TWO : Adaptation of the Country to the Technology											
CATEGORY A : COMMERCIALISED TECHNOLOGIES WITH CONSIDERABLE EXPERIENCE											
TECHNOLOGY: GAS PHASE CHEMICAL REDUCTION (GPCR)											
CRITERIA: RESOURCE NEEDS											
Power Reqmnts	Water Reqmnts	Labour Reqmnts	Technician Reqmnts	Laboratory Reqmnts	Haz Personnel	Reagents Volumes	Gas Volumes	Weather Proof Bldgs	Comms Systems	Sampling Reqmnts	Peer sampling
Scale											
Score											
Weight											
Net											
CRITERIA: COSTS											
Install & Commiss	Site Preparation	Energy & Comms	Monitoring Cost	Compliance Cost	Reporting costs	Running No waste	Running With waste	Decomm cost	Landfill Cost	Residue Transport	
Scale											
Score											
Weight											
Net											
CRITERIA: IMPACT				CRITERIA: DANGER			CRITERIA: CONSTRUCTABILITY				
Discharge to air	Discharge to water	Discharge to land	Social Impact	Reagents Danger	Technology Danger	Operations Danger	Ease Installation	Ease Shipping	Ease Operation	Ease Processing	
Scale											
Score											
Weight											
Net											
CRITERIA: OUTPUT WASTE											
Waste Volumes	Final Disposition	Quality & Properties									
Scale											
Score											
Weight											
Net											

TOTAL Score for Category A Technology 1 =

Figure 2 Matrix Two : Adaptation of the Country to the Technology Example page; each technology would have one page

5.0 CONCLUSIONS AND RECOMMENDATIONS

The purpose of this work was to review all existing technologies that were non-combustion in character and identify those technologies that are innovative and emerging and hold promise for the destruction of the POPs stockpiles.

5.1 Conclusions

Of the approximately 50 technologies reviewed, only five technologies were classified as promising, emerging and innovative (Category C). These are:

Ball milling;
GeoMelt™ Process;
Mediated Electrochemical Oxidation (CerOx);
Mediated Electrochemical Oxidation (AEA Silver II Process);
Catalytic Hydrogenation.

It is of concern that there are so few emerging technologies, especially those that may be suited for in situ destruction of POPs. To some extent this may be a reflection of the large amount of low cost high temperature incineration capacity in Europe, the ongoing POPs removal in developing countries to HTI coupled with a reluctance of research funding in this sector.

A number of technologies have been placed in Annexure 1 as technologies which have been insufficiently researched to indicate their promise. It is likely that some of these technologies should have been placed in Category D but there was insufficient information to place them in that category.

It is also possible that some technologies which were identified as unsuitable could be successfully developed as suitable technologies. However, with the direction of the research and the limited availability of information for some technologies, it was considered appropriate by the workshop to place them in Category E.

In addition, information was provided by Zoltan Csizer, Director, Cleaner Production and Environmental Management Branch, UNIDO on technologies acceptable for use in Japan for destroying PCBs (See Annexure 2). There was insufficient information provided to include them in this report although some of the technologies have been included as they are used elsewhere and data were available.

An additional goal of this work was to examine the criteria that a developing country could use to evaluate the application of a particular technology. A set of criteria was developed that has two elements. These criteria can be used as they stand for evaluative purposes but with an application of an ‘expert’ system a fully integrated and interactive evaluation model cam be achieved that is dynamic in that new technologies can be added to it as they become available.

5.2 Recommendations

It is recommended that the five identified emerging and promising technologies be further evaluated for the purpose of providing funding so that the technologies may become commercialised in the near future.

It is also recommended that a decision support system be developed which will assist users in deciding which technologies are appropriate for treating POPs wastes and contaminated soils in their region. Such a system should be developed as soon as possible to enable users around the world to make effective decisions on POPs management.

REFERENCES

Bollag, J.M., Shuttleworth, K.L., Anderson, D.H., 1988. Laccase- mediated detoxification of phenolic compounds. *Appl. Environ. Microbiol. 54: 3086-3091.*

Bridle, T. and K.R. Campbell, 1996. Destruction of Organiochlorine Compounds Using the Eco Logic Process. *3rd National Hazardous and Solid Waste Convention, Sydney, 26-30 May, 1996.*

Bumpus, J.A., Tien, M., Wright, D., Aust, S.D., 1985. Oxidation of persistent environmental pollutants by a white rot fungus. *Science 228: 1434-1436.*

Call, H.P., Mücke, I., 1997. History, overview and applications of mediated ligninolytic system, especially laccase-mediator-systems (Lignozym 1 -process). *J. Biotechnol. 53: 163-202.*

Catastini, C., M. Sarakha, G. Mailhot and M. Bolte, 2002. Iron (III) aquacomplexes as effective photocatalysts for the degradation of pesticides in homogeneous aqueous solutions, *The Science of The Total Environment 298(1-3): 219-228.*

CMPS&F – Environment Australia 1997. *Appropriate Technologies for the Treatment of Scheduled Wastes-Molten Media Processes (Review Report No. 1).* November. http://www/ea.gov.au/industry/chemicals/swm/swtt/molten.html.

CMPS&F – Environment Australia 1997. *Appropriate Technologies for the Treatment of Scheduled Wastes - Plasma Arc Systems (Review Report No. 4).* November. http://www.oztoxics.org/research/3000_hcbweb/library/gov_fed/appteck/plasma.html

Costner, P., D. Luscombe and M. Simpson, 1998. *Technical Criteria for the Destruction of Stockpiled Persistent Organic Pollutants*, Greenpeace International Service Unit.

Duffy, G.J. and C.J.R. Fookes, 1997. Development of a Catalytic Process for the Regeneration of Transformer Oils and the Destruction of Chlorinated Hydrocarbons. Presented at the I&EC Special Symposium, American Chemical Society, Pittsburgh, Pennsylvania, September 15-17, 1997.

Environment Australia, 1997. *Appropriate Technologies for the Treatment of Scheduled Wastes* Review Report Number 4-November 1997. http://www.ea.gov.au/industry/chemicals/swm/swtt/contents.html

Field, J.A., de Jong, E., Feijoo Costa, G., de Bont, J.A.M., 1993. Screening for ligninolytic fungi applicable to the degradation of xenobiotics. *TiBtech 14: 44-49.*

Guanrong, Y., G.D. Sayles, M.J. Kupferle, P.L. Bishop, S. K. In, 1996. Anaerobic DDT biotransformation: enhancement by application of surfactants and low oxidation reduction potential, *Chemosphere 32(11): 2269-2284.*

Hatakeda, K., Y. Ikushima, O. Sato, T. Aizawa, N. Saito, 1999. Supercritical water oxidation of polychlorinated biphenyls using hydrogen peroxide. *Chemical Engineering Science 54 (1999): 3079-3084.*

Huston, P.L. and Joseph J. Pignatello, 1999. Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction, *Water Research 33(5): 1238-1246.*

Johne, S., R. Watzke, K. Terytze,2001. Phytoremediation on HCH-contaminated soils. *6th International HCH and Pesticides Forum,* 20-22 March 2001, Poznan, Poland, *http://www.6thhchforum.com/forum_book/* .

Köller, G., M. Möder and K. Czihal, 2000. Peroxidative degradation of selected PCB: a mechanistic study, *Chemosphere 41(12): 1827-1834.*

Kronholm, J., T. Kuosmanen, K. Hartonen and M.L. Riekkola, 2003. Destruction of PAHs from soil by using pressurized hot water extraction coupled with supercritical water oxidation, *Waste Managemen 23(3): 253-260.*

Kubátová, A., P. Erbanová, I. Eichlerová, L. Homolka, F. Nerud and V. Šašek, 2001. PCB congener selective biodegradation by the white rot fungus *Pleurotus ostreatus* in contaminated soil, *Chemosphere 43(2): 207-215.*

Liu, Y., Z. Wei, Z. Feng, M. Luo, P. Ying and C. Li, 2001. Oxidative Destruction of Chlorobenzene and *o*-Dichlorobenzene on a Highly Active Catalyst: MnO_x/TiO_2–Al_2O_3, *Journal of Catalysis 202(1): 200-204.*

Lomnicki, S., J. Lichtenberger, Z. Xu, M. Waters, J. Kosman and M.D. Amiridis, 2003. Catalytic oxidation of 2,4,6-trichlorophenol over vanadia/titania-based catalysts, *Applied Catalysis B: Environmental, In Press, Corrected Proof, Available online 1 August 2003.*

Mester, T. and M. Tien, 2000. Oxidation mechanism of ligninolytic enzymes involved in the degradation of environmental pollutants**,** *International Biodeterioration & Biodegradation 46(1): 51-59.*

Molten Metal Technology, 1996. News release: "EPA Grants Molten Metal Technology Best Demonstrated Available Technology Status for All Wastes Previously Requiring Incineration," Waltham, Massachusetts, March 12, 1996.

Mori, T. and R. Kondo, 2002. Oxidation of chlorinated dibenzo-*p*-dioxin and dibenzofuran by white-rot fungus, *Phlebia lindtneri. FEMS Microbiology Letters 216(2): 223-227.*

Mougin, C., C. Pericaud, J. Dubroca and M. Asther, 1997. Enhanced mineralization of lindane in soils supplemented with the white rot Basidiomycete Phanerochaete chrysosporium, *Soil Biology and Biochemistry 29(9-10): 1321-1324.*

Nam, K., W, Rodriguez and J.J. Kukor, 2001. Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction, *Chemosphere 45(1): 11-20.*

National Research Council, 1993. *Alternative Technologies for the Destruction of Chemical Agents and Munitions*. Washington, D.C.: National Academy of Sciences.

Phillips, T., G. Bell, D. Raymond, K. Shaw, A. Seech, 2001. DARAMEND technology for in situ bioremediation of soil containing organochlorine pesticides. *6th International HCH and Pesticides Forum*, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/ .

Rahuman, M., L. Pistone, F. Trifiro and S. Miertus, 2000. *Destruction Technologies for Polychlorinated Biphenyls* (PCBs). UNIDO, Italy.

Ruiz-Aguilar, G.M.L., J.M. Fernández-Sánchez, R. Rodríguez-Vázquez and H. Poggi-Varaldo, 2002. Degradation by white-rot fungi of high concentrations of PCB extracted from a contaminated soil, *Advances in Environmental Research 6(4): 559-568.*

Rulkens, W.H, 2001. Perspectives of phytoremediation for soil contaminated with pesticides. 6th International HCH and Pesticides Forum, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/.

Sun, H., H. Felix, A. Nasciuti, Y Herieti and W. Hoffelner, 1998. Reduction of NO/NO2 & SO2 and destruction of VOCs & PCDD/F in industrial flue gas by electrical discharge, *Chemosphere 37(9-12): 2351-2359.*

Torres, E., I. Bustos-Jaimes and S. Le Borgne, 2003. Potential use of oxidative enzymes for the detoxification of organic pollutants, *Applied Catalysis B: Environmental, In Press, Corrected Proof, Available online 30 July 2003.*

United States Department of Energy, Idaho National Engineering and Environmental Laboratory. *Mixed Waste Focus Area Technology Profile*.

UNEP, 2003. *Technical Guidelines on the Environmentally Sound Management of Persistent Organic Pollutants as Wastes*. UNEP/CHW/OEWG/1/INF/6 25 March 2003.

USEPA, 2002. *Persistent Organic Pollutants, A Global Issue, A Global Response*. http://www.epa.gov/international/toxics/pop.pdf.

Vijgen, J., 2002. *Evaluation of Demonstrated and Emerging Remedial Action Technologies for the Treatment of Contaminated Land and Groundwater (Phase III) New, emerging and/or less expensive solutions for the destruction of land contaminated with pesticides*. NATO/CCMS Pilot Study, International HCH & Pesticides Association, Elmevej 14, DK-2840 Holte, Denmark.

Valli, K., Gold, M.H., 1991. Degradation of 2,4-dichlorophenol by the lignin-degrading fungus *Phanerochaete chrysosporium*. *J. Bacteriol. 173: 345-352.*

Valli, K., Wariishi, H., Gold, M.H., 1992. Degradation of 2,7-dichlorodibenzo-p-dioxin by the lignin degrading basidiomycete *Phanerochaete chrysosporium*. *J. Bacteriol. 174: 2131-2137.*

Weber, R. and T. Sakurai, 2001. Low temperature decomposition of PCB by TiO_2-based V_2O_5/WO_3 catalyst: evaluation of the relevance of PCDF formation and insights into the first step of oxidative destruction of chlorinated aromatics, *Applied Catalysis B: Environmental 34(2): 113-127.*

BIBLIOGRAPHY

Arienzo, M., J. Chiarenzelli, R. Scrudato, J. Pagano, L. Falanga and B. Connor, 2001. Iron-mediated reactions of polychlorinated biphenyls in electrochemical peroxidation process (ECP). *Chemosphere 44(6): 1339-1346.*

Badriyha, B.N., V. Ravindran, W. Den and M. Pirbazari, 2003. Bioadsorber efficiency, design, and performance forecasting for alachlor removal. *Water Research, Volume 37, Issue 17, October 2003, Pages 4051-4072.*

Bandala, E.R., S. Gelover, M.T. Leal, C. Arancibia-Bulnes, A. Jimenez and C. A. Estrada, 2002. Solar photocatalytic degradation of Aldrin. *Catalysis Today, Volume 76, Issues 2-4, 15 November 2002, Pages 189-199.*

Bending, G.D., M. Friloux and A. Walker, 2002. Degradation of contrasting pesticides by white rot fungi and its relationship with ligninolytic potential. *FEMS Microbiology Letters, Volume 212, Issue 1, 18 June 2002, Pages 59-63.*

Berg, H., M. Kiibus and N. Kautsky, 1992. DDT and other insecticides in the Lake Kariba Ecosystem, Zimbabwe. *Ambio*, 21 (7): 444-450.

Boethling, B., Buccini, J., Cowan-Ellsberry, C., Graham, D., Hansen, B., Murray, M., Rampy, L., Rodan, B., Wahlstrom, B., 2000. *Framework and Criteria for Evaluation of Persistence and Long-Range Transport. Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment.* Society of Environmental Toxicology and Chemistry (SETAC), FL., USA, 2000. P 315-334.

Bollag, J.M., Shuttleworth, K.L., Anderson, D.H., 1988. Laccase- mediated detoxification of phenolic compounds. *Appl. Environ. Microbiol*. 54: 3086-3091.

Bridle, T. and K.R. Campbell, 1996. Destruction of Organiochlorine Compounds Using the Eco Logic Process. *3rd National Hazardous and Solid Waste Convention*, Sydney, 26-30 May, 1996.

Bumpus, J.A., Tien, M., Wright, D., Aust, S.D., 1985. Oxidation of persistent environmental pollutants by a white rot fungus. *Science 228: 1434-1436.*

Bunce, N.J., S.G. Merica and J. Lipkowski, 1997. Prospects for the use of electrochemical methods for the destruction of aromatic organochlorine wastes. *Chemosphere 35(11): 2719-2726.*

Burrows, H. D., M. Canle L, J. A. Santaballa and S. Steenken, 2002. Reaction pathways and mechanisms of photodegradation of pesticides. *Journal of Photochemistry and Photobiology B: Biology 67(2): 71-108.*

Call, H.P., Mücke, I., 1997. History, overview and applications of mediated ligninolytic system, especially laccase-mediator-systems (Lignozym 1 -process). *J. Biotechnol. 53: 163-202.*

Catastini, C., M. Sarakha, G. Mailhot and M. Bolte, 2002. Iron (III) aquacomplexes as effective photocatalysts for the degradation of pesticides in homogeneous aqueous solutions. *The Science of The Total Environment 298(1-3): 219-228.*

Chaudhary, A.J., S.M. Grimes and M. ul-Hassan, 2001. Simultaneous recovery of copper and degradation of 2,4-dichlorophenoxyacetic acid in aqueous systems by a combination of electrolytic and photolytic processes. *Chemosphere 44(5): 1223-1230.*

Chen, A. S. C., A.R., Gavaskar, B.C. Alleman, A. M., D. Timberlake and E.H. Drescher, 1997. Treating contaminated sediment with a two-stage base-catalyzed decomposition (BCD) process: bench-scale evaluation. *Journal of Hazardous Materials 56(3): 287-306.*

Chiron, S., A. Fernandez-Alba, A. Rodriguez and E. Garcia-Calvo, 2000. Pesticide chemical oxidation: state-of-the-art. *Water Research 34(2): 366-377.*

CMPS&F – Environment Australia 1997. *Appropriate Technologies for the Treatment of Scheduled Wastes-Molten Media Processes (Review Report No. 1).* http://www/ea.gov.au/industry/chemicals/swm/swtt/molten.html.

CMPS&F – Environment Australia 1997. *Appropriate Technologies for the Treatment of Scheduled Wastes - Plasma Arc Systems (Review Report No. 4).* http://www.oztoxics.org/research/3000_hcbweb/library/gov_fed/appteck/plasma.html.

Cooper, W.J., Michael G. Nickelsen, Stephen P. Mezyk, G. Leslie, P. M. Tornatore, Wayne Hardison and Paris A. Hajali, 2002. MTBE and priority contaminant treatment with high energy electron beam injection. *Radiation Physics and Chemistry 65(4-5): 451-460.*

Costner, P., D. Luscombe and M. Simpson, 1998. *Technical Criteria for the Destruction of Stockpiled Persistent Organic Pollutants*, Greenpeace International Service Unit.

Duffy, G.J. and C.J.R. Fookes, 1997. Development of a Catalytic Process for the Regeneration of Transformer Oils and the Destruction of Chlorinated Hydrocarbons. Presented at the I&EC Special Symposium, American Chemical Society, Pittsburgh, Pennsylvania, September 15-17, 1997.

Environment Australia, 1997. *Appropriate Technologies for the Treatment of Scheduled Wastes.* Review Report Number 4-November 1997. http://www.ea.gov.au/industry/chemicals/swm/swtt/contents.html.

FAO, 2001. *Baseline study of the problem of obsolete pesticide stocks*. FAO Pesticide Disposal Series No. 9, Food and Agriculture Organization of the United Nations, Rome.

Field, J.A., de Jong, E., Feijoo Costa, G., de Bont, J.A.M., 1993. Screening for ligninolytic fungi applicable to the degradation of xenobiotics. *TiBtech 14: 44-49.*

Galadi, A., H. Bitar, M. Chanon and M. Julliard**,** 1995. Photosensitized reductive dechlorination of chloroaromatic pesticides. *Chemosphere* 30(9): 1655-1669.

Guanrong, Y., G.D. Sayles, M.J. Kupferle, P.L. Bishop, S. K. In, 1996. Anaerobic DDT biotransformation: enhancement by application of surfactants and low oxidation reduction potential. *Chemosphere, Volume 32, Issue 11, June 1996, Pages 2269-2284.*

Hatakeda, K., Y. Ikushima, O. Sato, T. Aizawa, N. Saito, 1999. Supercritical water oxidation of polychlorinated biphenyls using hydrogen peroxide. *Chemical Engineering Science* 54 (1999) 3079-3084.

Hayashi, J., J. Ikeda, K. Kusakabe and S. Morooka, 1993. Decomposition rate of volatile organochlorines by ozone and utilization efficiency of ozone with ultraviolet radiation in a bubble-column contactor. *Water Research* 27(6): 1091-1097.

Hema M. K., K. Pathirana and R. A. Maithreepala**,** 1997. Photodegradation of 3,4-dichloropropionamide in aqueous TiO_2 suspensions. *Journal of Photochemistry and Photobiology A: Chemistry* 102(2-3): 273-277.

Higarashi, M.M., and W. F. Jardim, 2002. Remediation of pesticide contaminated soil using TiO2 mediated by solar light. *Catalysis Today* 76 (2002) 201–207.

Hoffmann, M.R., I. Hua and R. Höchemer, 1996.Application of ultrasonic irradiation for the degradation of chemical contaminants in water. *Ultrasonics Sonochemistry 3(3): S163-S172.*

Huang, Q. and C.S. Hong, 2000. TiO_2 photocatalytic degradation of PCBs in soil-water systems containing fluoro surfactant. *Chemosphere* 41(6): 871-879.

Huston, P.L. and J. J. Pignatello, 1999. Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction. *Water Research* 33(5): 1238-1246.

Joint Service Pollution Prevention Opportunity Handbook. *Molten Metal Processing of Hazardous Waste*s. April, 2000.

Kearney, P.C., M.T. Muldoon and C.J. Somich, 1987. UV-ozonation of eleven major pesticides as a waste disposal pretreatment. *Chemosphere* 16(10-12): 2321-2330.

Klecka, G. and Buccini John. *Introduction. Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment*. Society of Environmental Toxicology and Chemistry (SETAC), FL., USA, 2000. P 1-6.

Köller, G., M. Möder and K. Czihal, 2000. Peroxidative degradation of selected PCB: a mechanistic study. *Chemosphere* 41(12): 1827-1834.

Konstantinou, I.K. and T.A. Albanis, 2003. Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways. *Applied Catalysis B: Environmental* 42(4): 319-335.

Kronholm, J., T. Kuosmanen, K. Hartonen and M.L. Riekkola, 2003. Destruction of PAHs from soil by using pressurized hot water extraction coupled with supercritical water oxidation.*Waste Management 23(3): 253-260.*

Kubátová, A., P. Erbanová, I. Eichlerová, L. Homolka, F. Nerud and V. Šašek, 2001. PCB congener selective biodegradation by the white rot fungus *Pleurotus ostreatus* in contaminated soil. *Chemosphere 43(2): 207-215*

Levin, L., A. Viale and A. Forchiassin, 2003. Degradation of organic pollutants by the white rot basidiomycete *Trametes trogii. International Biodeterioration & Biodegradation 52(1): 1-5.*

Lipnick, R. L.; Mason, R. P.; Phillips, M. L.; and Pittman, C. U., Jr.; Chemicals in the Environment: an Overview. In: *Chemicals in the Environment: Fate, Impacts, and Remediation. ACS Symposium Series 806*, ACS, Oxford University Press, 2002

Lomnicki, S., J. Lichtenberger, Z. Xu, M. Waters, J. Kosman and M.D. Amiridis, 2003. Catalytic oxidation of 2,4,6-trichlorophenol over vanadia/titania-based catalysts. *Applied Catalysis B: Environmental, In Press, Corrected Proof, Available online 1 August 2003*

Liu, Y., Z. Wei, Z. Feng, M. Luo, P. Ying and C. Li, 2001. Oxidative Destruction of Chlorobenzene and *o*-Dichlorobenzene on a Highly Active Catalyst: $MnO_x/TiO_2–Al_2O_3$. *Journal of Catalysis 202(1): 200-204.*

Malato, S., J. Blanco, C. Richter, B. Braun and M. I. Maldonado, 1998. Enhancement of the rate of solar photocatalytic mineralization of organic pollutants by inorganic oxidizing species. *Applied Catalysis B: Environmental 17(4): 347-356.*

Mester, T. and M. Tien, 2000. Oxidation mechanism of ligninolytic enzymes involved in the degradation of environmental pollutants. *International Biodeterioration & Biodegradation 46(1): 51-59.*

Meysami, P. and H. Baheri, 2003. Pre-screening of fungi and bulking agents for contaminated soil bioremediation. *Advances in Environmental Research 7(4): 881-887.*

Molten Metal Technology, 1996. News release: "EPA Grants Molten Metal Technology Best Demonstrated Available Technology Status for All Wastes Previously Requiring Incineration," Waltham, Massachusetts, March 12, 1996.

Mori, T. and R. Kondo, 2002. Oxidation of chlorinated dibenzo-*p*-dioxin and dibenzofuran by white-rot fungus, *Phlebia lindtneri*. *FEMS Microbiology Letters* 216(2): 223-227.

Morner, J., Bos, R., Fredrix, M., 2002. *Reducing and Eliminating the use of Persistent Organic Pesticides: Guidance on alternative strategies for sustainable pest and vector management*. http://www.chem.unep.ch/pops/pdf/redelepops/redelipops.pdf.

Mougin, C., C. Pericaud, J. Dubroca and M. Asther, 1997. Enhanced mineralization of lindane in soils supplemented with the white rot Basidiomycete Phanerochaete chrysosporium. *Soil Biology and Biochemistry* 29(9-10): 1321-1324.

Nam, K., W, Rodriguez and J.J. Kukor, 2001. Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction. *Chemosphere* 45(1): 11-20.

National Research Council, 1993. *Alternative Technologies for the Destruction of Chemical Agents and Munitions*. Washington, D.C.: National Academy of Sciences.

Oku, A., T. Nakaji, T. Kamada, H. Miyata and O. Aozasa, 1993. Destruction of PCDDs and PCDFs in laboratory-scale wastes. A convenient reductive method with sodium naphthalene. *Chemosphere* 27(8): 1433-1438.

Oku, A., K. Tomari, T. Kamada, E. Yamada, H. Miyata and O. Aozasa, 1995. Destruction of PCDDs and PCDFs. A convenient method using alkali-metal hydroxide in 1,3-dimethyl-2-imidazolidinone (DMI). *Chemosphere* 31(8): 3873-3878.

Ormad, P., S. Cortés, A. Puig and J. L. Ovelleiro, 1997. Degradation of Organochloride compounds by O_3 and O_3/H_2O_2. *Water Research* 31(9): 2387-2391.

Prevot, A.B., and Edmondo Pramauro, 1999. Analytical monitoring of photocatalytic treatments. Degradation of 2,3,6-trichlorobenzoic acid in aqueous TiO_2 dispersions. *Talanta* 48(4): 847-857.

Ritter, L.; Solomon, K.R.; Forget, J.; Stemeroff, M.; and O'Leary, C.; 1995. *Persistent Organic Pollutants. An Assessment Report on: DDT-Aldrin-Dieldrin-Endrin-Chlordane, Heptachlor-Hexachlorobenzene, Mirex-Toxaphene, Polychlorinated Biphenyls, Dioxins and Furans.* http://www.chem.unep.ch/pops/ritter/ritter.htm

Ruiz-Aguilar, G.M.L., J.M. Fernández-Sánchez, R. Rodríguez-Vázquez and H. Poggi-Varaldo, 2002. Degradation by white-rot fungi of high concentrations of PCB extracted from a contaminated soil. *Advances in Environmental Research 6(4): 559-568.*

Rusling, J.F., S. Schweizer, S. Zhang and G. N. Kamau, 1994. Microemulsions as media for destruction of organohalide pollutants by electrolysis. *Colloids and Surfaces A: Physicochemical and Engineering Aspects 88(1): 41-49.*

Sato, A., T. Watanabe, Y. Watanabe, K. Harazono and T. Fukatsu, 2002. Screening for basidiomycetous fungi capable of degrading 2,7-dichlorodibenzo-*p*-dioxin. *FEMS Microbiology Letters 213(2): 213-217.*

Schwinkendorf, W., McFee, J., Devarakonda, M., Nenninger, L., Fadullon, F., Donaldson, T., and Dickerson, K., 1995. *Alternatives to Incineration: Technical Area Status Report. Prepared for the Mixed Waste Integrated Program.* U.S. Department of Energy, Office of Technology Development, Washington, D.C., April 1995.

Shim, S. and K. Kawamoto, 2002. Enzyme production activity of *Phanerochaete chrysosporium* and degradation of pentachlorophenol in a bioreactor. *Water Research 36(18): 4445-4454.*

Skurlatov, Y.I., L. S. Ernestova, E. V. Vichutinskaya, D. P. Samsonov, I. V. Semenova, I. Ya. Rod'ko, V. O. Shvidky, R. I. Pervunina and T. J. Kemp, 1997. Photochemical transformation of polychlorinated phenols. *Journal of Photochemistry and Photobiology A: Chemistry 107(1-3): 207-213.*

Sun, H., H. Felix, A. Nasciuti, Y Herieti and W. Hoffelner, 1998. Reduction of NO/NO2 & SO2 and destruction of VOCs & PCDD/F in industrial flue gas by electrical discharge. *Chemosphere 37(9-12): 2351-2359.*

Top, E.M., M.P. Maila, M. Clerinx, J. Goris, P. De Vos and W. Verstraete, 1999. Methane oxidation as a method to evaluate the removal of 2,4-dichlorophenoxyactic acid (2,4-D) from soil by plasmid-mediated bioaugmentation. *FEMS Microbiology Ecology, 28(3): 203-213.*

Torres, E., I. Bustos-Jaimes and S. Le Borgne, 2003. Potential use of oxidative enzymes for the detoxification of organic pollutants. *Applied Catalysis B: Environmental, In Press, Corrected Proof, Available online 30 July 2003*

United States Department of Energy, Idaho National Engineering and Environmental Laboratory. *Mixed Waste Focus Area Technology Profile.*

UNECE, 2000. *Convention on Long-range Transboundary Air Pollution: Protocol to the 1979 Convention on Long-range Transboundary Air Pollution on Persistent Organic Pollutants*. http://www.uncec.org/env/lrtap/protocol/98p_dec.htm

UNEP, 2003. *Draft Technical Guidelines on the Environmentally Sound Management of Persistent Organic Pollutants as Wastes*. UNEP/CHW/OEWG/1/INF/6 25 March 2003.

UNEP Chemicals, 1998. *Inventory of World-wide PCB Destruction Capacity.* http://www.chem.unep.ch/pops/pdf/pcbrpt.pdf

UPEP Chemicals, 1999. *Inventory of Information Sources on Chemicals: Persistent Organic Pollutants*. http://www.chem.unep.ch/pops/pdf/invsrce/inventpopscomb.pdf

UNEP Chemicals, 2000. *Survey of Currently Available Non-Incineration PCB Destruction Technologies*. http://www.chem.unep.ch/pops/pdf/surveypcb/PCBdesteng.pdf

UNEP Chemicals, 2001. *Stockholm Convention on Persistent Organic Pollutants (POPs).* http://www.pops.int/documents/convtext/convtext_en.pdf

UNEP Chemicals, 2002. PCB *Transformers and capacitors: From Management to Reclassification and Disposal*. http://www.chem.unep.ch/pops/pdf/PCBtranscap.pdf

USEPA, 2002. *Persistent Organic Pollutants, A Global Issue, A Global Response.* http://www.epa.gov/international/toxics/pop.pdf

Valli, K., Gold, M.H., 1991. Degradation of 2,4-dichlorophenol by the lignin-degrading fungus, *Phanerochaete chrysosporium*. *J. Bacteriol. 173: 345-352.*

Valli, K., Wariishi, H., Gold, M.H., 1992. Degradation of 2,7-dichlorodibenzo-p-dioxin by the lignin degrading basidiomycete *Phanerochaete chrysosporium*. *J. Bacteriol. 174: 2131-2137.*

Vidal, A., A. I. Díaz, A. El Hraiki, M. Romero, I. Muguruza, F. Senhaji and J. González, 1999. Solar photocatalysis for detoxification and disinfection of contaminated water: pilot plant studies**.** *Catalysis Today 54(2-3): 283-290.*

Weber, R., K. Nagai, J. Nishino, H. Shiraishi, M. Ishida, T. Takasuga, K. Konndo and M. Hiraoka, 2002. Effects of selected metal oxides on the dechlorination and destruction of PCDD and PCDF. *Chemosphere 46(9-10): 1247-1253.*

Weber, R., T. Takasuga, K. Nagai, H. Shiraishi, T. Sakurai, T. Matuda and M. Hiraoka, 2002. Dechlorination and destruction of PCDD, PCDF and PCB on selected fly ash from municipal waste incineration. *Chemosphere 46(9-10): 1255-1262.*

Weber, R., M. Plinke, Z. Xu and M. Wilken Destruction efficiency of catalytic filters for polychlorinated dibenzo-*p*-dioxin and dibenzofurans in laboratory test and field operation—insight into destruction and adsorption behavior of semivolatile compounds. *Applied Catalysis B: Environmental 31(3): 195-207.*

Weber, R. and T. Sakurai, 2001. Low temperature decomposition of PCB by TiO_2-based V_2O_5/WO_3 catalyst: evaluation of the relevance of PCDF formation and insights into the first step of oxidative destruction of chlorinated aromatics. *Applied Catalysis B: Environmental 34(2): 113-127.*

Zaleska, A., J. Hupka, M. Wiergowski and M. Biziuk, 2000. Photocatalytic degradation of lindane, *p,p*'-DDT and methoxychlor in an aqueous environment. *Journal of Photochemistry and Photobiology A: Chemistry 135(2-3): 213-220.*

Zheng, Z. and J.P. Obbard, 2002. Oxidation of polycyclic aromatic hydrocarbons (PAH) by the white rot fungus, *Phanerochaete chrysosporium*. *Enzyme and Microbial Technology 31(1-2): 3-9.*

Zouari, H., M. Labat and S. Sayadi, 2002. Degradation of 4-chlorophenol by the white rot fungus *Phanerochaete chrysosporium* in free and immobilized cultures. *Bioresource Technology 84(2): 145-150.*

REVIEWED ABSTRACTS

Baillet, C., A. Fadli and J-P Sawerysyn, 1996. Experimental study on the thermal oxidation of 1,3-hexachlorobutadiene at 500 - 1100° C, *Chemospher 32(7): 1261-1273.*

Bonte, J.L., K.J. Fritsky, M.A. Plinke and M. Wilken, 2002. Catalytic destruction of PCDD/F in a fabric filter: experience at a municipal waste incinerator in Belgium, *Waste Management 22(4): 421-426.*

Davies, W.A., Prince, R.G.H., 1994. Comparative feasibilities of processes for the destruction of organochlorines: Base-catalyzed dechlorination, sodium metal, hydrogen and electrolytic reduction processes. *Process Safety and Environmental Protection: Transactions of the Institution of Chemical Engineers, Part B* 72(2):113-115

El Mejdoub, N., A. Souizi and L. Delfosse, 1998. Experimental and numerical study of the thermal destruction of hexachlorobenzene, *Journal of Analytical and Applied Pyrolysis 47(1): 77-94.*

Goncharuk, V.V., Vakulenko, V.F., Samsoni-Todorov, A.O., Podrezov, A.N., Badekha, V.P., Shevchenko, T.L., 1996. Decomposition of pesticides, derivatives of triazole, during ozonization. *Khimiya i Tekhnologiya Topliv i Masel* 6(Nov-Dec, 1996):339-345

Johne, S., R. Watzke, K. Terytze,2001. Phytoremediation on HCH-contaminated soils. 6th international HCH and Pesticides Forum, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/.

Kümmling, K.E., D. J. Gray, J.P. Power, S.E. Woodland, 2001. Gas-phase chemical reduction of hexachlorobenzene and other chlorinated compounds: Waste treatment experience and applications. *6th international HCH and Pesticides Forum*, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/.

Langenhoff, A., S. Staps, C. Pijls, A. Alphenaar, G. Zwiep, H. Rijnaarts, 2001. Intrinsic and stimulated in situ biodegradation of Hexachlorocyclohexane (HCH). *6th International HCH and Pesticides Forum*, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/.

Phillips, T., G. Bell, D. Raymond, K. Shaw, A. Seech, 2001. DARAMEND technology for in situ bioremediation of soil containing organochlorine pesticides. *6th International HCH and Pesticides Forum*, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/.

Rulkens, W.H, 2001. Perspectives of phytoremediation for soil contaminated with pesticides. *6th International HCH and Pesticides Forum*, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/

Schramm, J.D. and I. Hua, 2000. Ultrasonic Irradiation of Dichlorvos: Decomposition Mechanism, *Water Research 35(3): 665-674.*

Sharma, A.K. , Josephson, G.B., Camaioni, D.M., Goheen, S.C., 2000. Destruction of pentachlorophenol using glow discharge plasma process. *Environmental Science and Technology, 34(11): 2267-2272.*

Zhang G. and I. Hua, 2000. Ultrasonic degradation of trichloroacetonitrile, chloropicrin and bromobenzene: design factors and matrix effects, *Advances in Environmental Research 4(3): 219-224.*

ANNOTATED LITERATURE REVIEW

GPCR – Gas phase chemical reduction

Gas-phase chemical reduction of hexachlorobenzene and other chlorinated compounds: Waste treatment experience and applications - 271
K. Elisabeth (Beth) Kümmling, Douglas J. Gray, Jim P. Power, Sherri E. Woodland
6th international HCH and Pesticides Forum, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/.

BCD - Base catalyzed decomposition

Abraham S. C. Chen, Arun R. Gavaskar, Bruce C. Alleman, Audrey Massa, Dennis Timberlake and Eric H. Drescher
Treating contaminated sediment with a two-stage base-catalyzed decomposition (BCD) process: bench-scale evaluation, *Journal of Hazardous Materials, Volume 56, Issue 3, October 1997, Pages 287-306*
Effective treatment of >99.65% of PCDD and >97.8% PCB at low levels in soils using a two stage BCD process; the treatment of pesticides is possible but was not measured. Gives costings and cost comparisons

Solvated electron process

Akira Oku, Kohei Tomari, Tohru Kamada, Etsu Yamada, Hideaki Miyata and Osamu Aozasa
Destruction of PCDDs and PCDFs. A convenient method using alkali-metal hydroxide in 1,3-dimethyl-2-imidazolidinone (DMI), *Chemosphere, Volume 31, Issue 8, October 1995, Pages 3873-3878*
PCDD and PCDF (10-12,000ppb) were extracted using hexane then treated with NaOH or KOH dissolved in DMI to achieve reductions >99.999% within 5 hrs and T=90^{o}C; up to 5% H2O acceptable

Chemical oxidation methods

Serge Chiron, Amadeo Fernandez-Alba, Antonio Rodriguez and Eloy Garcia-Calvo
Pesticide chemical oxidation: state-of-the-art, *Water Research, Volume 34, Issue 2, February 2000, Pages 366-377*
Overview of chemical oxidation of pesticides in wastewaters. photo-Fenton's reagent and TiO_2 photocatalysis together with ozonation are the most promising; TiO_2 is effective in large scale wastewaters with available sunlight and concentrations <50ppm Ozonation more easily controlled, can be implemented with UV/H_2O_2 but dependant on pollutant and mineralisation not always complete.

The various currently used chemical oxidation processes (AOPs), for pesticide elimination from wastewater are reported. Heterogeneous TiO_2 photocatalysis, ozonation and photo-Fenton's reagent are the most intensively investigated technologies. Theoretical and practical advantages and limitations of each method are discussed. Degradation mechanism and experimental conditions employed for the optimization of each technology are reviewed. Performances such as the achieved degree of mineralization and obtained degradation rates are detailed. The various analytical approaches for studying pesticide degradation by AOPs are also discussed. Formation of by-products is unavoidable during cost e•ective treatments. Their detection and identification are required in order to determine which kind of chemical structures are left at the end of the process. For this purpose, the crucial role of gas and liquid mass spectrometry is emphasized. The review reveals a general lack of data on kinetics of formation and disappearance of the major by-products. The effciency of AOPs has scarcely been investigated at industrial scales, i.e. in presence of a mixture of active ingredients

together with their formulating agents and at concentration levels above 10 mg/l. The more polar by-products are largely unknown and their toxicity is usually not addressed.

Nigel J. Bunce, Simona G. Merica and Jacek Lipkowski
Prospects for the use of electrochemical methods for the destruction of aromatic organochlorine wastes**,** *Chemosphere, Volume 35, Issue 11, December 1997, Pages 2719-2726*
Evaluation of the potential for electrochemical destruction of pesticides; potential is high for aqueous solutions such as leachate from stockpiles or treated soil.

William J. Cooper, Michael G. Nickelsen, Stephen P. Mezyk, Greg Leslie, Paul M. Tornatore, Wayne Hardison and Paris A. Hajali
MTBE and priority contaminant treatment with high energy electron beam injection, *Radiation Physics and Chemistry, Volume 65, Issues 4-5, November 2002, Pages 451-460*
Advanced oxygenation technology which effectively treated organochlorines in aqueous solution at very low concentrations (ug/l).

A study was conducted to examine the removal of methyl tert butyl ether (MTBE) and 15 other organic compounds, as well as perchlorate ion,in waters of different quality.The 15 organic compounds consisted of halogenated solvents (chlorination),disinfection by-products,pesticides,and nitrosodimethylamine (NDMA).These studies were conducted using a pilot scale 20 kW mobile electron beam system at Water Factory 21, Orange County, CA where wastewater is treated and re-injected into the ground as a barrier to salt water intrusion.Future applications for this treated water include water reuse.Ground water and treated wastewater,after having gone through a reverse osmosis-polishing step (RO permeate),were used to prepare mixtures of the compounds.Using fundamental radiation chemistry,it was possible to examine the factors effectingremoval ef .ciency of all the compounds as well as MTBE destruction and reaction by-product formation and removal.All of the organic compounds were destroyed in the studies and we also observed the destruction of perchlorate ion in one of the waters.

Electrochemical peroxidation process (Fenton's reaction)
(aqueous solution)
M. Arienzo, J. Chiarenzelli, R. Scrudato, J. Pagano, L. Falanga and B. Connor
Iron-mediated reactions of polychlorinated biphenyls in electrochemical peroxidation process (ECP), *Chemosphere, Volume 44, Issue 6, September 2001, Pages 1339-1346*
Complete removal of PCBs in 0.061ppm aqueous solutions of PCBs using iron powder and iron electrodes.

Yan Liu, Zhaobin Wei, Zhaochi Feng, Mengfei Luo, Pinliang Ying and Can Li
Oxidative Destruction of Chlorobenzene and *o*-Dichlorobenzene on a Highly Active Catalyst: $MnO_x/TiO_2–Al_2O_3$, *Journal of Catalysis, Volume 202, Issue 1, 15 August 2001, Pages 200-204*
A highly active catalyst, $MnO_x/TiO_2 –Al_2 O_3$, was prepared by mpregnating MnO_x species on TiO_2 -modified $Al_2 O_3$. The TiO species in $TiO_2 –Al_2 O_3$ support is in a monolayer dispersion, and the MnO_x species is again highly dispersed on $TiO_2 –Al_2 O_3$ support. The total oxidation of chlorobenzene and *o*-dichlorobenzene on $MnO_x/TiO_2 –Al2 O_3$ catalyst can be achieved at 300^oC and 250^oC respectively, at the space velocity of 8000 h¡ 1 . The activity of $MnO_x/TiO_2 –Al_2 O_3$ catalyst (Mn loading 11.2 wt%) is gradually increased in the first 10–20 h and then keeps stable at least for the measured 52 h at 16,000 h¡ 1 . Furthermore, no chlorinated organic byproducts are detected in the effluent during the oxidative de-struction of

chlorobenzene and o-dichlorobenzene. It is proposed that the partially chlorinated and highly dispersed manganese oxide on a monolayer TiO_2 -modified Al_2O_3 is responsible for the high and stable activity for the total oxidation of chlorinated aromatics.

Slawomir Lomnicki, Janine Lichtenberger, Zhengtian Xu, Michelle Waters, Joe Kosman and Michael D. Amiridis
Catalytic oxidation of 2,4,6-trichlorophenol over vanadia/titania-based catalysts, *Applied Catalysis B: Environmental, In Press, Corrected Proof, Available online 1 August 2003.*
The catalytic oxidation of 2,4,6-trichlorophenol (TCP) was investigated over two commercial vanadia/titania-based catalysts both in the presence and the absence of water. The two catalysts exhibited significant activity for the oxidation of TCP-producing carbon dioxide and HCl as the main reaction products. Furthermore, these catalysts-as well as the bare titania support-have a high capacity for the reversible adsorption of TCP at 200^{o}C. The presence of water affects the adsorption capacity, steady state activity and product distribution observed. This behavior can be attributed to the competitive adsorption of TCP and water, and the surface reactions of hydroxyl groups with Cl species and adsorbed chlorinated hydrocarbon derivatives. In situ FTIR studies indicate the presence of phenolate, catecholate, ether, benzoquinone, aldehyde and carboxylate species on the catalyst surface following the adsorption of TCP as well as under reaction conditions. These partial oxidation products are formed during the reaction of TCP with surface oxygen and are intermediates of the oxidation process.
These catalysts are used commercially for PCDD control

James F. Rusling, Silvia Schweizer, Shiping Zhang and Geoffrey N. Kamau
Microemulsions as media for destruction of organohalide pollutants by electrolysis, *Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 88, Issue 1, 19 August 1994, Pages 41-49*
This paper reviews recent work on the dehalogenation of organohalide pollutants by electrochemical catalysis in bicontinuous microemulsions of didodecyldimethylammonium bromide (DDAB)-water-dodecane. Compared with alternative toxic, expensive organic solvents, the catalytic efficiency for the dehalogenations was enhanced for non- polar organohalides in DDAB microemulsions. Using metal phthalocyanine tetrasulfonates as catalysts, the catalytic efficiencies for the reactions of 1,2-dibromobutane and 1,2-dibromocyclohexane were much larger in a microemulsion than in a homogeneous solvent. The reverse was found for trichloroacetic acid. Since DDAB and the catalysts adsorb on the carbon cathode, results suggest that a DDAB layer on the cathode preconcentrates non-polar dibromides but not the polar trichloroacetic acid. For complex mixtures of polychiorinated biphenyls, DDAB microemulsions performed better in bench-scale catalytic dechlorinations than aqueous DDAB dispersions, which performed better than aqueous CTAB micelles. Complete conversion of 100 mg of a 60% chlorine industrial PCB mixture in a 20 ml microemulsion could be carried out overnight using an activated lead cathode, zinc phthalocyanine as catalyst, and ultrasonic mass transport. Finally, the dechlorination of DDT (l,l-bis(4-chlorophenyl)-2,2,2-trichloroethane), which has both aliphatic and aromatic chlorines, was also explored in the microemulsions. Preliminary results suggest that oxygen may be an effective catalyst for the dechlorination of DDT in DDAB microemulsions to l,l-diphenylethane using a carbon cathode.

Ozonation
Jun-ichiro Hayashi, Joji Ikeda, Katsuki Kusakabe and Shigeharu Morooka

Decomposition rate of volatile organochlorines by ozone and utilization efficiency of ozone with ultraviolet radiation in a bubble-column contactor, *Water Research, Volume 27, Issue 6, June 1993, Pages 1091-1097*
Use of UV and ozone to degrade low levels of organochlorines in aqueous solution

Philip C. Kearney, Mark T. Muldoon and Cathleen J. Somich
UV-ozonation of eleven major pesticides as a waste disposal pretreatment, *Chemosphere, Volume 16, Issues 10-12, 1987, Pages 2321-2330*
Low levels of pesticides in aqueous solution

P. Ormad, S. Cortés, A. Puig and J. L. Ovelleiro
Degradation of Organochloride compounds by O_3 and O_3/H_2O_2, *Water Research, Volume 31, Issue 9, September 1997, Pages 2387-2391*
Degradation of a wastewater containing a mixture of organochlorines using O3 and H2O2 in a basic (pH - 9.4) medium; trichlorobenzene and others degraded but DDE not affected
This paper presents the results obtained from oxidation with O_3 and O_3/H_2O_2 of a residual water coming from the production of dicofol and tetradifon pesticides, where chlorobenzenes, DDTs and its metabolites and other organochloride compounds were found. The oxidation processes were carried out using ozone (O_3) in basic medium (pH 9.4) at low dosage (0-1.5 g O_3 g^{-1} initial TOC) and in the presence of hydrogen peroxide (H_2O_2), with a 0.5 H_2O_2/O_3 molar ratio. During the treatment, many compounds were removed (dichlorobenzophenone, tetradifon, chlorobenzene, trichlorobenzene) and their change in concentration at different ozonation contact time was monitored. Other compounds like DDE remained practically invariable. This study investigated the formation of first ozonation by-products (FOBPs) in the wastewater, specifically chlorophenols, by means of gas chromatography/mass spectrometry (GC/MS) and gas chromatography/electron capture detection (GC/ECD) analysis in terms of the amount of time the O_3 has been in contact with the processed sample. *o*-Chlorophenol, *p*-chlorophenol, benzenemethanol, *n*-chlorohydroxibenzaldehyde, *n*-chlorobenzenemethanol, chlorobenzoic acid, etc., were formed during the treatment, due to the mechanism of fast and non-selective oxidation which ozone has through OH radicals, formed by the decomposition of the O_3 molecule and accelerated by the presence of H_2O_2 in water.

Photodegradation
Abdul J. Chaudhary, Susan M. Grimes and Mukhtar-ul-Hassan
Simultaneous recovery of copper and degradation of 2,4-dichlorophenoxyacetic acid in aqueous systems by a combination of electrolytic and photolytic processes, *Chemosphere, Volume 44, Issue 5, August 2001, Pages 1223-1230*
Complete degradation of 2,4D in a 50ppm aqueous solution by a photolytic process

Yu. I. Skurlatov, L. S. Ernestova, E. V. Vichutinskaya, D. P. Samsonov, I. V. Semenova, I. Ya. Rod'ko, V. O. Shvidky, R. I. Pervunina and T. J. Kemp
Photochemical transformation of polychlorinated phenols, *Journal of Photochemistry and Photobiology A: Chemistry, Volume 107, Issues 1-3, 15 July 1997, Pages 207-213*

Photocatalyst (Fe(III)) degradation
Carole Catastini, Mohamed Sarakha, Gilles Mailhot and Michèle Bolte, Iron (III) aquacomplexes as effective photocatalysts for the degradation of pesticides in homogeneous aqueous solutions, *The Science of The Total Environment, Volume 298, Issues 1-3, 21*

October 2002, Pages 219-228
Complete degradation of asulam

Photocatalyst (TiO_2) degradation
Hema M. K. K. Pathirana and R. A. Maithreepala
Photodegradation of 3,4-dichloropropionamide in aqueous TiO_2 suspensions, *Journal of Photochemistry and Photobiology A: Chemistry, Volume 102, Issues 2-3, 22 January 1997, Pages 273-277*
Complete destruction of 265ppm DPA in aqueous TiO_2 within 5 hr

Alessandra Bianco Prevot and Edmondo Pramauro, Analytical monitoring of photocatalytic treatments. Degradation of 2,3,6-trichlorobenzoic acid in aqueous TiO_2 dispersions, *Talanta, Volume 48, Issue 4, 5 April 1999, Pages 847-857*
Degradation of aqueous solutions of 34mg/L 236 TBA using 340mg/L TiO_2 with a surfactant at a pH of 3 and T=25^{o}C after 90 minutes

Martha M. Higarashi, Wilson F. Jardim, Remediation of pesticide contaminated soil using TiO_2 mediated by solar light. Catalysis Today 76 (2002) 201–207
Soil at 100ppm contamination of Diuran (Nortex) a haloaromatic pesticide degraded with 90% degradation at 2cm depth and 120h; dependant on light intensity

Qingdong Huang and Chia-Swee Hong
TiO_2 photocatalytic degradation of PCBs in soil-water systems containing fluoro surfactant, *Chemosphere, Volume 41, Issue 6, May 2000, Pages 871-879*
Low level contaminated soil (including age-contaminated soils) degraded with TiO_2 and fluoro surfactants

Ioannis K. Konstantinou and Triantafyllos A. Albanis
Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways, *Applied Catalysis B: Environmental, Volume 42, Issue 4, 10 June 2003, Pages 319-335*
Review of TiO_2 photodegradation in aqueous solution; lindane, DDT, methoxychlor are mineralised with various intermediates

Adriana Zaleska, Jan Hupka, Marek Wiergowski and Marek Biziuk
Photocatalytic degradation of lindane, *p,p'*-DDT and methoxychlor in an aqueous environment, *Journal of Photochemistry and Photobiology A: Chemistry, Volume 135, Issues 2-3, 26 July 2000, Pages 213-220*
Aqueous solutions containing 40 mg/dm 3 of lindane, p,p0 -DDT and methoxychlor were photodegraded in a UV/TiO_2/O_2 system yielding different degradation products. Powdered anatase and rutile, and anatase supported on glass hollow microspheres served as photocatalysts. The destruction degree of pesticides was evaluated and oxidation products identified by gas chromatography with an electron capture detector (GC–ECD) and a mass spectroscopy detector (GC–MS). From 68 to 90% of pesticides investigated was eliminated after 30 min irradiation in the presence of anatase supported on glass microspheres. The lowest efficiency was obtained for rutile as a catalyst. One hundred and fifty minutes of processing resulted in 50% elimination for g-HCH, 85% for DDT and over 99% for methoxychlor.

H. D. Burrows, M. Canle L, J. A. Santaballa and S. Steenken

Reaction pathways and mechanisms of photodegradation of pesticides, *Journal of Photochemistry and Photobiology B: Biology, Volume 67, Issue 2, June 2002, Pages 71-108*

Evaluation of photodegradation of pesticides in aqueous solution

A. Vidal, A. I. Díaz, A. El Hraiki, M. Romero, I. Muguruza, F. Senhaji and J. González
Solar photocatalysis for detoxification and disinfection of contaminated water: pilot plant studies, *Catalysis Today, Volume 54, Issues 2-3, 3 December 1999, Pages 283-290*
Photocatalytic processes in the presence of titanium dioxide provide an interesting route to destroy hazardous organic contaminants, being operational in the UV-A domain with a potential use of solar radiation. A preliminary evaluation of a photocatalytic process for water purification has been made to assess its effectiveness in reducing contaminant concentrations of drinking water standards. Studies reported in this paper also evaluate the performance of a low-cost compound parabolic concentrator (CPC) prototype built along this work and explore the feasibility of this concept as the basis for the solar pho-tocatalytic oxidation facilities of water supplies. From our observations, a solar throughput value of 42 l/h m 2 for the low-cost CPC reactor tested at our facilities has been obtained. These calculations are based on the time required for the destruction of 20-500 μg/l of selected pesticides to maximum permitted levels (0.1 mg/l) and four-log inactivation of microorganisms. From the research performed, cost analyses have been made for a full-scale commercial system using the data available in this project. For a 500 m^2 facility, the estimated total costs for photocatalytic degradation is competitive with conventional technologies and estimated to be ca. 0.7 $/$m^3$.

A. Vidal, Z. Dinya, F. MogyorodiJr. and F. Mogyorodi
Photocatalytic degradation of thiocarbamate herbicide active ingredients in water, *Applied Catalysis B: Environmental, Volume 21, Issue 4, 2 August 1999, Pages*
It has been shown that a wide range of organic compounds in aqueous solutions is photocatalytically oxidized to carbon dioxide in the presence of titanium dioxide with near-UV radiation. The photocatalytic mineralization of thiocarbamate derivative pesticides (EPTC, butylate, molinate, vernolate and cycloate) in water by illuminated TiO_2 has been studied. The determination of the effects of various kinetic factors on the photocatalytic degradation and the determination of the nature of the principal intermediates form part of the focus of this study. The degradation rate of these thiocarbamates in a continuous recirculation mode approximates first-order kinetics. It was demonstrated that photocatalyzed degradation of thiocarbamate active ingredients does not occur instantaneously to form carbon dioxide, but through the formation of long-lived intermediate species. Photocatalytic intermediates detected during the degradation of thiocarbamates were identified by GC/MS techniques. Intermediates detected in the photocatalytic oxidation of thiocarbamates in water solutions are in excellent agreement with products identified from the atmospherically important reactions of OH radical with thiocarbamates. Particular attention will be paid to the carbon dioxide formed from the illuminated suspension in order to demonstrate not only apparent destruction but also complete mineralization. The degradation of a two-component mixture was carried out and compared to results obtained with single-component studies.

Erick R. Bandala, Silvia Gelover, Maria Teresa Leal, Camilo Arancibia-Bulnes, Antonio Jimenez and Claudio A. Estrada
Solar photocatalytic degradation of Aldrin, *Catalysis Today, Volume 76, Issues 2-4, 15 November 2002, Pages 189-199*
90% degradation of aldrin from 5ppm aqueous solutions using light, hydrogen peroxide and TiO_2

Photocatalytic degradation of the pesticide Aldrin dissolved in water was carried out, in one case, using concentrated solar radiation and, in another case, using non-concentrated solar radiation. In these experiments, the effects of catalyst concentration, oxidant agent concentration, and solar irradiation were tested. In experiments without irradiation, strong adsorption of the pesticide over titanium dioxide was observed in the first few minutes of contact in the presence of titanium dioxide (TiO_2). These results can be explained by means of Coulombic interactions between the catalyst surface and the pesticide molecules. During the photodegradation process, results show a residual degradation (photolysis) in both the cases, when no catalyst was added. In the case of the non-concentrated solar system, the achieved results suggest that the use of H_2O_2 increased the degradation rate. For concentrated sunlight, an increase of the Aldrin concentration was observed during the first few minutes of irradiation. This can be explained as a desorption process that is triggered by a change in surface charge of the catalyst in the presence of hydrogen peroxide (H_2O_2) during irradiation. When photocatalysis was performed with TiO_2 alone, no Aldrin was detected in the water solutions throughout the entire experiment. This result was unexpected; however, it might be explained by the adsorption of the pesticide on the catalyst surface and by the absence of the oxidant's effect. Three transformation products (TPs) of the degradation process were identified: dieldrin, chlordene and 12-hydroxy-dieldrin. The results presented here are in agreement with previously reported results for photocatalytic degradation of other chlorinated pesticides using lamps as radiation sources.

S. Malato, J. Blanco, C. Richter, B. Braun and M. I. Maldonado
Enhancement of the rate of solar photocatalytic mineralization of organic pollutants by inorganic oxidizing species, *Applied Catalysis B: Environmental, Volume 17, Issue 4, 31 August 1998, Pages 347-356*
Particulate suspensions of TiO_2 irradiated with natural solar light in a large experimental plant catalyze the oxidation of a typical organic contaminant: pentachlorophenol (PCP). The addition of oxidants, concentration of which is kept constant during treatment, such as hydrogen peroxide, peroxymonosulphate (oxone) and peroxydisulphate increases the rate of photodegradation of PCP in the following order: $S_20_8^{2-}$> Oxone > H_2O_2. Peroxydisulphate (10 mM), selected as the best oxidant studied, has been applied to the development of a solar photocatalytic plant for the treatment of commercial pesticide rinsates found in the wastewater produced by a pesticide container recycling plant, which includes the correct treatment of this highly contaminating effluent. The first results, without process or hardware optimisation, show that peroxydisulphate enhances the photocatalytic mineralization rate at least five times. Low concentrations of pesticides treated

Fenton reaction
A. Galadi, H. Bitar, M. Chanon and M. Julliard
Photosensitized reductive dechlorination of chloroaromatic pesticides, *Chemosphere, Volume 30, Issue 9, May 1995, Pages 1655-1669*
Use of electron donor photosensitizer in improving the efficiency of photodegradation of pesticides in aqueous solution

Patrick L. Huston and Joseph J. Pignatello
Degradation of selected pesticide active ingredients and commercial formulations in water by the photo-assisted Fenton reaction, *Water Research, Volume 33, Issue 5, April 1999, Pages 1238-1246*
Degradation of pesticides in water at solubility levels using Fe(III)/H_2O_2/UV. Most 100% degraded but some were lower with concerns re toxic daughter products.

The destruction of pesticide active ingredients (AI) and commercial formulations in acidic aqueous solution with the catalytic photo-Fenton, Fe(III)/H_2O_2 /UV, advanced oxidation process has been studied. The AI are alachlor, aldicarb, atrazine, azinphos-methyl, captan, carbofuran, dicamba, disulfoton, glyphosate, malathion, ethoxylchlor, metolachlor, picloram and simazine. Complete loss of pure AI occurred in most cases in <30 min under the following conditions: $5.0X10^{5}$M Fe(III), $1.0X10^{-2}$M H_2O_2 , T =25°C, pH 2.8 and $1.2X10^{-19}$ quanta $1^{-1}s^{-1}$ with fluorescent blacklight UV irradiation (300±400 nm). Considerable mineralization over 120 min occurred in most cases as evidenced by the appearance of inorganic ions and the decline in total organic carbon (TOC) of the solution. Intermediate products such as formate, acetate and oxalate appeared in early stages of degradation in some cases. Observed rate constants calculated from initial rates varied by a factor of <03. The commercial products, Furadan (AI, carbofuran), Lasso 4EC (AI, alachlor) and Lasso Microtech (AI, alachlor) were also tested. The "inert ingredients" (adjuvants) present in these products had no effect (Furadan), a slight effect (Lasso 4EC), or a strong effect (Lasso Microtech) on the rate of degradation of the AI. Lasso Microtech, in which the AI is micro-encapsulated in a polymeric shell wall micro-sphere, required slightly elevated temperatures to effect removal of alachlor in a timely manner. The results show that many pesticides and their commercial formulations in dilute aqueous solution are amenable to photo-Fenton treatment.

Supercritical water oxidation

K. Hatakeda, Y. Ikushima, O. Sato, T. Aizawa, N. Saito. Supercritical water oxidation of polychlorinated biphenyls using hydrogen peroxide. Chemical Engineering Science 54 (1999) 3079-3084

Degradation of 9000ppm PCBs using H_2O_2 and scwo at 30Mpa and 673°C to a level of 99.999% releasing HCl and CO_2

Hawthorne, S.B, Lagadec, A.J.M., Kalderis, D., Lilke, A.V., Miller, D.J.
Pilot-scale destruction of TNT, RDX, and HMX on contaminated soils using subcritical water. Environmental Science & Technology. Vol. 34, no. 15, pp. 3224-3228. Aug 2000.
Use of subcritical water to degrade explosives at up to 12% contamination at 275°C and 60bar pressure; lower temperatures and pressures for longer times achieved >98%.
Estimates based on Montero et al. predict a cost of $125/ton compared to $125-210/ton for composting, $220-650/ton for supercritical water oxidation, and ca. $1600/ton for incineration.

Juhani Kronholm, Teemu Kuosmanen, Kari Hartonen and Marja-Liisa Riekkola
Destruction of PAHs from soil by using pressurized hot water extraction coupled with supercritical water oxidation, *Waste Management, Volume 23, Issue 3, 2003, Pages 253-260*
Technically the PHWE-SCWO provided safe and effective extraction of organic compounds from sea sand and delivery of the compounds into the reaction tube for oxidation. The oxidation process is in need of further optimization (higher temperature, use of oxidant gradient, turbulence in the reaction tube) to provide destruction of all the compounds. The oxidation of PAHs was not investigated separately from toluene; however, real environmental samples often contain a mixture of pollutants, and in this sense the problems with toluene were of interest. With real environmental samples, extraction can also remove salts and halogenated compounds, which can damage the oxidation reactor through corrosion. Consequently, the equipment used in the remediation of contaminated soil needs careful design.

Ultrasonic irradiation

Jennifer D. Schramm and Inez Hua, Ultrasonic Irradiation of Dichlorvos: Decomposition Mechanism, *Water Research, Volume 35, Issue 3, February 2001, Pages 665-674*

The sonochemical degradation of dichlorvos in a batch reactor is investigated. Dichlorvos was irradiated with 500 kHz ultrasound at input powers ranging from 86 to 161 W. Acoustic power and sparge gas are two factors which greatly affect sonochemical degradation efficiency. Increasing total acoustic power input from 86 to 161 W resulted in a change in the rate constant from 0.018±0.001 min^{-1} to 0.037±0.002 min^{-1}. The change in rate constant due to sparge gas (Argon, Oxygen, and Argon/Oxygen (60/40% v/v) mixture) at a power of 161 W is also investigated, with the Argon/Oxygen mixture giving the highest rate constant (0.079±0.005 min^{-1}). Total organic carbon and ion chromatographic analyses are employed to determine and quantify major degradation products, including dimethyl phosphate, formate, carbon dioxide, chloride, and phosphate. The extent of mineralization, indicated by a decrease in the total organic carbon, and the formation of the various intermediates and products, varies with saturating gas. A pathway for dichlorvos decomposition is proposed, based upon formation rates of the various intermediates and products and the rate of decrease of the total organic carbon in the system. The limiting steps in the mineralization pathway appear to be transformation of dimethyl phosphate and formate.

Guangming Zhang and Inez Hua,
Ultrasonic degradation of trichloroacetonitrile, chloropicrin and bromobenzene: design factors and matrix effects, *Advances in Environmental Research, Volume 4, Issue 3, August 2000, Pages 219-224*

Power ultrasound has been employed to degrade numerous environmental pollutants. Through a series of experiments, the viability of sonication for pollution control in higher complexity systems was investigated. First, a mixture of chloropicrin (CCl_3NO_2), trichloroacetonitrile (C_2Cl_3N), and bromobenzene (C_6H_5Br) was irradiated in a batch system. At a frequency of 20 kHz and a sound intensity of 30.8 W cm^{-2}, a minimal difference was observed between rate constants during sonication of a mixture and rate constants during sonication of individual compounds. Ultrasonic irradiation at 358 kHz was also viable for treatment of a mixture characterized by a high chemical oxygen demand (COD=3470 ppm). Sonication in a complex aqueous matrix, river water, demonstrated minimal to moderate decreases in efficiency compared to sonication in reagent grade water. The recovery ratios for chloride, bromide, and inorganic nitrogen (nitrite plus nitrate) were 72±1, 56±3 and 91±2%, demonstrating the extent of mineralization of the parent compounds. A flow-through reactor was also studied. Higher flow rates and appropriate positioning of the ultrasonic probe accelerated the observed reaction rates. For example, increasing the flow rate from 4.4 to 34 ml min^{-1} doubled the sonication coefficient for bromobenzene in a mixture, possibly due to better temperature control and mixing. Also, the sonication coefficient was 34% higher for chloropicrin degradation when the probe was positioned 1 cm from the entrance than when the probe was positioned 14.2 cm from the entrance.

Michael R. Hoffmann, Inez Hua and Ralf Höchemer
Application of ultrasonic irradiation for the degradation of chemical contaminants in water, *Ultrasonics Sonochemistry, Volume 3, Issue 3, November 1996, Pages S163-S172*

The degradation of chemical compounds by electrohydraulic cavitation involves three distinct pathways. The pathways include oxidation by hydroxyl radicals, pyrolytic decomposition and supercritical water oxidation. It has been shown that transient supercritical water is obtained during the collapse of cavitation bubbles generated sonolytically. The sonochemical degradation of a variety of chemical contaminants in aqueous solution has been investigated.

Substrates such as chlorinated hydrocarbons, pesticides, phenols, explosives such as TNT, and esters are transformed into short-chain organic acids, CO_2, and inorganic ions as the final products. Time scales of treatment in simple batch reactors over the frequency range of 20 to 500 kHz are reported to range from minutes to hours for complete degradation. Ultrasonic irradiation appears to be an effective method for the rapid destruction of organic contaminants in water because of localized high concentrations of oxidizing species such as hydroxyl radical and hydrogen peroxide in solution, high localized temperatures and pressures, and the formation of transient supercritical water. The degradation of chemical compounds by acoustic cavitation is shown to involve three distinct pathways: 1) oxidation by hydroxyl radicals, 2) pyrolytic decomposition and 3) supercritical water oxidation. Detailed reaction mechanisms for the degradation of p-nitrophenol, carbon tetrachloride, parathion, p-nitrophenyl acetate and trinitrotoluene are presented.

Electrical discharge

Haiyan Sun, H. Felix, A. Nasciuti, Y Herieti and W. Hoffelner
Reduction of NO/NO_2 & SO_2 and destruction of VOCs & PCDD/F in industrial flue gas by electrical discharge, *Chemosphere, Volume 37, Issues 9-12, 11 October 1998, Pages 2351-2359*
A systematic study with the aim to reduce NO/NO_2, SO_2 and to destroy VOCs and PCDD/F in flue gas by electrical discharge both in laboratory and at a pilot plant has been performed. Results show that 1) both indirect and direct treatment by electrical discharge can reduce NO/NO_2 and SO_2 and can destroy PCDD/F in flue gas; 2) Indirect treatment destroys about 90% of PCDD/F in real industrial flue gas; and 3) It is possible to destroy NO/NO_2, SO_2 and PCDD/F in one step.

Roland Weber and Takeshi Sakurai
Low temperature decomposition of PCB by TiO_2-based V_2O_5/WO_3 catalyst: evaluation of the relevance of PCDF formation and insights into the first step of oxidative destruction of chlorinated aromatics, *Applied Catalysis B: Environmental, Volume 34, Issue 2, 5 November 2001, Pages 113-127*
In this study, PCB were destroyed on a V_2O_5/WO_3 supported titanium catalyst at low temperature in the range of 150–300°C. At a space velocity of 5000 h 1 more than 98% could be removed. Below 250°C, the higher chlorinated PCB remained partly unchanged on the catalyst for several minutes. In contrast, the oxidation process lasted up to hours at a temperature of 150°C. At around 200°C and below a significant part of the PCB were oxidised to the more toxic polychlorinated dibenzofurans (PCDF). The PCDF remained mainly adsorbed on the catalyst. At 250°C, no significant amount of PCDF were detected and at 300°C no byproducts were found.

Roland Weber, Marc Plinke, Zhengtian Xu and Michael Wilken
Destruction efficiency of catalytic filters for polychlorinated dibenzo-*p*-dioxin and dibenzofurans in laboratory test and field operation—insight into destruction and adsorption behavior of semivolatile compounds, *Applied Catalysis B: Environmental, Volume 31, Issue 3, 17 May 2001, Pages 195-207*
Catalytic destruction of chlorinated dibenzodioxins and dibenzofurans for environmental protection is one of the key subjects of applied catalysis in combustion facilities. For catalytic filters, the removal and destruction efficiencies (RE and DE) for polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) were tested in the laboratory and compared with data from field operation. The comparison shows very similar values of laboratory measurements and actual field measurements for fresh samples, used samples without catalyst

deactivation, and used samples with varying degrees of deactivation. The non-poisoned catalytic filter showed destruction and removal efficiencies for PCDD/PCDF and the "toxic equivalents" (TEQ) of more than 99%. The laboratory comparison confirmed this activity did not decrease after 2 years of operation in a municipal waste incinerator.

R. Weber, K. Nagai, J. Nishino, H. Shiraishi, M. Ishida, T. Takasuga, K. Konndo and M. Hiraoka
Effects of selected metal oxides on the dechlorination and destruction of PCDD and PCDF, *Chemosphere, Volume 46, Issues 9-10, March 2002, Pages 1247-1253*
OCDD and OCDF spiked silica/graphite based model fly ash containing various copper compounds and metal oxides were thermally treated under oxygen deficient conditions. All copper compounds tested showed a considerable dechlorination/hydrogenation reaction at 260°C. After 30 min at 340°C less than 1%of the spiked OCDD and OCDF was recovered as TCDD/F to OCDD/F.Other compounds tested demonstrated a lower rate of dechlorination compared to the copper compounds.However,all other metal oxides showed a small dechlorination effect at 260°C which was considerably increased at 340°C.

R. Weber, T. Takasuga, K. Nagai, H. Shiraishi, T. Sakurai, T. Matuda and M. Hiraoka
Dechlorination and destruction of PCDD, PCDF and PCB on selected fly ash from municipal waste incineration, *Chemosphere, Volume 46, Issues 9-10, March 2002, Pages 1255-1262*
The potential of fly ash to dechlorinate and destroy PCDD,PCDF and PCB was tested under oxygen deficient conditions in the laboratory. Specifically, two types of fly ash were compared, originating either from a fluidized bed incinerator using $Ca(OH)_2$ spray (FA1),or a stoker incinerator without $Ca(OH)_2$ impact (FA2). Results from the present study indicate that on FA2 type fly ash, the degradation processes of OCDD,OCDF and D10CB occurred primarily via dechlorination/hydrogenation up to temperature settings of 340°C In contrast, FA1 type fly ash was found to effect both dechlorination and destruction of these compounds already at temperature settings of 260°C. The dechlorination velocity of PCDD and PCDF did not differ significantly. However, the first dechlorination step of OCDF in the 1,9-position occurred faster compared to the first dechlorination step of OCDD. The isomer pattern resulting from the dechlorination processes was quite similar on both FA1 and FA2, indicating that differences in alkalinity or elemental composition of the two types of fly ashes do not have a significant influence on the position of dechlorination. PCDD and PCDF dechlorination of the 2,3,7,8-positions was not favoured over de-chlorination of the 1,4,6,9-positions on either type of fly ash. In contrast, dechlorination of PCB occurred predominantly on the toxicological relevant 3-and 4-positions. The dechlorination/destruction processes were completed on both types of fly ash at 380°C within one hour, which correlates well with results obtained from actual plant operation practices.

Vinod K. Gupta, C. K. Jain, Imran Ali, S. Chandra and S. Agarwal, Removal of lindane and malathion from wastewater using bagasse fly ash—a sugar industry waste, *Water Research, Volume 36, Issue 10, May 2002, Pages 2483-2490*
The bagasse fly ash, obtained from the local sugar industry, has been used as inexpensive and effective adsorbent for the removal of lindane and malathion from wastewater. The optimum contact needed to reach equilibrium was found to be 60 min. Maximum removal takes place at pH 6.0. The removal of the pesticides increases with an increase in adsorbent dose and decreases with adsorbent particle size. The optimum adsorbent dose is 5 g/l of particle size 200 – 250μm. Removal of the two pesticides was achieved up to 97–98%under optimum conditions. The material exhibits good adsorption capacity and follows both Langmuir and Freundlich models. Thermodynamic parameters also indicate the feasibility of the process.

The adsorption was found to be exothermic in nature. At lower concentrations, adsorption is controlled by .lm diffusion, while at higher concentrations, it is controlled by particle diffusion mechanisms. The adsorbent is a very useful and economic product for the removal of lindane and malathion.

Vinod K. Gupta and Imran Ali, Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste, *Water Research, Volume 35, Issue 1, January 2001, Pages 33-40*
Bagasse fly ash, a waste from the sugar industry, was converted into an effective adsorbent and was used for the removal of DDD [2,2-Bis(4-chlorophenyl)-1,1-dichloroethane] and DDE [2,2-Bis(4-chlorophenyl)-1,1-dichloroethene] pesticides from wastewater. The DDD and DDE are removed by the developed adsorbent up to 93% at pH 7.0, with the adsorbent dose of 5 g/l of particle size 200–250µm at 30°C. The removal of these two pesticides was achieved up to 97–98% in column experiments at a flow rate of 0.5 ml/min. The adsorption was found to be exothermic in nature. The bagasse fly ash system has been used for the removal of DDD and DDE from the wastewater. The developed system is very useful, economic, and reproducible.

Bioremediation
Bioactive activated charcoal
Badri N. Badriyha, Varadarajan Ravindran, Walter Den and Massoud Pirbazari
Bioadsorber efficiency, design, and performance forecasting for alachlor removal, *Water Research, Volume 37, Issue 17, October 2003, Pages 4051-4072*
Complete removal of alachlor from 5ppm aqueous solutions

Kyoungphile Nam, Wilson Rodriguez and Jerome J. Kukor
Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction, *Chemosphere, Volume 45, Issue 1, October 2001, Pages 11-20*
Using Fe ions and a chelating agent (catechol and gallic acid) combined with H_2O_2, a Fenton reaction at neutral pH was combined with in situ soil bacteria to degrade polycyclic aromatic hydrocarbons at 600 ug/g by 98% for 2-3 ring and 70-85% 4-5ring hydrocarbon molecules.

Eva M. Top, Mphekgo P. Maila, Marleen Clerinx, Johan Goris, Paul De Vos and Willy Verstraete
Methane oxidation as a method to evaluate the removal of 2,4-dichlorophenoxyactic acid (2,4-D) from soil by plasmid-mediated bioaugmentation, *FEMS Microbiology Ecology, Volume 28, Issue 3, March 1999, Pages 203-213*
The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is known to inhibit methanotrophic bacteria. Methane oxidation was therefore used as a parameter to evaluate the residual 2,4-D after bioaugmentation of an agricultural soil. Several strains harbouring catabolic plasmids which code for the degradation of this pesticide, were compared for their potential to alleviate the negative impact of 2,4-D on methane oxidation by soil microorganisms. Three indigenous soil bacteria which contain the 2,4-D degradative plasmid pEMT1k, obtained from a donor by in situ plasmid transfer in previous experiments, were compared with *Ralstonia eutropha* JMP134, which harbours the well studied 2,4-D degradative plasmid pJP4. In addition a *Pseudomonas putida* UWC3(pEMT1k), which does not degrade 2,4-D, was used as donor to investigate the potential bioaugmentation through in situ transfer of the catabolic genes towards the indigenous soil bacteria. Both the strains that can degrade 2,4-D as well as the *P. putida* donor strain could enhance the recovery of methane oxidation by increasing the rate of degradation of 2,4-D and thus removing its toxic effect on the methane oxidising microbial populations. In all cases the time needed to oxidise methane was consistently shorter (4-10

days) in a 2,4-D treated soil inoculated with the strains, than in the non-inoculated 2,4-D treated soil, but still longer (5-10 days) than in the soil without 2,4-D. These data indicate that pesticide residues as well as their toxic effect on important soil microbial processes could be successfully removed from the soil by addition of well adapted specialised strains with the genetic information required to degrade the applied pesticides.

In situ bioremediation

Biodegradation of DDT

You Guanrong, Gregory D. Sayles, Margaret J. Kupferle, Paul L. Bishop, S. Kim In Anaerobic DDT biotransformation: enhancement by application of surfactants and low oxidation reduction potential, Chemosphere, Volume 32, Issue 11, June 1996, Pages 2269-2284.

Anaerobic degradation of 2500ppm DDT in saturated soil of 99.3% with use of surfactants and reducing agents

Enhancement of anaerobic DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane) biotransformation by mixed cultures was studied with application of surfactants and oxidation reduction potential reducing agents. Without amendments, DDT transformation resulted mainly in the production of DDD (1,1-dichloro-2,2-bis(p-chlorophenyl) ethane) upon removal of one aliphatic chlorine. The DDT transformation rate increased with the addition of the nonionic surfactants Triton X-114 or Brij 35. The addition of either surfactant or reducing agents did not significantly extend the DDT transformation. Addition of both surfactant and reducing agents extended DDT transformation by reducing the accumulation of DDD and increasing the accumulation of less chlorinated products. It is important to minimize the accumulation of DDD because it is a regulated pesticide and is recalcitrant to aerobic transformation. Controlled experiments revealed that the transformation of DDT requires microbial culture, but the culture need not be biologically active. Transformation results are presented for aqueous and soil phase contamination.

Enzyme degradation

G. Köller, M. Möder and K. Czihal

Peroxidative degradation of selected PCB: a mechanistic study, *Chemosphere, Volume 41, Issue 12, December 2000, Pages 1827-1834*

The enzyme-induced decomposition and biodegradation of PCB were investigated. 2,5-Dichlorobiphenyl (PCB 9) and $2,2^1,5,5^1$-tetrachlorobiphenyl (PCB 52) were used as example compounds to study efficiency and mechanism of the degradation processes. It was found that the application of horseradish peroxidase (HRP) together with defined amounts of hydrogen peroxide removed 90% of the initial concentration of PCB 9 and 55% of the initial concentration of PCB 52 from an aqueous solution after a reaction period of 220 min. Dechlorination was observed as the initial step. Although the metabolites identified were mainly chlorinated hydroxybiphenyls, benzoic acids and non-substituted 1,10 -biphenyl, some higher chlorinated biphenyl isomers also appeared. The biodegradation of PCB 9 using the white rot fungus, *Trametes multicolor,* took about four weeks and reduction was about 80% of the initial concentration. The metabolites produced (dichlorobenzenes, chlorophenols and alkylated benzenes) were not quite the same as those observed upon incubation with HRP.

Eduardo Torres, Ismael Bustos-Jaimes and Sylvie Le Borgne

Potential use of oxidative enzymes for the detoxification of organic pollutants, *Applied Catalysis B: Environmental, In Press, Corrected Proof, Available online 30 July 2003,*

The ability of peroxidases and laccases enzymes to treat organic pollutants is reviewed. Enzymatic methods generally have low energy requirements, are easy to control, can operate

over a wide range of conditions and have a minimal environmental impact. Peroxidases and laccases have broad substrate specificities and can catalyze the oxidation of a wide range of toxic organic compounds. The results show that an enzymatic oxidation can diminish the toxicity of some polycyclic aromatic hydrocarbons (PAHs), phenols, organophosphorus pesticides and azo dyes in laboratory and some field conditions. Due to the hydrophobicity and low aqueous solubility of these substrates, reactions are usually performed in the presence of organic solvents. However, it was detected that organic solvents can provoke enzyme denaturation, unfavorable substrate partition, inhibition or stabilization of enzyme–substrate complexes, depending on the enzyme, substrate and organic solvent used.

White rot

Gary D. Bending, Maxime Friloux and Allan Walker
Degradation of contrasting pesticides by white rot fungi and its relationship with ligninolytic potential, *FEMS Microbiology Letters, Volume 212, Issue 1, 18 June 2002, Pages 59-63*
Biobeds are on-farm pesticide bioremediation systems developed in Sweden to retain pesticides and facilitate natural attenuation, and are currently being evaluated in a number of other European countries. Biobed matrix was prepared by mixing together on a w/w basis 50% barley straw, 25% topsoil (Wick series sandy loam,1% organic C)and 25% compost, according to Fogg.

However, there were significant positive correlations between the rates of degradation of the different pesticides. Greatest degradation of all the pesticides was achieved by *Coriolus versicolor*, *Hypholoma fasciculare* and *Stereum hirsutum*. After 42 days, maximum degradation of diuron, atrazine and terbuthylazine was above 86%,but for metalaxyl less than 44%. When grown in the organic matrix of an on-farm 'biobed' pesticide remediation system, relative degradation rates of the highly available pesticides by *C. versicolor, H. fasciculare* and *S. hirsutum* showed some differences to those in liquid culture.

Christian Mougin, Claude Pericaud, Jaqueline Dubroca and Marcel Asther
Enhanced mineralization of lindane in soils supplemented with the white rot Basidiomycete Phanerochaete chrysosporium, *Soil Biology and Biochemistry, Volume 29, Issues 9-10, 10 September 1997, Pages 1321-1324*
Degradation of 8µg/g lindane in soil by white rot to 8% of original after 9 weeks

Toshio Mori and Ryuichiro Kondo
Oxidation of chlorinated dibenzo-*p*-dioxin and dibenzofuran by white-rot fungus, *Phlebia lindtneri, FEMS Microbiology Letters, Volume 216, Issue 2, 5 November 2002, Pages 223-227*
The actions of a white-rot fungus on two chlorinated aromatic compounds, known to be persistent environmental contaminants, were studied. Two models, both-ring chlorinated dioxin,2,7-dichlorodibenzo-*p*-dioxin (2,7-diCDD)and 2,8-dichlorodibenzofuran (2,8-diCDF), were metabolized by the white-rot fungus *Phlebia lindtneri*. 2,7-DiCDD disappeared linearly in the culture of *P. lindtneri*; over a 20-day incubation period, with only 45% remaining in the culture. One of the metabolites produced by *P.lindtneri* from a 5-day incubated culture with 2,7-diCDD or 2,8-diCDF was identified by gas chromatography mass spectrometry. *P. lindtneri* was shown to metabolize 2,7- diCDD and 2,8-diCDF to hydroxy-diCDD and hydroxy-diCDF, respectively.

A. Kubátová, P. Erbanová, I. Eichlerová, L. Homolka, F. Nerud and V. Šašek
PCB congener selective biodegradation by the white rot fungus Pleurotus ostreatus in contaminated soil, Chemosphere, Volume 43, Issue 2, April 2001, Pages 207-215

Four strains of *P. ostreatus* able to degrade 40% Delor 103 in 2 months; efficiency decreased with increasing number of chlorination.

L. Levin, A. Viale and A. Forchiassin
Degradation of organic pollutants by the white rot basidiomycete *Trametes trogii*, *International Biodeterioration & Biodegradation, Volume 52, Issue 1, July 2003, Pages 1-5*
The ability of the white rot basidiomycete *Trametes trogii* (strain BAFC 463)to degrade in vitro concentrations of 250 –500 ppm of nitrobenzene and anthracene was analyzed. Within 12 –24 days, more than 90% of the organic pollutants added to the fungal cultures were removed.

Tünde Mester and Ming Tien
Oxidation mechanism of ligninolytic enzymes involved in the degradation of environmental pollutants, *International Biodeterioration & Biodegradation, Volume 46, Issue 1, July 2000, Pages 51-59*
White rot fungi are the most significant lignin degraders among the wood inhabiting microorganisms. They degrade lignin by extracellular oxidative enzymes. The ligninolytic enzymes also oxidize various environmental pollutants such as polycyclic aromatic hydrocarbons, chlorophenols, and aromatic dyes. The most ubiquitous ligninolytic enzymes produced by these fungi are lignin peroxidases (LP), manganese peroxidases (MnP), and laccases (phenol oxidases). The peroxidases are heme-containing enzymes having typical catalytic cycles, which are characteristic of other peroxidases as well. One molecule of hydrogen peroxide oxidizes the resting (ferric) enzyme withdrawing two electrons. Then the peroxidase is reduced back in two steps of one electron oxidation in the presence of appropriate reducing substrate. The range of the reducing substrates of the two peroxidases is very different due to their altered substrate binding sites. LP is able to oxidize various aromatic compounds, while MnP oxidizes almost exclusively Mn(II) to Mn(III), which then degrades phenolic compounds. Laccases are copper-containing oxidases. They reduce molecular oxygen to water and oxidize phenolic compounds. In this paper, the mechanism of pollutant oxidation by ligninolytic enzymes is discussed giving an overview on the recent results of enzyme kinetics and structure.

P. Meysami and H. Baheri
Pre-screening of fungi and bulking agents for contaminated soil bioremediation, *Advances in Environmental Research, Volume 7, Issue 4, June 2003, Pages 881-887*
This paper discusses methods to promote fungal growth and penetration in a soil contaminated with weathered crude oil. The ligninolytic enzyme activity and toxicity threshold of several white-rot fungi known for their hydrocarbon degradation ability was studied. Pine wood chips, peat moss and Kellogg ’s Bran Flakes were examined for their properties as the bulking agents and solid amendments. The results showed all strains developed severe toxicity at concentrations higher than 10 000 ppm. Two strains of *Bjerkandera adusta* UAMH 7308 and 8258 showed the highest ligninolytic enzyme activity. Furthermore, white-rot fungi did not colonize the soil without bulking agents being present in the soil. A mixture of peat moss with bran flakes resulted in the best growth, penetration and enzyme activity in the soil.

Graciela M. L. Ruiz-Aguilar, José M. Fernández-Sánchez, Refugio Rodríguez-Vázquez and Héctor Poggi-Varaldo
Degradation by white-rot fungi of high concentrations of PCB extracted from a contaminated soil, *Advances in Environmental Research, Volume 6, Issue 4, October 2002, Pages 559-568.*
White-rot fungi are known to degrade a wide variety of recalcitrant pollutants. In this work,

three white-rot fungi were used to degrade a mixture of PCBs at high initial concentrations from 600 to 3000 mg /l, in the presence of a non-ionic surfactant, Tween 80 . The PCBs were extracted from a historically PCB-contaminated soil. Preliminary experiments showed that Tween 80 exhibited the highest emulsification index of the three surfactants tested, Tergitol .NP-10, Triton X-100 and Tween 80 . Tween 80 had no inhibitory effect on fungal radial growth, whereas the other surfactants inhibited the growth rate by 75-95%. Three initial PCB concentrations 600, 1800 and 3000 mg /l were assayed with three fungi for the PCB degradation tests. The extent of PCB modification was found to depend on PCB concentration P_0.001 and fungal species P_0.001 . PCB degradation ranged from 29 to 70%, 34 to 73% and 0 to 33% for *Trametes v ersicolo*r, *Phanerochaete chrysosporium* and *Lentinus edode*s, respectively, in 10-day incubation tests. The highest PCB transformation 70% was obtained with *T. versicolor* at an initial PCB concentration of 1800 mg/l, whereas *P. chrysosporium* could modify 73% at 600 mg/l. Interestingly, *P. chrysosporium* was the most effective for PCB metabolization at an initial concentration of 3000 mg /l, and it reduced up to 34% of the PCB mixture. As an overall effect, an increase in the initial PCB concentration led to a decrease in the pollutant degradation, from 57% to 21%. *P. chrysosporium* and *L. edodes* accumulated low chlorinated congeners. In contrast, *T. versicolor* removed both low and high-chlorinated congeners of PCBs.

Soon-Seop Shim and Katsuya Kawamoto
Enzyme production activity of *Phanerochaete chrysosporium* and degradation of pentachlorophenol in a bioreactor, *Water Research, Volume 36, Issue 18, November 2002, Pages 4445-4454*
Lignin peroxidase production by a white rot fungus, *Phanerochaete chrysosporium* was experimentally investigated using a batch system and a reactor system with various carriers. Immobilization of mycelia cell culture was more effective in promoting cell growth and lignin peroxidase production compared to conventional stationary liquid culture. Biostage carrier, commonly used for biochemical treatment in a fluidized bed disposal system, greatly improved production of lignin peroxidase up to 8.1 U/mL in the batch system. The packed bed reactor system was operated using a repeated batch technique, consisting of alternating growth and production phases, to sustain lignin peroxidase growth and production during the entire experiment period. Steady-state continuous PCP degradation over an extended period was accomplished with a mineralization ratio exceeding 80%. These systems and operation methods are promising techniques for the treatment of hazardous waste.

Akira Sato, Tsuneo Watanabe, Yoshio Watanabe, Koichi Harazono and Takema Fukatsu
Screening for basidiomycetous fungi capable of degrading 2,7-dichlorodibenzo-*p*-dioxin, *FEMS Microbiology Letters, Volume 213, Issue 2, 6 August 2002, Pages 213-217*
Degradation of 10uM PCDD after 40 days in aqueous medium

Zhongming Zheng and Jeffrey Philip Obbard
Oxidation of polycyclic aromatic hydrocarbons (PAH) by the white rot fungus, *Phanerochaete chrysosporium*, *Enzyme and Microbial Technology, Volume 31, Issues 1-2, 1 July 2002, Pages 3-9*
Key factors affecting the oxidation of polycyclic aromatic hydrocarbons (PAH) by the white rot fungus, *Phanerochaete chrysosporiu*m, including Mn 2^{+}concentrations on extracellular enzyme production and PAH source were investigated. *P. chrysosporium* acted synergis-tically with soil indigenous microorganisms in the oxidation of low molecular weight PAH (i.e. acenaphthene, fluorene, phenanthrene, fluoranthene and pyrene) in a soil-slurry, where oxidation was enhanced by up to 43% in the presence of fungus. However, limited oxidation

occurred for high molecular weight PAH (i.e. chrysene, benzo(a)pyrene, dibenz(*a*h)anthracene and benzo(*gh*i)perylene). This was also the case for the oxidation of solid phase PAH (i.e. phenanthrene, pyrene and benzo(a)pyrene) when added in acetone to cultures, where less than 12% of the high molecular weight PAH benzo(a)pyrene was oxidized, compared to up to 84% for relatively soluble phenanthrene. In contrast, surfactant dissolved PAH pyrene and benzo(a)pyrene were efficiently oxidized (i.e. recovery was less than 16.3 and 0.35%, respectively). Results collectively show that PAH dissolution rate is the limiting factor in the oxidation of PAH from contaminated soil and when added in acetone. However, the presence of fungal biomass is a pre-requisite for the oxidation of surfactant dissolved pyrene as the biomass-free supernatant did not result in the oxidation of pyrene, despite the presence of extracellular enzyme activity.

Hèla Zouari, Marc Labat and Sami Sayadi
Degradation of 4-chlorophenol by the white rot fungus *Phanerochaete chrysosporium* in free and immobilized cultures, *Bioresource Technology, Volume 84, Issue 2, September 2002, Pages 145-150*
4-Chlorophenol (4-CP) degradation was investigated by suspended and immobilized *Phanerochaete chrysosporium* conducted in static and agitated cultures. The best results were achieved when experiment was carried out in a rotating biological contactor instead of an Erlenmeyer flask, for both batch degradation and repeated batch degradation. The relative contribution of lignin peroxidase (LiP) versus manganese peroxidase (MnP) to the 4-CP degradation by *P.chrysosporium* was investigated. 4-CP degradation slightly increased and a high level of MnP (38 nKat ml 1) was produced when *P.chrysosporium* was grown at high MnII concentration.High LiP production in the medium had no significant effect on 4-CP degradation.4-CP degradation occurred when *P.chrysosporium* was grown in a medium that repressed LiP and MnP production.This result indicates that LiP and MnP are not directly involved in 4-CP degradation by *P.chrysosporium*.

Alette Langenhoff, Sjef Staps, Charles Pijls, Arne Alphenaar, Gerard Zwiep, Huub Rijnaarts
Intrinsic and stimulated in situ biodegradation of Hexachlorocyclohexane (HCH) - 181
6th International HCH and Pesticides Forum, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/

Theresa Phillips, G. Bell, D. Raymond, K. Shaw, Alan Seech
DARAMEND technology for in situ bioremediation of soil containing organochlorine pesticides 6th International HCH and Pesticides Forum, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/
Patented technology that uses soil specific solid phase organic amendments to increase activity of contaminant degrading microorganisms. Will biodegrade DDT, DDD, DDE, lindane, toxaphene, chlordane, dieldrin.

Phytoremediation
Siegfried Johne, Roland Watzke, Konstantin Terytze
Phytoremediation on HCH-contaminated soils - 187 6th International HCH and Pesticides Forum, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/
Full scale of HCH remediation is limited due to high cost, treatment requirements for off-gases for thermal processes, further optimisation requirements and the slow rate of biological treatment. Full scale bioreactors and insitu bioremediation have not been put into practice. Research is focused on phytoremediation, using HCH tolerant plants to reduce HCH mobility, particularly the role played by mycorrhizal fungi.

Wim H. Rulkens
Perspectives of phytoremediation for soil contaminated with pesticides - 191
6th International HCH and Pesticides Forum, 20-22 March 2001, Poznan, Poland,
http://www.6thhchforum.com/forum_book/
Use of phytoremediation to enhance bioremediation by improved soil aeration and release of plant enzymes and exudates, phytodegredation and phytovolatilisation; used for aldrin, dieldrin (spikerush), PCBs (plant cells, enzymes); enhanced by compost and fungi addition; large scale experience absent.

ANNEXURE 1

Undeveloped Technologies

Technologies which are still at research level but their applicability is still unknown.

Microemulsion Electrolysis

Process: From Rusling et al., 1994:

'This paper reviews recent work on the dehalogenation of organohalide pollutants by electrochemical catalysis in bicontinuous microemulsions of didodecyldimethylammonium bromide (DDAB)-water-dodecane. Compared with alternative toxic, expensive organic solvents, the catalytic efficiency for the dehalogenations was enhanced for non-polar organohalides in DDAB microemulsions. Using metal phthalocyanine tetrasulfonates as catalysts, the catalytic efficiencies for the reactions of 1,2-dibromobutane and 1,2-dibromocyclohexane were much larger in a microemulsion than in a homogeneous solvent. The reverse was found for trichloroacetic acid. Since DDAB and the catalysts adsorb on the carbon cathode, results suggest that a DDAB layer on the cathode preconcentrates non-polar dibromides but not the polar trichloroacetic acid. For complex mixtures of polychiorinated biphenyls, DDAB microemulsions performed better in bench-scale catalytic dechlorinations than aqueous DDAB dispersions, which performed better than aqueous CTAB micelles. Complete conversion of 100 mg of a 60% chlorine industrial PCB mixture in a 20 ml microemulsion could be carried out overnight using an activated lead cathode, zinc phthalocyanine as catalyst, and ultrasonic mass transport. Finally, the dechlorination of DDT (l,l-bis(4-chlorophenyl)-2,2,2-trichloroethane), which has both aliphatic and aromatic chlorines, was also explored in the microemulsions. Preliminary results suggest that oxygen may be an effective catalyst for the dechlorination of DDT in DDAB microemulsions to l,l-diphenylethane using a carbon cathode.'

Pre-treatment: N/A

Configuration: N/A

Capacity/Throughput: N/A

Efficacy: 100% conversion

Applicability: 60% PCB; likely to treat all POPs including high strength wastes.

Emissions: N/A

By-products: Cl^-; CO_2; potential for daughter product formation

Practical Issues: N/A

Licensing: N/A

Vendor(s): N/A

Info Sources: Rusling, Schweizer, Zhang and Kamau, 1994.

Ultrasonic irradiation

Process: From Hoffman, Hua and Höchemer, 1996:

'The degradation of chemical compounds by electrohydraulic cavitation involves three distinct pathways. The pathways include oxidation by hydroxyl radicals, pyrolytic decomposition and supercritical water oxidation. It has been shown that transient supercritical water is obtained during the collapse of cavitation bubbles generated sonolytically. The sonochemical degradation of a variety of chemical contaminants in aqueous solution has been investigated. Substrates such as chlorinated hydrocarbons, pesticides, phenols, explosives such as TNT, and esters are transformed into short-chain organic acids, CO_2, and inorganic ions as the final products. Time scales of treatment in simple batch reactors over the frequency range of 20 to 500 kHz are reported to range from minutes to hours for complete degradation. Ultrasonic irradiation appears to be an effective method for the rapid destruction of organic contaminants in water because of localized high concentrations of oxidizing

species such as hydroxyl radical and hydrogen peroxide in solution, high localized temperatures and pressures, and the formation of transient supercritical water. The degradation of chemical compounds by acoustic cavitation is shown to involve three distinct pathways: 1) oxidation by hydroxyl radicals, 2) pyrolytic decomposition and 3) supercritical water oxidation. Detailed reaction mechanisms for the degradation of p-nitrophenol, carbon tetrachloride, parathion, p-nitrophenyl acetate and trinitrotoluene are presented.'

Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: N/A
Applicability: Potentially all POPs
Emissions: N/A
By-products: short chain organic acids; CO_2; inorganic acids
Practical Issues: Effectiveness on POPs at high concentrations is unknown; however, if the SCWO pathway does occur, it is likely to be a less expensive option than SCWO although pitting due to localised cavitation effects may be an issue. Use of krypton or argon/oxygen gas would be a significant expense. Research into effective liquids, gases and limits of concentration is also required.
Licensing: N/A
Vendor(s): N/A
Info Sources:
Schramm, and Hua, 2000; Zhang and Hua, 2000; Hoffmann, Hua and Höchemer, 1996.

Photocatalytic degradation using TiO_2
Process: Higarashi and Jardim (2000) found that soil at 0.1ppm contamination of Diuran (Nortex) a haloaromatic pesticide degraded with 90% degradation at 2cm depth and 120h; rate was dependant on light intensity and addition of water improved the reaction. Bandala et al. (2002) used TiO_2 to degrade aldrin; H_2O_2 increased reaction time. Low levels of PCBs degraded in soil with addition of TiO_2; a fluoro surfactant assisted the TiO_2 with degradation of aged PCB contaminated soil (Huang and Hong, 2002). Malato et al. (1998) found peroxydisulphate to increase the reaction rate over H_2O_2 in degrading PCP. Powdered anatase and rutile, anatase and TiO_2 supported on glass hollow microspheres served as photocatalysts for Zaleska et al. (2000). The aqueous solution was then subjected to irradiation in the presence of oxygen. Vidal et al. (1999) used a parabolic concentrator to supplement a high pressure xenon arc lamp to degrade lindane.
Pre-treatment: Extraction from soils or sludges by water
Configuration: Mostly lab or pilot plant based
Capacity/Throughput: N/A
Efficacy: 50 – 99% after 150 minutes for lindane, methoxychlor, DDT (Zaleska et al., 2000); lindane 99.9% (Vidal et al., 1999); aldrin 90% (Bandala et al, 2002)
Applicability: organochlorine pesticides (0.1-40 ppm)
Emissions: CO_2
By-products: Cl^-, CO_2; some toxic breakdown products may occur
Practical Issues: This process treats low levels in aqueous solutions or top soil layers. Research is required to increase the treatable concentration to treat higher strength POP wastes.
Licensing: N/A
Vendor(s): N/A
Info Sources:
Konstantinou and Albanis, 2003; Higarashi and Jardim, 2000; Huang and Hong, 2002;

Bandala et al., 2002; Zaleska, Hupka, Wiergowski and Biziuk, 2000; Vidal et al., 1999; Prevot, and Pramauro, 1999; Vidal, Dinya, Mogyorodi Jr. and Mogyorodi, 1999; Malato, Blanco, Richter, Braun and Maldonado, 1998; Hema, Pathirana and Maithreepala, 1997.

Electron Beam Injection

Process: From Cooper et al., 2002:

'A study was conducted to examine the removal of methyl tert butyl ether (MTBE) and 15 other organic compounds, as well as perchlorate ion, in waters of different quality. The 15 organic compounds consisted of halogenated solvents (chlorination), disinfection by-products, pesticides, and nitrosodimethylamine (NDMA). These studies were conducted using a pilot scale 20 kW mobile electron beam system at Water Factory 21, Orange County, CA where wastewater is treated and re-injected into the ground as a barrier to salt water intrusion. Future applications for this treated water include water reuse. Ground water and treated wastewater, after having gone through a reverse osmosis-polishing step (RO permeate), were used to prepare mixtures of the compounds. Using fundamental radiation chemistry, it was possible to examine the factors effecting removal efficiency of all the compounds as well as MTBE destruction and reaction by-product formation and removal. All of the organic compounds were destroyed in the studies and we also observed the destruction of perchlorate ion in one of the waters.'

Pre-treatment: N/A

Configuration: N/A

Capacity/Throughput: N/A

Efficacy: 68 – 99.8% removal of MTBE, pesticides etc.

Applicability: (20-200 ppb) low levels in aqueous solution

Emissions: N/A

By-products: short chain organic acids; CO_2; inorganic acids

Practical Issues: Achieved pilot plant level but only at low concentrations. Significant research is necessary to assess application to destruction of POPs at higher concentrations.

Licensing:

Vendor(s):

Info Sources: Cooper, et al., 2002.

Ozonation

Process: Degradation of a wastewater containing a mixture of organochlorines using O_3 and H_2O_2 in a basic (pH - 9.4) medium; trichlorobenzene and others degraded but DDE not affected; Hayashi et al. (1993) found UV and ozone to be effective for degrading chlorohydrocarbons and destruction rate to be correlated to UV intensity

From Ormad et al., 1997:

'This paper presents the results obtained from oxidation with O_3 and O_3/H_2O_2 of a residual water coming from the production of dicofol and tetradifon pesticides, where chlorobenzenes, DDTs and its metabolites and other organochloride compounds were found. The oxidation processes were carried out using ozone (O_3) in basic medium (pH 9.4) at low dosage (0-1.5 g O_3 g^{-1} initial TOC) and in the presence of hydrogen peroxide (H_2O_2), with a 0.5 H_2O_2/O_3 molar ratio. During the treatment, many compounds were removed (dichlorobenzophenone, tetradifon, chlorobenzene, trichlorobenzene) and their change in concentration at different ozonation contact time was monitored. Other compounds like DDE remained practically invariable. This study investigated the formation of first ozonation by-products (FOBPs) in the wastewater, specifically chlorophenols, by means of gas chromatography/mass spectrometry (GC/MS) and gas chromatography/electron capture detection (GC/ECD) analysis in terms of the amount of time the O_3 has been in contact with the processed sample.

o-Chlorophenol, *p*-chlorophenol, benzenemethanol, *n*-chlorohydroxibenzaldehyde, *n*-chlorobenzenemethanol, chlorobenzoic acid, etc., were formed during the treatment, due to the mechanism of fast and non-selective oxidation which ozone has through OH radicals, formed by the decomposition of the O_3 molecule and accelerated by the presence of H_2O_2 in water.'

Pre-treatment: extraction into water
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: N/A
Applicability: low levels of pesticides in aqueous solutions
Emissions: N/A
By-products: Cl^-, CO_2
Practical Issues: Potential for breakdown product formation. Significant work is required to upgrade this process for destruction of POPs stockpiles. Advanced oxygenation processes are likely to be more effective.
Licensing:
Vendor(s):
Info Sources: Ormad, Cortés, Puig and Ovelleiro, 1997; Chiron, Fernandez-Alba, Rodriguez and Garcia-Calvo, 2000; Hayashi, Ikeda, Kusakabe and Morooka, 1993; Kearney, Muldoon and Somich., 1987.

REFERENCES

Bandala, E.R., S. Gelover, M.T. Leal, C. Arancibia-Bulnes, A. Jimenez and C. A. Estrada, 2002. Solar photocatalytic degradation of Aldrin. *Catalysis Today 76(2-4): 189-199.*

Chiron, S., A. Fernandez-Alba, A. Rodriguez and E. Garcia-Calvo, 2000. Pesticide chemical oxidation: state-of-the-art. *Water Research 34(2): 366-377.*

Cooper, W.J., Michael G. Nickelsen, Stephen P. Mezyk, Greg Leslie, Paul M. Tornatore, Wayne Hardison and Paris A. Hajali, 2002. MTBE and priority contaminant treatment with high energy electron beam injection. *Radiation Physics and Chemistry 65(4-5): 451-460.*

Hayashi, J., J. Ikeda, K. Kusakabe and S. Morooka, 1993. Decomposition rate of volatile organochlorines by ozone and utilization efficiency of ozone with ultraviolet radiation in a bubble-column contactor. *Water Research 27(6): 1091-1097.*

Hema M. K., K. Pathirana and R. A. Maithreepala**,** 1997. Photodegradation of 3,4-dichloropropionamide in aqueous TiO_2 suspensions. *Journal of Photochemistry and Photobiology A: Chemistry 102(2-3): 273-277.*

Higarashi, M.M., and Wilson F. Jardim, 2002. Remediation of pesticide contaminated soil using TiO2 mediated by solar light. *Catalysis Today 76(2002): 201–207.*

Hoffmann, M.R., I. Hua and R. Höchemer, 1996.Application of ultrasonic irradiation for the degradation of chemical contaminants in water. *Ultrasonics Sonochemistry 3(3): S163-S172.*

Huang, Q. and C.S. Hong, 2000. TiO_2 photocatalytic degradation of PCBs in soil-water systems containing fluoro surfactant. *Chemosphere 41(6): 871-879.*

Kearney, P.C., M.T. Muldoon and C.J. Somich, 1987. UV-ozonation of eleven major pesticides as a waste disposal pretreatment. *Chemosphere 16(10-12): 2321-2330.*

Konstantinou, I.K. and T.A. Albanis, 2003. Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways. *Applied Catalysis B: Environmental 42(4): 319-335.*

Malato, S., J. Blanco, C. Richter, B. Braun and M. I. Maldonado, 1998. Enhancement of the rate of solar photocatalytic mineralization of organic pollutants by inorganic oxidizing species. *Applied Catalysis B: Environmental 17(4): 347-356.*

Ormad, P., S. Cortés, A. Puig and J. L. Ovelleiro, 1997. Degradation of Organochloride compounds by O_3 and O_3/H_2O_2, *Water Research 31(9): 2387-2391*

Prevot, A.B., and Edmondo Pramauro, 1999. Analytical monitoring of photocatalytic treatments. Degradation of 2,3,6-trichlorobenzoic acid in aqueous TiO_2 dispersions. *Talanta 48(4): 847-857.*

Rusling, J.F., S. Schweizer, S. Zhang and G. N. Kamau, 1994. Microemulsions as media for destruction of organohalide pollutants by electrolysis. *Colloids and Surfaces A: Physicochemical and Engineering Aspects 88(1): 41-49.*

Schramm, J.D. and I. Hua, 2000. Ultrasonic Irradiation of Dichlorvos: Decomposition Mechanism. *Water Research 35(3): 665-674*

Vidal, A., A. I. Díaz, A. El Hraiki, M. Romero, I. Muguruza, F. Senhaji and J. González, 1999. Solar photocatalysis for detoxification and disinfection of contaminated water: pilot plant studies**.** *Catalysis Today 54(2-3): 283-290.*

Vidal, A., Z. Dinya, F. Mogyorodi Jr. and F. Mogyorodi, 1999. Photocatalytic degradation of thiocarbamate herbicide active ingredients in water, *Applied Catalysis B: Environmental 21(4): 283-290.*

Zaleska, A., Jan Hupka, Marek Wiergowski and Marek Biziuk, 2000. Photocatalytic degradation of lindane, *p,p'*-DDT and methoxychlor in an aqueous environment. *Journal of Photochemistry and Photobiology A: Chemistry 135(2-3): 213-220.*

Zhang G. and I. Hua, 2000. Ultrasonic degradation of trichloroacetonitrile, chloropicrin and bromobenzene: design factors and matrix effects. *Advances in Environmental Research 4(3): 219-224.*

ANNEXURE 2

Japanese Technologies for Destruction of PCBs

PCB Treatment Technologies based on the Waste Disposal and Clean-Up Law, Japan

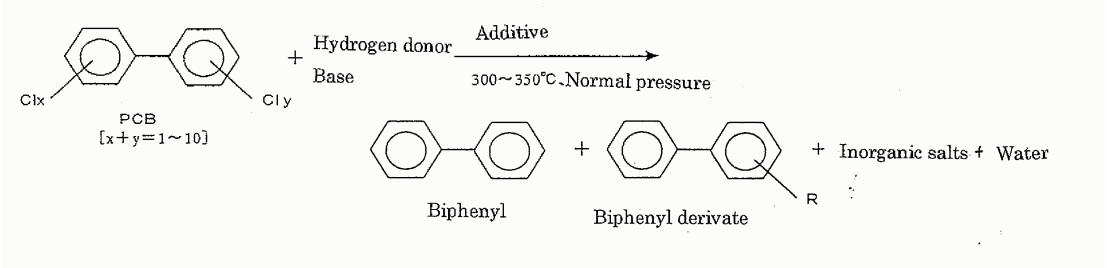
(Current as of September, 2003; information provided by Zoltan Csizer, Director, Cleaner Production and Environmental Management Branch, UNIDO)

Applicable substance	Treatment system	Treatment technology name	Developed by (Company name)
Waste PCB etc. (Liquid PCB wastes)	Dechlorination decomposition	Base catalyzed decomposition method (BCD method)	Ebara Corporation
		Chemical extraction decomposition method	Tokyo Electric Power Co., Ltd., Mitsui & Co., Ltd., Neos Co., Ltd.
		Organic alkali metal decomposition method (1-BuOK method)	Kansai Electric Power Co., Ltd., KansaiTech Corporation
		Catalytic hydrogen dechlorination method (Pd/C method)	
		Metallic sodium oil dispersion dechlorination method (OSD method)	Nuclear Fuel Industries, Ltd., Sumitomo Corp.
		Metallic sodium dispersion method (SD method)	Nippon Soda Co., Ltd.
		Metallic Na dispersion method (SP method)	Shinko Pantec Co., Ltd, Okinawa Plant Kogyo Ltd.
		Metallic Na dechlorination method (PCB Gone method)	Organo Corporation
		Metallic Na dechlorination method (MC method)	Kyoeigiken Co., Ltd., Tokyo Institute of Technology, NTRK Corp.
		Catalytic hydrogen reduction method	Nikko Rica Corporation, Takaoka Electric Mfg. Co., Ltd., Showa Engineering Co., Ltd., Kanae Corporation
	Hot water oxidation decomposition	Supercritical water oxidation decomposition method	Organo Corporation
		Hot water decomposition method	Mitsubishi Heavy Industries, Ltd.
	Reduction heat chemical decomposition	Molten catalyst extraction method (CEP method)	Ebara Corporation, Mitsubishi Chemical Corporation
		Gas phase hydrogen reduction method	Nippon Sharyo, Ltd., Tokyo Boeki Ltd.

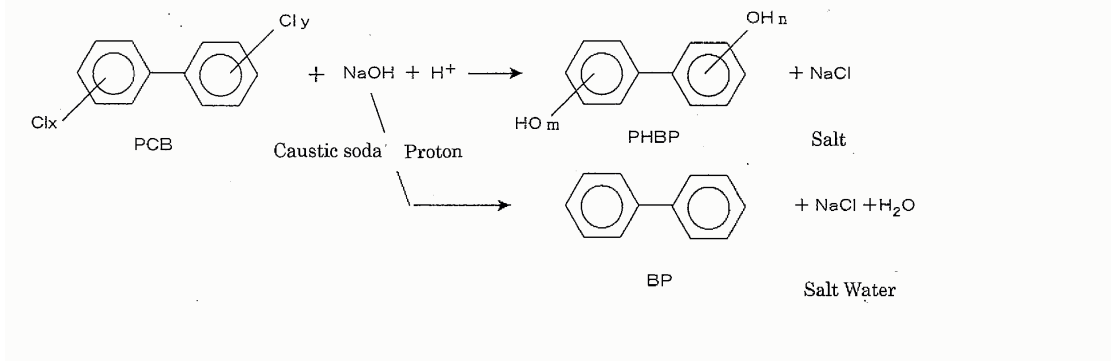
Applicable substance	**Treatment system**	**Treatment technology name**	**Developed by (Company name)**
Waste PCB etc. (Liquid PCB wastes)	Photo decomposition	UV decomposition, biodegradation method	Railway Technical Research Institute, Mitsubishi Heavy Industries, Ltd.
		UV/Catalytic decomposition method	Toshiba Corporation
	Plasma decomposition	Plasma Decomposition Method (PLASCON method)	ITOCHU Corporation
PCB pollutants (Solid PCB wastes)	Hot water oxidation decomposition	Supercritical water oxidation decomposition method	Organo Corporation
		Hot water decomposition	Mitsubishi Heavy Industries, Ltd.
	Reduction heat chemical decomposition	Gas phase hydrogen reduction method	Nippon Sharyo, Ltd., Tokyo Boeki Ltd.
	Separation	Vacuum thermal separation (VTR method)	Zero Japan Co., Ltd.
		Vacuum thermal separation	Aichi Electric Co., Ltd.
	Cleaning	Precision reconditioning and cleaning method	Tokyo Electric Power Co., Ltd., Mitsui & Co., Ltd.
		S-DEC method	Nuclear Fuel Industries, Ltd.
		Solvent extraction decomposition method (SED method)	Shinko Pantec Co., Ltd
		Solvent cleaning method (Decontaksolv method)	Ebara Corporation
		Solvent cleaning method (SD Myers method)	Organo Corporation
		MHI chemical cleaning method	Mitsubishi Heavy Industries, Ltd.

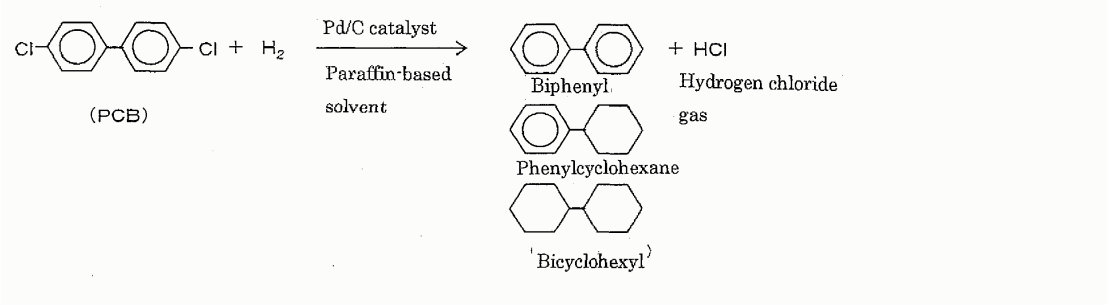
Overview of dechlorination decomposition/treatment technologies

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Base catalyzed decomposition method (BCD method) [Ebara Corporation]	In the reaction of the BCD method, a hydrogen donor, additive and a base are added to an organic chlorine compound, and the mixture is heated to 300 – 350°C in a nitrogen atmosphere at normal pressure, thereby eliminating the chlorine in the organic chlorine compound. The products are biphenyl, biphenyl derivatives, inorganic salts of neutral products, and water.	Alkali reagent: KOH Hydrogen donor: Hydrocarbon Additive: Unsaturated hydrocarbon	Temperature: 300 – 350°C Pressure: Normal pressure Reaction time: 4 hours when treating high-concentration insulation oil (Treated oil: 100% capacitor oil) 30 minutes when treating low-concentration insulation oil (Treated oil: 50ppm transformer oil)

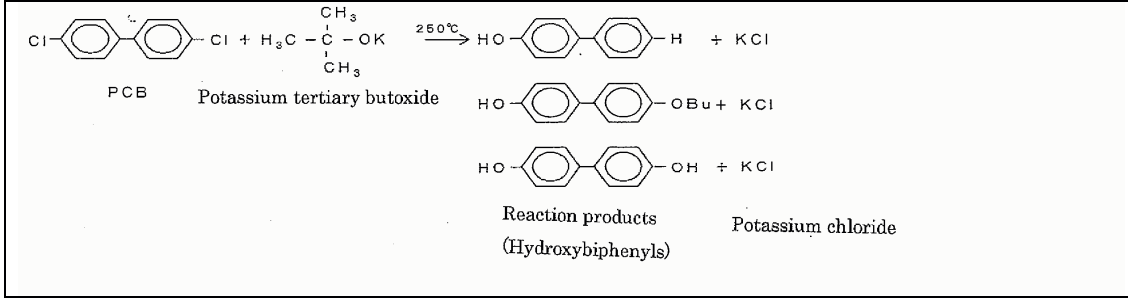


Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Chemical extraction decomposition method [Tokyo Electric Power Co., Ltd.] [Mitsui & Co., Ltd.] [Neos Co., Ltd.]	In this technology, the chlorine in PCB is changed to alkali salts like NaCl by placing the PCB in the presence of a base (like caustic soda or KOH) and an aprotic polar solvent (like 1,3 Dimethyl-2-Imidazolidinone (DMI) or Sulfolane (SF)), thereby changing the PCB into substances like mono- and polyhydroxybiphenyl (PHBP) and biphenyl (BP).	Alkali reagent: NaOH Hydrogen donor: Insulation oil etc. Catalyst: Aprotic polar solvent like DMI or SF	Temperature: 200 – 210^{o}C Pressure: Normal pressure Reaction time: 1 - 6 hours (Treated oil: 19, 64 ppm transformer oil) 15 - 18 hours (Treated oil: 66% transformer oil) Amount of solvent (DMI/insulation oil): 1 - 14, depending on PCB concentration

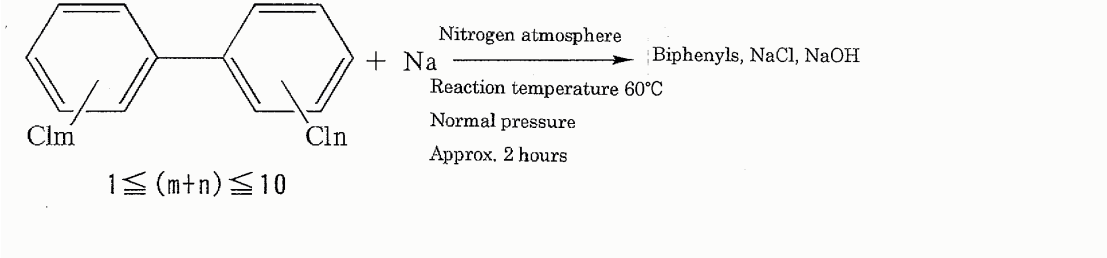


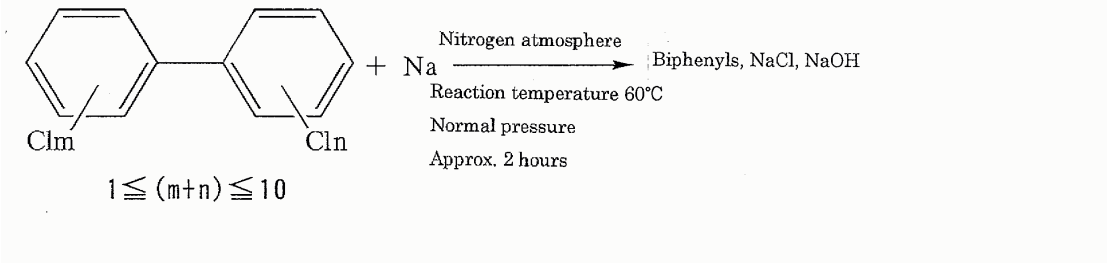
Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Catalytic hydrogenation dechlorination method (Pd/C method) -t-BuOK method [Kansai Electric Power Co., Ltd.] [KansaiTech Corporation]	In the reaction of the Pd/C method, PCB is dechlorinated at normal pressure using hydrogen gas in the presence of palladium/carbon catalyst. The reaction products are biphenyl, hydrides of biphenyl and hydrogen chloride. A 2-stage reaction is also possible by combining with the t-BuOK method.		Hydrogen donor: Hydrogen gas Catalyst: Pd/C (Palladium/Carbon) Temperature: 180 °C Pressure: Normal pressure Reaction time: 5 hours (Conditions for bringing 10% of treated oil to 10ppm)
	2-stage reaction (Pd/C method – t-BuOK method) Method where treatment is done using the t-BuOK method after bringing concentration to 100ppm or less using the Pd/C method.	Same as t-BuOK method	Same as t-BuOK method
			

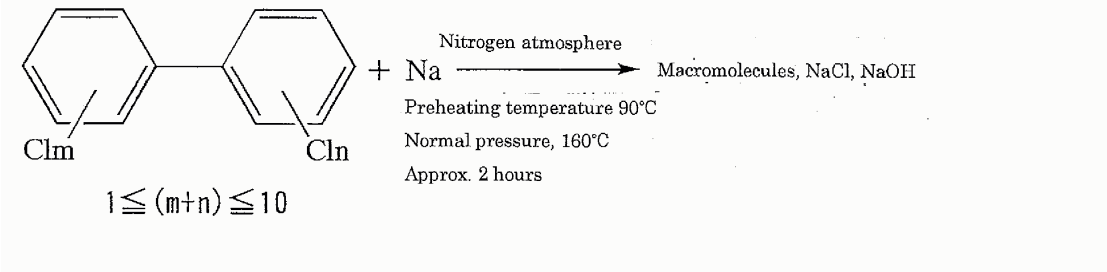
Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Organic alkali metal decomposition method (1-BuOK method) [Kansai Electric Power Co., Ltd.] [KansaiTech Corporation]	The organic metal compound potassium tertiary butoxide (t-BuOK) reacts easily with the chlorine in PCB and dissolves easily in oil. The chlorine in PCB is removed as harmless KCl by adding t-BuOK to oil containing PCB, and reacting with heat. After chlorine is eliminated from PCB, it is replaced by butoxide, OH or H.	Alkali reagents: t-BuOK (Potassium tertiary butoxide) Hydrogen donor: Insulation oil etc. Catalyst: None	Temperature: 200 - 250 °C Pressure: Normal pressure Reaction time: 3 - 9 minutes (Treatable concentration: 17 - 130ppm)

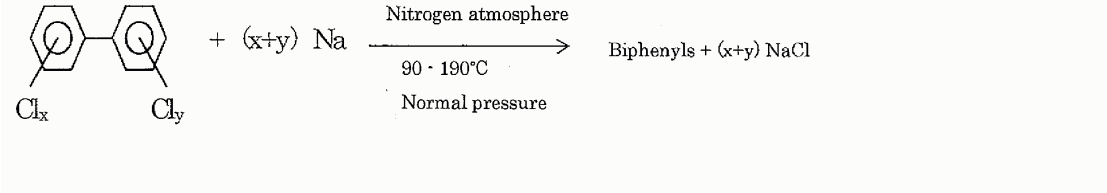


Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Metallic sodium oil dispersion dechlorination method (OSD method) [Nuclear Fuel Industries, Ltd.] [Sumitomo Corp.]	With this method, low-concentration PCB is mixed with SD, and high-concentration PCB is added in an appropriate amount to a mixture of low-concentration PCB contaminated oil or uncontaminated oil with an oil dispersion of metallic sodium (SD: Sodium Dispersion; metallic sodium of size about 5μm dispersed in mineral oil. Na content is 40wt%). The reaction proceeds by agitating in a nitrogen environment and thereby eliminating the chlorine in PCB. Degassing treatment is performed on the oil before dechlorination treatment, and chlorbenzene removal treatment is performed if necessary. After the reaction is finished, H2O is added to change residual Na to NaOH. Products include: biphenyls, NaCl and NaOH.	Alkali reagent: Oil dispersion of metallic sodium	Temperature:80 - 140 °C (preheating temperature) depending on PCB concentration Pressure: Normal pressure Reaction time: Approx. 0.5 - 3 hours for both low and high concentration

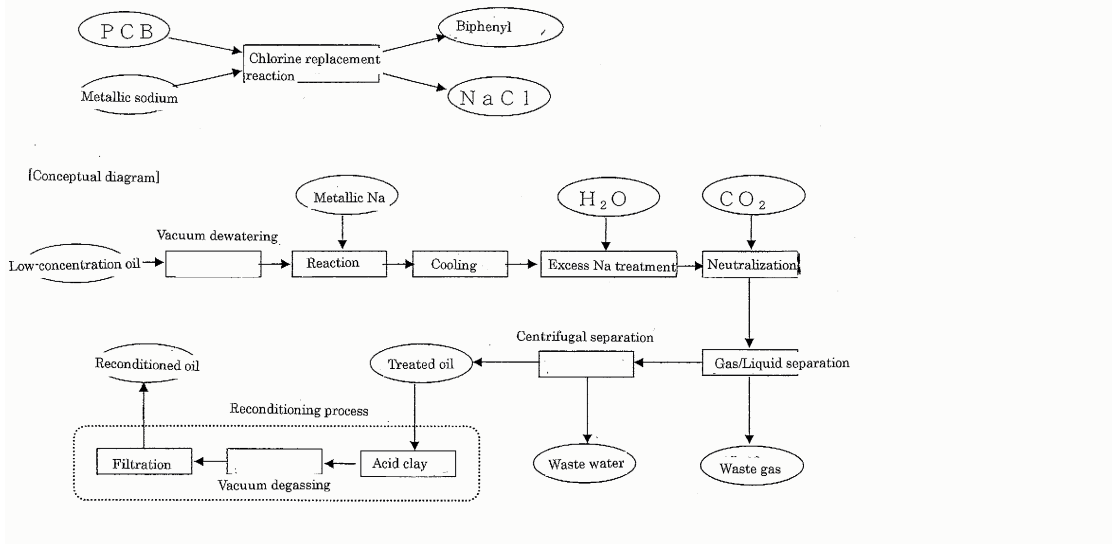


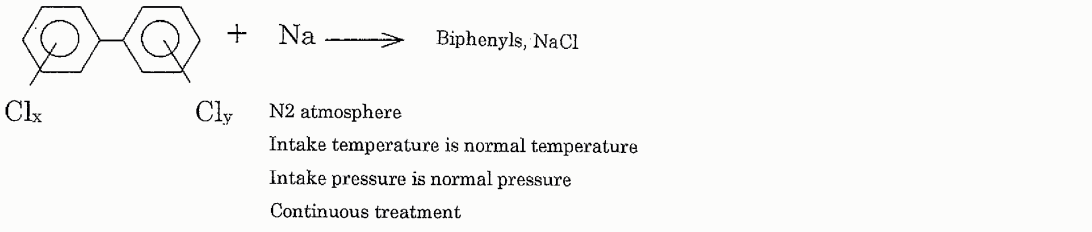
Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Metallic sodium dispersion method (SD method) [Nippon Soda Co., Ltd.] Low-concentration insulation oil treatment (Decomposition and detoxification method)	This reaction aims to dechlorinate PCB (from low-concentration to 100%) in a nitrogen atmosphere by using a metallic sodium dispersion (SD: Sodium Dispersion: metallic sodium of size about 5 - 10μm dispersed in insulation oil. Na content is 10 - 20wt%). Admixed chlorbenzene is also dechlorinated, so there is no need to perform chlorobenzene separation treatment prior to the reaction. SD is added to low-concentration PCB, and the reaction temperature is controlled to 60±10 °C. After dripping in an activator over one hour, the reaction is continued for another hour, thereby completing dechlorination. After the reaction is finished, quenching water is added to change the residual excess Na to NaOH. Products includce biphenyls, NaCl and NaOH, but the biphenyls dissolve in the insulation oil layer, while NaCl and NaOH dissolve in the water layer, so almost no formation of solids is seen.	Alkali reagent: SD Catalyst (Additive): Activator	Temperature: 60±10 °C Pressure: Normal pressure Reaction time: Approx. 2 hours
			

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Metallic sodium dispersion method (SD method) [Nippon Soda Co., Ltd.] High-concentration insulation oil treatment (Polymerization detoxification method)	Reaction temperature is controlled to 160±10 °C, and PCB fluid is dripped over one hour. The reaction is continued for another hour to complete dechlorination. After the reaction is finished, the minimal amount of quenching water is added to change the residual excess Na to NaOH. Products include polyphenylene macromolecules, NaCl and NaOH. Afterwards, insulation oil is separated from solids via centrifugation. If necessary, chlorine in the solids can be dechlorinated separately using hot water cleaning treatment.	Alkali reagent: SD Catalyst (Additive): None	Temperature: 60±10 °C Pressure: Normal pressure Reaction time: Approx. 2 hours
			

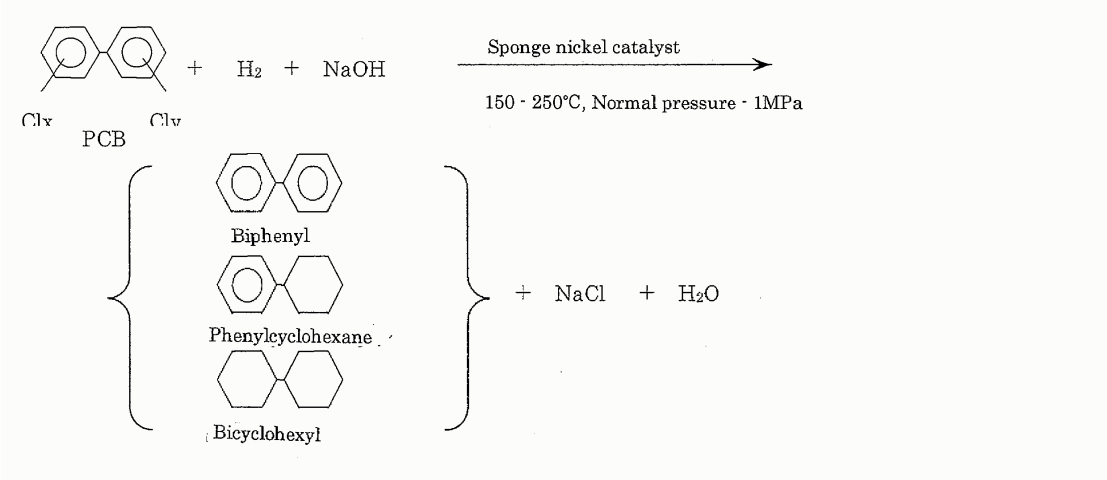
Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Metallic Na dispersion method (SP method) [Shinko Pantec Co., Ltd] [Okinawa Plant Kogyo Ltd.]	For low-concentration treatment, a metallic Na dispersion is added, and a dechlorination reaction is performed at a temperature of 90 °C and normal pressure. For high-concentration treatment, oil contaminated at high concentration and a reaction promoter are added to a metallic Na dispersion bath, and the reaction is performed at a temperature of 170 - 190 °C and normal pressure. In both cases, excess moisture is removed prior to the reaction by vacuum distillation, and during the reaction, the mixture is agitated in a nitrogen atmosphere. Residual Na is neutralized with CO_2 gas. Chlorine produced by the reaction and neutralization is extracted into water, and the produced waste water is released after improving its quality via bio-treatment.	Alkali reagent: Metallic Na dispersion Hydrogen donor: Reaction promoter (Isopropyl alcohol) Other: CO_2 gas for neutralization	Temperature: 90 - 190 °C Pressure: Normal pressure Reaction time: 10 mins. - 3 hours
			

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Metallic Na dechlorination method (PCB Gone method) [Organo Corporation]	A dechlorination reaction is performed by mixing the PCB oil with a metallic sodium dispersion. After the reaction, PCB becomes biphenyl, and chlorine is discharged as sodium chloride. PCB concentration of the treated oil is at or below the standard value (0.5ppm).	Metallic sodium reagent (Fine metallic sodium dispersed uniformly in mineral oil, concentration 10%)	Temperature: 120 °C Reaction time: 15 secs. Pressure: 2kg/cm2 MAX.

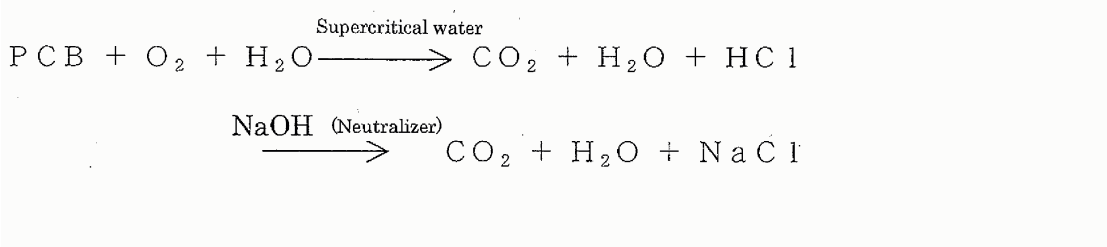


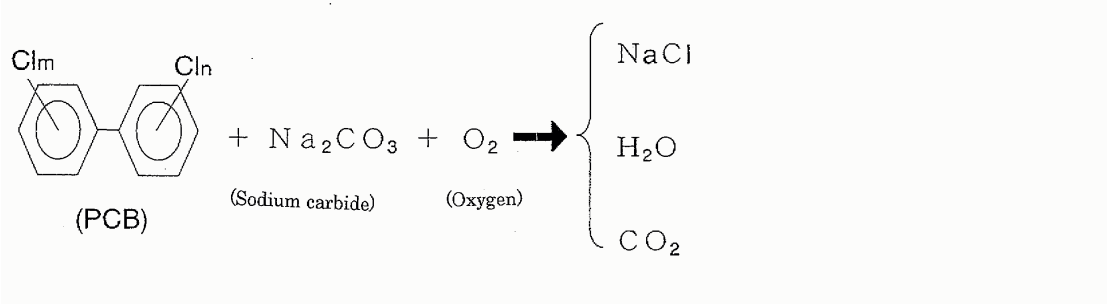
Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Metallic Na dechlorination method (MC method) [Tokyo Institute of Technology] [Kyoeigiken Co., Ltd.] [NTRK Corp.]	The raw PCB liquid is blended with kerosene (a hydrogen donor) in a nitrogen atmosphere and adjusted to be a PCB liquid with concentration of 10 - 30%. Metallic sodium is added (10% more than the amount appropriate for the adjusted concentration), and a mechanochemical reaction is performed in a reaction vessel using a high-speed rotating disk, thereby completing dechlorination. In the reaction vessel, the reaction proceeds at a rapid speed due to the local high-temperature and high-pressure, so the reaction finishes in a short time. After the reaction is finished, the liquid layer and solid layer are separated, and the liquid layer with decomposed PCB can be used as a hydrogen donor, and as fuel. Excess sodium present in the solid layer becomes NaOH when water is added. The NaOH dissolves in the water layer, so there is almost no evident formation of solids other than NaCl. In the solid layer to which water is supplied, water and solids are separated using a mechanochemical reaction vessel following the same system, and only a slight amount of solids remain. Water can also be used as cooling water. Admixed chlorohexane can also be dechlorinated in the same way using metallic sodium.	Alkali reagent: Metallic reagent Hydrogen donor: Kerosene Atmosphere in reaction vessel: N_2 gas (To prevent oxidation)	Temperature: Temperature in reaction vessel 110 - 200 °C Pressure: Normal pressure Average retention time: 2 - 8 mins. per unit For continuous treatment, equipment is staged to suit the capacity.
			

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Catalytic hydrogen reduction method [Nikko Rica Corporation] [Takaoka Electric Mfg. Co., Ltd.] [Showa Engineering Co., Ltd.] [Kanae Corporation]	In the reaction of the catalytic hydrogen reduction method, PCB is dechlorinated and decomposed using a sponge nickel catalyst in the presence of hydrogen gas and caustic soda. The reaction products are biphenyl, biphenyl compounds and salt water.	Catalyst: Sponge Ni Hydrogen donor: Hydrogen gas Alkali reagent: NaOH (Alkali)	Temperature: 150 - 250 °C Pressure: Normal pressure - 1MPa Reaction time*1: 1.2 hours (Low-concentration: 100ppm) 7*2 - 20 hours (High-concentration 1%) *1 When treating at 250 °C, normal pressure - 0.3MPa *2Depends on reactor switching.

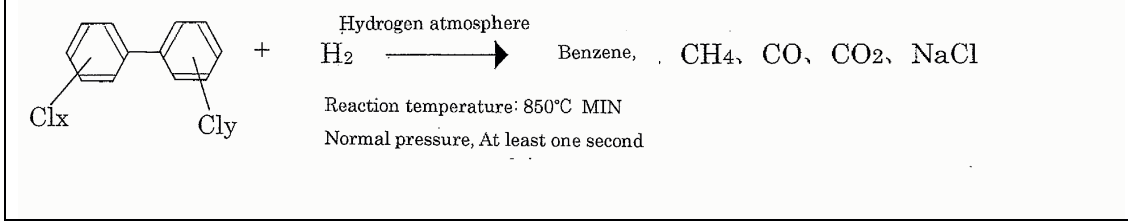


Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Supercritical water oxidation decomposition method [Organo Corporation]	This method completely oxidizes and decomposes toxic organic substances like PCB using the characteristics of water (supercritical water) exceeding critical conditions (374 °C, 22MPa). (Supercritical water has extremely good characteristics as an oxidation decomposition reaction catalyst for freely dissolving organic material and oxygen.) Typical reaction conditions are: temperature 400 - 650 °C, pressure 25MPz, reaction time 1 - 5 mins. When this technique is applied to PCB treatment, the carbon in PCB is changed to carbon dioxide, hydrogen is converted to water, and chlorine is ionized and discharged as chlorine. If the PCB concentration is high, the pH of treatment water drops, and this may lead to corrosion of the reactor and piping, so pH is neutralized by adding alkali.	Catalyst: Supercritical water Oxidizers: Air, oxygen, hydrogen peroxide etc. Neutralizer: Alkali	Typical conditions Temperature: 400 - 500 °C Pressure: 25Mpa Reaction time: 1 - 5 mins. (Treatable concentration: 0.1 - 10%)



Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Hot water decomposition method [Mitsubishi Heavy Industries, Ltd.]	Sodium carbide crystals are precipitated in hot water at 350 °C or higher, and reacted with PCB. The sodium carbide dechlorinates PCB, producing sodium chloride. The remaining biphenyl is decomposed into carbon dioxide and water using an oxidizer.	Oxidizers: Oxygen, air, hydrogen peroxide etc. Solvent: Hot water Catalyst: Sodium carbide	Typical conditions Temperature: 380°C Pressure: 26.5MPa Reaction time: A few mins. - 30 mins.
			

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Gas phase hydrogen reduction method [Tokyo Boeki Ltd.] [Nippon Sharyo, Ltd.]	Gas phase hydrogen reduction method uses a reduction reaction where organic compounds are heated to at least 850□ in a non-oxygen hydrogen atmosphere, at normal pressure, and decomposed/dechlorinated without using catalyst in a reaction time (retention time) of at least one second. This process decomposes organic chlorine compounds like PCB and dioxin into hydrogen chloride, methane, carbon monoxide, carbon dioxide, hydrogen and slight amounts of low-grade hydrocarbons like benzene. Hydrogen chloride is neutralized with NaOH, and recovered as NaCl. The advantage of using a hydrogen reducing atmosphere is that no dioxins are produced, and the dioxins in the waste are decomposed. The benzene, methane and carbon monoxide produced by the decomposition reaction under the above conditions become hydrogen, carbon monoxide and carbon dioxide due to a water shift reaction. Therefore, the efficiency of the reduction reaction increases in the presence of water, and the water acts not only as a thermal transfer catalyst, but also as the source of hydrogen supply for the system.	Hydrogen NaOH	Temperature: 850 °C MIN Pressure: Normal pressure Reaction time (Retention time): 1 sec. MIN



Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Molten catalyst extraction method (CEP method) [Ebara Corporation] [Mitsubishi Chemical Corporation]	1) PCB oil is loaded, together with oxygen, into molten metal (Ni-Cu) maintained at high temperature. The PCB is immediately broken down into elements by carbon removing catalytic action of the high-temperature molten metal. 2) The decomposed elemental components form intermediates with the molten metal, and are reconstituted into CO/H2/HCl gas etc. The "intermediates" formed by carbon and the molten metal are powerful in separating carbon from the PCB, and as a result, it is possible to attain a high decomposition efficiency.	Molten metal: Catalyst (Ni-Cu) Oxygen: Reaction agent	Temperature: Approx. 1300 - 1500 °C Pressure: Approx. 0.3MPa Reaction time: Approx. 0.5secs MIN.

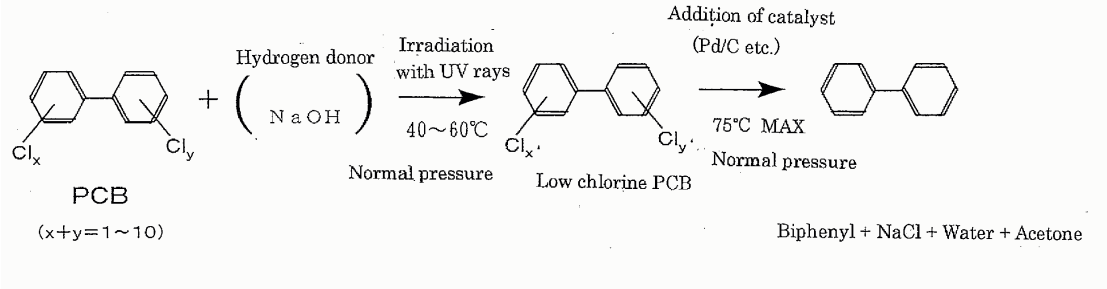
Decomposition process: $C_{12}H_7CL_3 + O_2 \rightarrow 12\underline{C}(L) + 7\underline{H}(L) + 3\underline{CL}(L) + 2\underline{O}(L)$

Synthesis process $\underline{C} + \underline{O} \rightarrow CO(g)$

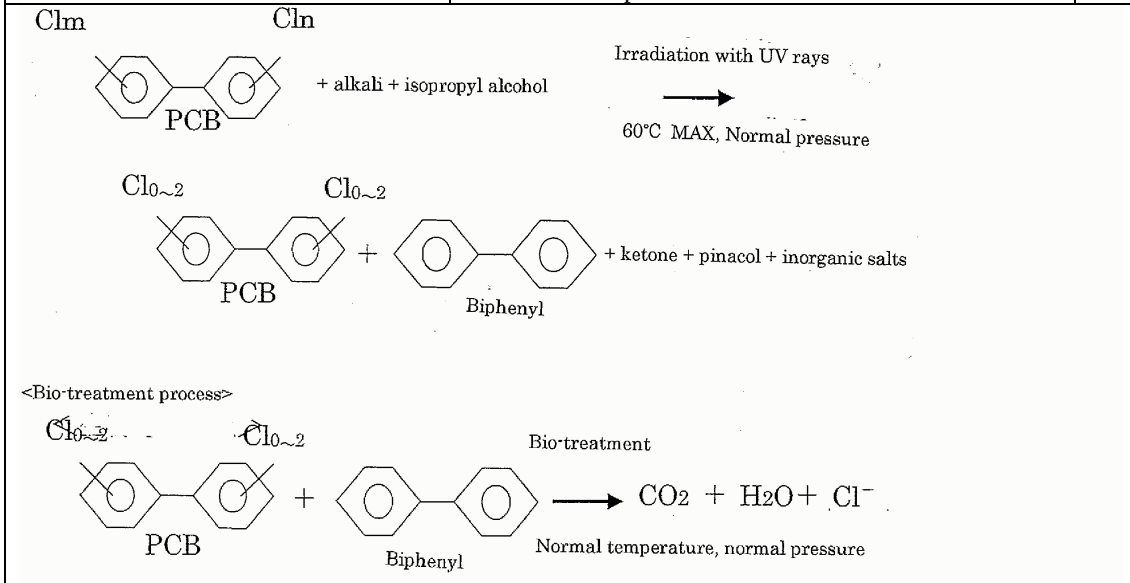
$2\underline{H} \rightarrow H_2(g)$

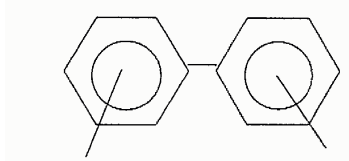
$\underline{CL} + \underline{H} \rightarrow HCL(g)$ or $yCL + xM \rightarrow MxCLy$

(Note) M indicates the metal forming the bath.

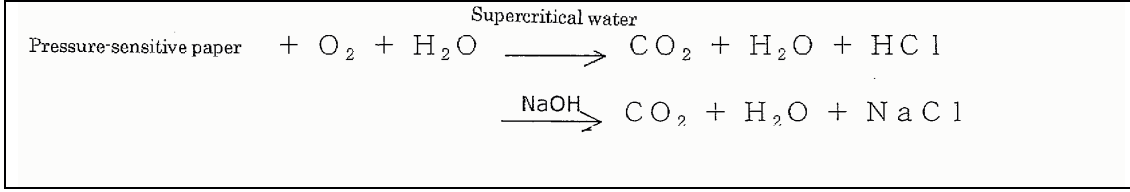
Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
UV/Catalytic decomposition method [Toshiba Corporation]	PCB and NaOH are dissolved in a hydrogen donor, and this is irradiated with UV light. After chlorine separates from PCB, it pulls off hydrogen from the hydrogen donor. The separated chlorine reacts with NaOH, and is removed as NaCl. After irradiation, the solution is heated to approx. 75°C, and the remaining PCB is subjected to a dechlorination reaction in the presence of a catalyst like palladium/carbon (Pd/C), thereby changing it to biphenyl. The chlorine from PCB becomes NaCl. The substances produced after the reaction ends are biphenyl, NaCl, acetone and water.	Hydrogen donor: Isopropyl alcohol Alkali: NaOH Catalyst: Precious metal catalyst like Pd/C etc.	[Light irradiation process] Temperature: 50±10 °C Pressure: Normal pressure Reaction time: The time where the irradiated energy becomes - 3kJ/g, when normalized by the initial dissolved weight of PCB. This is about 30 - 60 mins. with a concentration of I% in the catalyst. [Catalyst reaction process] Temperature: 75 °C MAX Pressure: Normal pressure Reaction time: Approx. 15 mins.
			

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
UV decomposition, biodegradation method [Railway Technical Research Institute] [Mitsubishi Heavy Industries, Ltd.]	Basic principle, Chemical reaction formula PCB is made into an alcohol solution using an alcohol like isopropyl alcohol to which an alkali like caustic soda has been added. In the UV decomposition process, dechlorination is achieved by the alcohol radicals formed by irradiation with UV rays, thereby changing PCB into monochlorobiphenyl, dichlorobiphenyl, biphenyl, ketone and inorganic salts. In the biodegradation process, the residual PCB produced in the UV decomposition process is made inorganic by bio-treatment, and converted to carbon dioxide, water and chlorine ions. Detoxification process	<UV decomposition process> Alkali reagent: NaOH water solution etc. Radical donor: Isopropyl alcohol etc. <Bio-treatment process> PCB decomposing bacteria: *Comamonas testosteroni* (TK 102 strain) *Rhodococcus opacus* (TSP 203 strain)	<UV decomposition process> Temperature: 60 °C MAX Pressure: Normal pressure <Bio-treatment process> Temperature: Normal temperature Pressure: Normal pressure

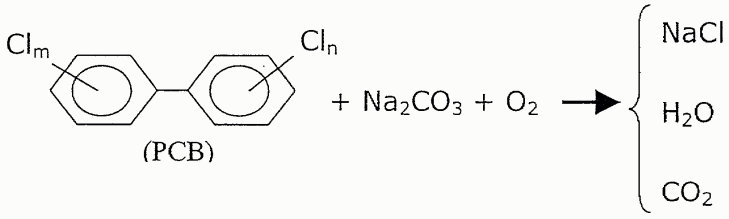


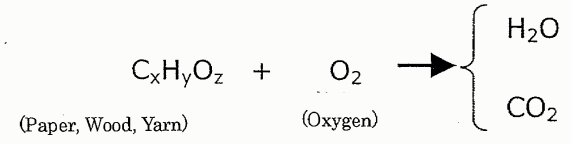
Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Plasma Decomposition Method (PLASCON method) [SRL Plasma Limited] [ITOCHU Corporation]	The principle of this technology is to dissociate the atoms comprising PCB using a plasma at high temperatures up to 3,000 °C (MIN). PCB is detoxified and rendered harmless with extremely high efficiency due to decomposition at extremely high temperatures. Due to the principle of high temperature dissociation, it is suitable for treatment of highly concentrated PCB, and the formation of harmful by-products is controlled by rapid cooling after decomposition.	Argon Oxygen	Temperature: 3,000 °C MIN Pressure: Normal pressure Reaction time: 30milliseconds or less
 Clx Cly $+O_2 \rightarrow CO, CO_2, HCl, H_2 H_2O$			

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Supercritical water oxidation decomposition method [Organo Corporation]	This method completely oxidizes and decomposes toxic organic substances like PCB using the characteristics of water (supercritical water) exceeding critical conditions (374 °C, 22MPa). (Supercritical water has extremely good characteristics as an oxidation decomposition reaction catalyst for freely dissolving organic material and oxygen.) Typical reaction conditions are: temperature 400 - 650 °C, pressure 25MPz, reaction time 1 - 5 mins. When this technique is applied to treatment of waste pressure-sensitive paper, both the PCB and paper component are simultaneously and completely decomposed. With this technique, the carbon in waste pressure-sensitive paper is converted to carbon dioxide, and the hydrogen is converted to water. Chlorine is ionized and discharged as HCl. If the PCB concentration is high, the concentration of the produced HCl increases, so it is neutralized by adding alkali	Catalyst: Supercritical water Oxidizers: Air, oxygen, hydrogen peroxide etc. Neutralizer: Alkali	Typical conditions Temperature: 400 - 500 °C Pressure: 25MPa Reaction time: 1 - 5 mins.

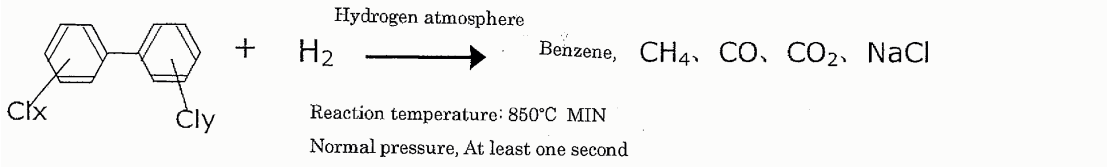


Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Hot water decomposition method [Mitsubishi Heavy Industries, Ltd.]	Sodium carbide crystals are precipitated in hot water at 350 °C or higher, and reacted with things like paper, wood or yarn containing PCB. The sodium carbide dechlorinates PCB, producing sodium chloride. The remaining biphenyl and contaminants (paper, wood, yarn etc.) are decomposed into carbon dioxide and water using an oxidizer.	Oxidizers: Oxygen, air, hydrogen peroxide etc. Solvent: Hot water Catalyst: Sodium carbide	Typical conditions Temperature: 380 °C Pressure: 26.5MPa Reaction time: A few mins. - 30 mins.



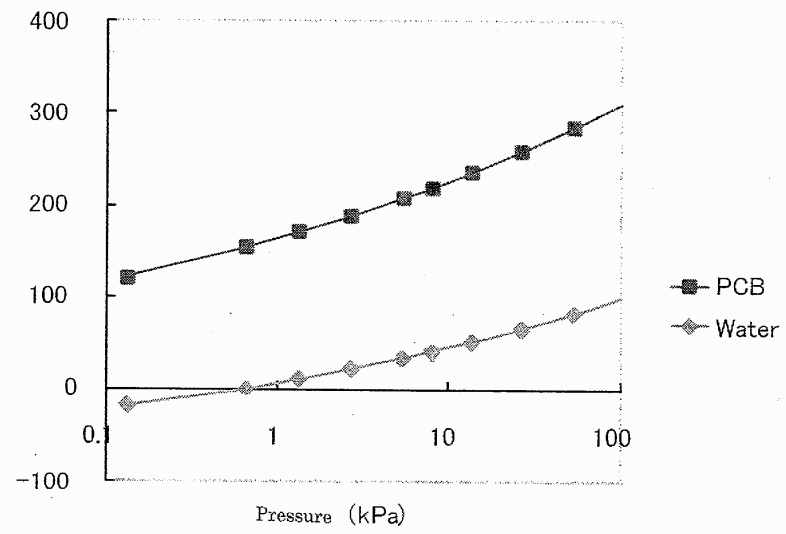


Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Gas phase hydrogen reduction method [Tokyo Boeki Ltd.] [Nippon Sharyo, Ltd.]	Gas phase hydrogen reduction method uses a reduction reaction where organic compounds are heated to at least 850 °C in a non-oxygen hydrogen atmosphere, at normal pressure, and decomposed/dechlorinated without using catalyst in a reaction time (retention time) of approximately second. This process decomposes organic chlorine compounds like PCB and dioxin into hydrogen chloride, methane, carbon monoxide, carbon dioxide, hydrogen and slight amounts of low-grade hydrocarbons like benzene. Hydrogen chloride is neutralized with NaOH, and recovered as NaCl. The advantage of using a hydrogen reducing atmosphere is that no dioxins are produced, and the dioxins in the waste are decomposed. The benzene, methane and carbon monoxide produced by the decomposition reaction under the above conditions become hydrogen, carbon monoxide and carbon dioxide due to a water shift reaction. Therefore, the efficiency of the reduction reaction increases in the presence of water, and the water acts not only as a thermal transfer catalyst, but also as the source of hydrogen supply for the system.	Hydrogen NaOH	Temperature: 850 °C MIN Pressure: Normal pressure Reaction time: 1 sec. MIN



Overview of separation technology

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Vacuum thermal separation (VTR method) Zero Japan Co., Ltd.	The vacuum thermal separation (VTR method) is a technology for evaporating, separating and recovering PCB contained in the treated material using a vacuum sealed system. When electrical devices like transformers and capacitors containing PCB are treated using the drop in boiling point which accompanies a drop in pressure, the PCB evaporates, leaving iron, copper and aluminum, and paper and wood become carbides. The PCB vaporized here is condensed and recovered by cooling in a cooling condenser.	None	Typical conditions Temperature: 200 - 600 °C Treatment pressure: 0.1 - 10kP Treatment time: 2 - 10 hours/batch



Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Vacuum thermal separation Aichi Electric Co., Ltd.	The vacuum thermal separation method is a technology for heating and evaporating substances like PCB (deposited on or impregnated in the treated material) at a temperature lower than the boiling point at normal pressure. This is done using the physical phenomenon whereby the boiling point drops at lower temperatures. Thus the PCB is removed while minimizing deterioration of the treated material. PCB, solvents and other substances which evaporate and separate from the parts of a capacitor or transformer, are cooled, condensed and recovered. When this technology is used for electrical equipment containing high-concentration PCB (high-voltage transforms, high-voltage capacitors etc.), detoxification can be achieved by reducing the rate of PCB residue in the treated material using techniques like solvent washing beforehand.	None	Treatment conditions Temperature: 200 ^{o}C Pressure: 6.7Pa (0.05mmHg) Vacuum hold time: 2 hours MIN.

Overview of cleaning technology

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Solvent cleaning method (Precision reconditioning and cleaning method) [Tokyo Electric Power Co., Ltd.] [Mitsui & Co., Ltd.]	The solvent cleaning method (precision reconditioning and cleaning method) is a technology for dissolving and removing PCB insulation oil using a cleaning solvent. After removing PCB insulation oil from the treated equipment (high-voltage transformer, high-voltage capacitor etc.), the treatment equipment is roughly disassembled into its container and contents (core, element etc.), and placed in cleaning baskets. These are each given a first cleaning for a specified time, and after materials which have been given a first cleaning are disassembled and sorted into non-impregnated parts (iron, copper, ceramics etc.) and impregnated parts (paper, wood, element etc.) and the impregnated parts are crushed. Non-impregnated parts are placed in a cleaning basket, and impregnated parts are placed in a cleaning barrel, and the parts are then given a second cleaning for a specified time. The treated materials from which deposited and impregnated PCB has been removed are obtained in the dry state. For the solvent containing PCB (and some TCB) is reused after clean solvent has been recovered via distillation recovery at reduced pressure. Distillation residue containing PCB is subjected to separate PCB decomposition treatment. The cleaning system in the precision reconditioning and cleaning method, the three operations (reduced pressure immersion cleaning, reduced pressure wapor cleaning, and vacuum drying) must be repeated the necessary number of items. The role of each operation is as follows: Reduced pressure immersion cleaning: The unit operation of cleaning by immersion the material to be	Cleaning solvent Hydrocarbon-based solvent (NS clean 220P)	Typical treatment conditions Cleaning solvent: NS220P Cleaning temperature: 50□ Cleaning time: -Non-impregnated parts 1st cleaning: 1 hour 2nd cleaning: 1 hour -Impregnated cleaning 1st cleaning: 3 hours 2nd cleaning: 3 hours

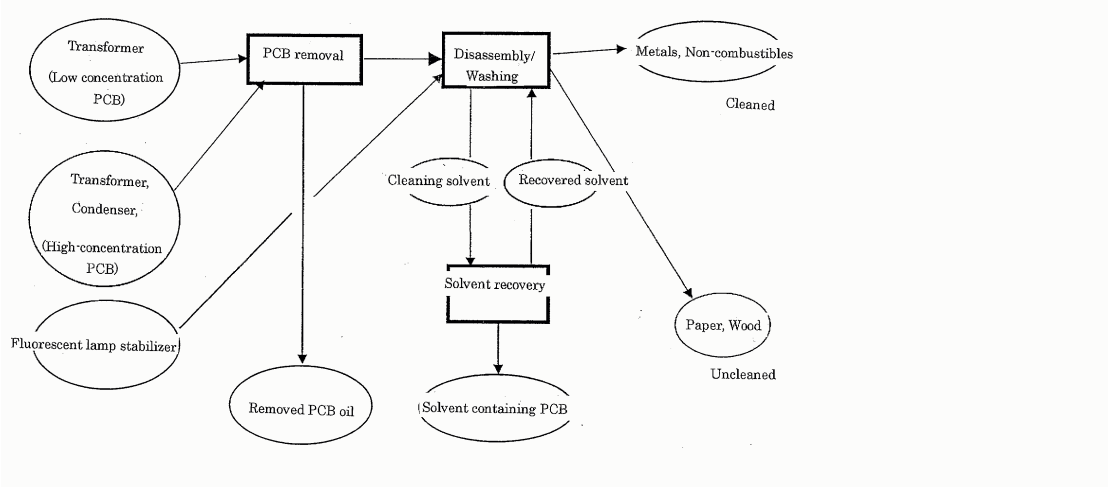
Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Solvent cleaning method (Precision reconditioning and cleaning method) [Tokyo Electric Power Co., Ltd.] [Mitsui & Co., Ltd.] (Continued from above)	cleaned in solvent. Both reduced pressure and ultrasonic waves are used to improve cleaning effectiveness. -Reduced pressure vapor cleaning: A unit operation where solvent vapor is supplied to heat the treated parts (materials to be dried) as a pretreatment for vacuum drying, and to rinse away condensed solvent. -Vacuum drying: A unit operation where a vacuum state is produced to remove cleaning fluid from the cleaned material.		
S-DEC method [Nuclear Fuel Industries, Ltd., Sumitomo Corp.]	With this method, the material to be cleaned is cleaned in a sealed system using an organic solvent as the cleaning agent. Non-impregnated substances like containers are washed clean of PCB contaminated oil by spraying cleaning agent in a cleaning tank equipped with internal spray nozzles, or they are cleaned by solvent in a rotating drum in a cleaning tank filled with cleaning fluid. Impregnated materials at finely shred with a shredder, and then subjected to solvent extraction cleaning in a rotating drum in the cleaning tank. One cleaning cycle involves: introduction of cleaning agent, cleaning and draining. Cleaning is repeated for a number of cycles. Cleaning agent is removed in a drying process, after cleaning and before removal of the cleaned materials. Cleaning agent contained PCB produced by washing is separated into PCB contaminated oil and cleaning agent using distillation equipment, and the cleaning agent is reused. The separated PCB or PCB contaminated oil is decomposed and treated using liquid treatment equipment (the OSD method).	Organic solvent	Temperature: Normal temperature - Approx. 80 °C Cleaning time (per cycle): 30 mins. (Non-impregnated material) 30 mins. - Approx. 1 hour (Impregnated material) Number of cleaning cycles: 3 - Approx. 10 cycles (Non-impregnated material) 5 - Approx. 15 cycles (Impregnated material)

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Solvent extraction decomposition method (SED method) Shinko Pantec Co., Ltd	This technology is comprised of a solvent extraction method and the metallic Na dispersion method (SP method). In the solvent extraction process, vapor or immersion cleaning is done using perchloroethylene or a hydrocarbon-based solvent*1 as the cleaning solvent, and the PCB deposited on the container is extracted into the solvent. If necessary, vacuum thermal drying*2 is performed as the final step in decontamination. The cleaning solvent containing PCB is separated into clean solvent and concentrated PCB using distillation equipment. The separated concentrated PCB, and PCB contaminated oil sealed into the PCB contaminated container, are detoxified by performing a dechlorination reaction at a temperature of 90 - 190^{o}C and normal pressure. This is achieved by adding a metallic Na dispersion and using the metallic Na dispersion method.	[Solvent extraction method] Cleaning solvent: Perchloroethylene or a hydrocarbon-based solvent*1 [Metallic Na dispersion method] Alkali reagent: Metallic Na dispersion Hydrogen donor: Reaction promoter (Isopropyl alcohol etc.) Other: CO_2 gas for neutralization	[Solvent extraction method] Temperature: Normal temperature - 120 ^{o}C Pressure: Atmospheric pressure of less Decontamination time: -Cleaning: - 72 hours -Final decontamination: - 16 hours [Metallic Na dispersion method] Temperature: 90 - 190^{o}C Pressure: Normal pressure Reaction time: 10 mins. - 3 hours

*1) Hydrocarbon-based solved was added as an additional condition

*2) Vacuum thermal drying was added as an additional condition

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Solvent cleaning method (SD Meyers method) Organo Corporation	PCB oil is removed from the contaminated container, and after disassembly into parts, the contaminated parts which are metal or non-combustible are placed in a special-purpose cleaning machine, bathed in a solvent (trichloroethylene), and each part is cleaned to below the treatment standard value. After cleaning, the solvent is reconditioned (distilled) and reused, and the PCB in the solvent finally concentrates in the distillation residue and is discharged.	Solvent used: Trichloroethylene	Cleaning time: Approx. 24h



Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Solvent cleaning method (Decontaksolv method) [Ebara Corporation]	This method involves cleaning equipment (transformers etc.) from which substances like waste PCB have been removed. The solvent is recovered and reconditioned by distillation so the solvent is always kept clean, and reused in a cyclic fashion. After cleaning, the solvent is adequately removed and dried before the equipment is opened. This is done to prevent vaporization of the solvent. Large transformers are directly connected, and small devices and disassembled parts are cleaned by placing them in a cleaning unit. After the first cleaning, the device is disassembled, and porous materials like paper and wood are separated out, and the disassembled metal parts are given a second cleaning. The first cleaning can be omitted for devices like transformers contaminated with low-concentration PCB, or when the concentration of contaminants like waste PCB is low.	Solvent: Tetrachloroethylene (PCE) Note) Solvent is reconditioned by distillation and cycled through the system, so it is not discharged.	Treatment temperature: In cleaning process: less than 140°C In drying process: less than 230 °C

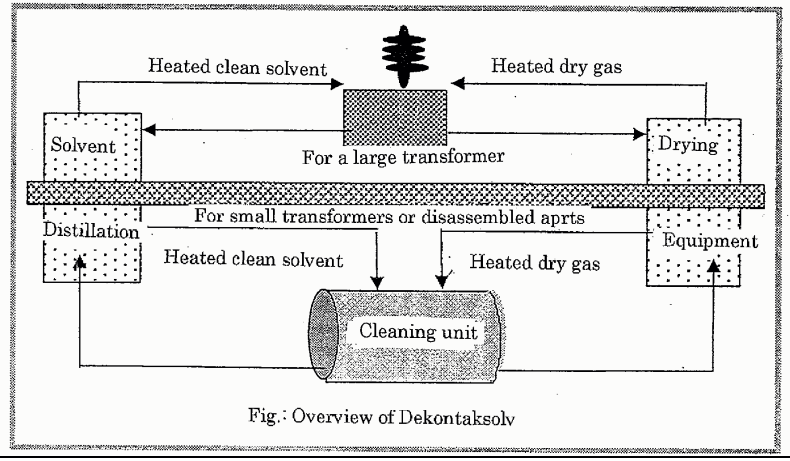


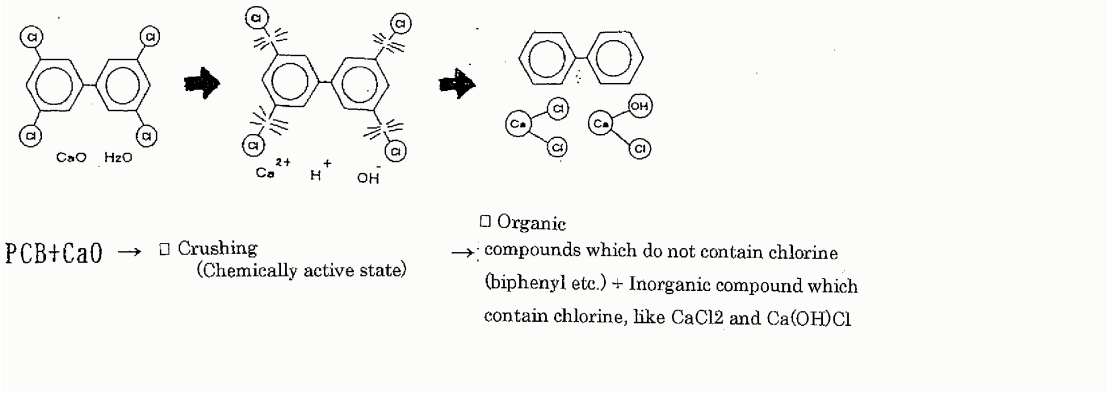
Fig.: Overview of Dekontaksolv

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
MHI chemical cleaning method [Mitsubishi Heavy Industries, Ltd.]	This method removes PCB deposited on the surface of substances like metal, to the level where the material can be handled safely. Cleaning of material deposited with low-concentration PCB (- 100ppm): *Surfactant method -The oil removing effect of surfactant achieves cleaning up to a safe level. Cleaning of material deposited with high-concentration PCB (- 100%PCB) -Cleaning is done to safe level by repeatedly using oil removal by surfactant and PCB dilution cleaning with oil. *Organic solvent method -Cleaning is done to safe level by using the oil removing effect of organic solvent, and cleaning multiple times.	Cleaning fluid for material deposited with low-concentration PCB *Surfactant method -Surfactant -Water Cleaning fluid for material deposited with high-concentration PCB *Surfactant method -Surfactant -Water -Oil (Kerosene etc.) *Organic solvent method -Organic solvent (n-benzene etc.)	Typical conditions Cleaning of material deposited with low-concentration PCB *Surfactant method -Ultrasound cleaning or spray cleaning -One cycle: 5-15mins. (surfactant)/5mins (water) Cleaning of material deposited with high-concentration PCB *Surfactant method -Ultrasound cleaning -Repeat 3 times: 15 mins. (surfactant)/5 mins. (water)/30 minutes (oil). Then repeat one time: 15 mins. (surfactant)/5 mins. (water) *Organic solvent method -Ultrasound cleaning -15 mins. (organic solvent): 5 time

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Solvent cleaning method [Toshiba Corporation]	The solvent cleaning method decontaminates PCB by cleaning PCB contaminated substances with solvent. After PCB is removed from PCB contaminated equipment, the equipment is disassembled and sorted. Non-impregnated materials like metal are cut to a size which will fit in the cleaning basket, and impregnated materials like paper and wood are crushed to an appropriate size to facilitate removal of PCB soaked into the parts. A light precleaning is done using a small amount of cleaning solvent to wash off PCB deposited on the surface, and then the cleaning solvent is heated and cleaning is done until PCB is below the standard value. Cleaning solvent is reconditioned and reused, and the PCB extracted at that time (and the PCB removed from the contaminated equipment) and decomposed and treated using a separate fluid treatment process.	Cleaning solvent Hydrocarbon-based solvent	Non-impregnated materials (Metals) Precleaning Temperature: Normal temperature Pressure: Atmospheric pressure Cleaning time: About 5 mins. Main cleaning Temperature: 100 °C Pressure: Atmospheric pressure - Vacuum Cleaning time: - 1 hour Impregnated materials (Paper) Precleaning Temperature: Normal temperature Pressure: Atmospheric pressure Cleaning time: About 5 mins. Main cleaning Temperature: 100 °C Pressure: Atmospheric pressure - Vacuum Cleaning time: - 4 hours

Overview of dechlorination decomposition/treatment technology (Technology in revision of the Waste Disposal and Clean-Up Law which is being prepared)

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Radical planet method (RP method) [PX Project] (Sumitomo Metal Industries, Ltd.) (Sumitomo Heavy Industries, Ltd.)	The RP method is a non-thermal decomposition method which uses the principle of mechanochemical reaction, causing a chemical reaction in the solid state by crushing action which provides mechanical energy. An organic chlorine compound is placed in a sealed vessel together with raw lime, and mechanical energy is applied to cut the chlorine-hydrogen bond in the organic chlorine compound (i.e. to perform dechlorination). When a chemical reaction with lime is produced in this way, the chlorine in the organic compound is removed as harmless inorganic compounds, $CaCl_2$ and Ca(OH)Cl, thereby producing an organic compound which does not contain chlorine.	Dechlorination agent: Raw lime Additive: Silica sand Dilution agent: Insulation oil	Temperature: Non-thermal However, the temperature rises in the range from normal temperature to 140°C due to the chemical reaction Pressure: Normal pressure However, pressure may rise to approx. 1.4atmospheres due to the reaction in the sealed vessel. Reaction time: 16 - 64 hours However, there are differences in reaction time depending on the initial concentration, shape, and mechanical energy application conditions.



Overview of Geomelt technology (Technology in revision of the Waste Disposal and Clean-Up Law which is being prepared)

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Geomelt method ISV Japan Co., Ltd. Ube Industries, Ltd. Konoike Construction Co., Ltd. The Japan Research Institute, Ltd. Hazama Corporation	1. Principle of reaction The Geomelt method is an electrical resistance based batch melting technology. Its distinguishing features are that it uses mineral components like soil as the melting medium, and that the melting range gradually expands from upper to lower layers. In the batch melting process, organic substances like PCB are decomposed into reducing gases like CO, H_2, CH_4 and HCl, in the presence of superheated water vapor produced by heating the melting medium in the non-oxygen high-temperature range within or around the melted object. Note 1) Furthermore, these reducing gases move to the upper gas layer of a furnace operated with the oxidizing atmosphere, and are converted to CO_2 or H_2O. Note 2) Unreacted CO and trace amounts of organic compounds are completely converted to CO_2 and H_2O in a high-temperature oxidizing atmosphere by a downstream thermal oxidizer. On the other hand, the inorganic components contained in PCB contaminated materials (containers, parts, soil, sludge, balas, wood etc.) are recovered after melting as harmless glass solids and metals. Note 1): These reducing gases are thought to have the same composition as gas generated by the molten catalyst extraction method. In the Geomelt method, PCB decomposed in a reducing atmosphere is decomposed into reducing gases by a reaction with the superheated water vapor supplied from sources like the melting medium.	Melting medium: Soil, Silica sand Melting regulation agent: $CaCO_3$, Na_3CO_3 (added if necessary)	Reaction in melted object Temperature: 1,600 - 2,000^oC Pressure: Slight negative pressure Reaction time (Melting speed): Varies depending on batch treatment volume and amount of electric power applied. (Power unit requirement: 0.7 - 1.0 kwh/kg) Reaction in thermal oxidizer Temperature: 850^oC MIN. Pressure: Slight negative pressure Reaction time: 2 secs. MIN.

Name of technology [Name of Japanese developer]	**Principle of reaction**	**Reaction reagents etc.**	**Reaction conditions**
Geomelt method ISV Japan Co., Ltd. Ube Industries, Ltd. Konoike Construction Co., Ltd. The Japan Research Institute, Ltd. Hazama Corporation (Continued from above)	Note 2): The basic approach of the Geomelt method is batch treatment, and the pressure in the equipment is kept slightly negative to keep decomposition gases and produced gases from escaping to the outside of the equipment. (Reduction of environmental effects) However, a small amount of air flows from the outside into the equipment and mixes with produced gases, so there is a possibility of inducing an explosion of the produced gas. So safe operation of equipment in the Geomelt method requires planning and operation to ensure that the produced gas which passes through the melted object is mixed upside-down with a large volume of external air in a hood, and converted to CO_2 or H_2O.		
Reaction in melted object (Thermal decomposition, Production reaction): $PCB+H_2O \rightarrow CO+H_2+CH_4+HC\ell$ Reaction in off-gas hood and in thermal oxidizer (Oxidation reactions) $2CO+O_2 \rightarrow 2CO_2$ $2H_2+O_2 \rightarrow 2H_2O$ $CH_4+2O_2 \rightarrow CO_2+2H_2O$			

ANNEXURE 3

Evaluation of Demonstrated and Emerging Remedial Action Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)

John Vijgen
International HCH & Pesticides Association