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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 draft document is provided ahead of the emerging and promising non-combustion technologies for POPs workshop in October 2003. Please note that the referencing is at this time non regularised. Some of the technolgies that are reviewed and presented here may well be on the margin of non-combustion but have been included for completeness. Note that the criteria section is still under development as is the final table of promising technolopgies. These to be confirmed during the workshop and then fully reported on in the final draft.

[This section to be completed post workshop – Washington 3 October 2003]

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EXECUTIVE SUMMARY

[This section to be completed post workshop – Washington 3 October 2003]

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 Conventions

1.4 Overview of non–combustion technology

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.

A number of technologies exist which are not clearly incineration but are similar to pyrolysis destruction. Steam reforming uses a pyrolysis reactor and has therefore been considered as a combustion process. Molten salt, molten metal and molten slag also both operate at high temperatures but claim to use the salt, metal or slag as both a solvent and a catalyst for destruction and have therefore been included. In addition, there are also variants of the technologies that have been included here and some are also known under different names.

It should be noted that in the emerging technologies category, there are a number of concepts that could be combined to achieve better performance, such as limitations of solubility solved using surfactants or microemulsions and use of catalysts combined with UV, hydrogen peroxide, ozone or biological remediation.

This summary classifies the technologies into five categories:

1. Direct applicable 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 Catalyzed Decomposition
   - Solvated electron technology

2. Applicable technologies on the stage of a 'breaking through and/or start of commercialisation'
   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
   - Super-critical water oxidation (SCWO)
   - Sodium Reduction
   - Mediated electrochemical oxidation (CerOx)
   - GeoMelt™ Process

3. Technologies that given the right financial circumstances could be full scale within approximately five years
   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:

Mediated electrochemical oxidation (AEA Silver II Process)
Ball milling
TiO_2-based V_2O_5/WO_3 Catalysis
Photochemically enhanced microbial degradation of environmental pollutants
Molten Metal

4. Technologies in the stage of laboratory scale testing

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.

These include:

Microemulsion Electrolysis
$MNO_x/TiO_2–Al_2O_3$ Catalyst Degradation
Catalytic hydrogenation
Self-Propagating High Temperature Dehalogenation (SPHTG)
Ultrasonic irradiation
Photocatalytic degradation using TiO_2
Fe(III) Photocatalyst Degradation
Electron Beam Injection
Ozonation
Biodegradation/Fenton's reaction
White rot fungi biodegradation
Ozonation/Electrical Discharge Destruction
In situ bioremediation of soils
DARAMEND bioremediation
Fly Ash Destruction
Molten Slag

5. 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 100% POPs

These include:

Phytoremediation

2.1 Direct applicable technologies with considerable experience

2.1.1 Gas Phase Chemical Reduction (GPCR) – GPCR Process

Info sources: Detailed description given in UNIDO Annex 7, based on info provided by vendor. Also Vijgen, 2002 and UNEP, 2003.
Process: Hydrogen reacts with chlorinated organic compounds, such as PCBs, at high temperatures (≥850C) and low (ambient?) 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 throughput 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 600C 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 (ie. coupled with the TBRP or TORBED systems).
Efficacy: Demonstrated high destruction efficiencies for PCBs, dioxins/furans, HCB, DDT. (Note vendor info refers to 6 & 7 nines DRE, but UNEP, 2003, says only 4 nines)
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.
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).

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 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. 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)

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 Catalyzed Decomposition

Info Sources: BCD International literature and Vijgen, 2002.
Process: The BCD process involves batch treatment of liquid and solid wastes in the presence of a reagent mixture consisting of a high boiling point hydrocarbon (eg. No.6 fuel oil), sodium hydroxide and a proprietary catalyst. When heated to about 300C the reagent produces highly reactive atomic hydrogen, which reacts with organochlorines and other wastes. The residues produced from decomposition are an inert carbon residue, and sodium salts of the anions liberated during decomposition. After the reaction, solid residues are separated from the residual oil by gravity of centrifugation. The oil and catalyst may be recovered for reuse.

Note: the earliest version of this process used polyethylene glycol as the hydrogen donor and operated at temperatures of 100-180C. The process was more selective, but also shown to produce measurable emissions of dioxins and furans. It has since been superceded by the use of hydrocarbon oils as hydrogen donor and a new catalyst, resulting in shorter treatment times, greater destruction efficiencies, and the ability to process high strength wastes (up to 100%). The process has been renamed "decomposition" (vs dechlorination) in recognition of these changes.
Pre-treatment: The system has been developed for both solid and liquid phase processes. However the latter appears to be most commonly used, and in this case requires a pre-treatment process such as thermal desorption for use with contaminated soils and other solid wastes.

According to the company "for contaminated soil or sediment treatment, the contaminated material is pre-mixed with a BCD solids catalyst and fed into a heated indirect thermal desorption unit of either batch or continous flow design. Depending on PCB concentration levels in the feed material little or no PCB is collected in the ITD condensate. If PCB levels in the feed material are high and PCB decomposition is not complete, then the resulting condensate is treated in a liquid PCB reactor."
The system can tolerate other inorganic and organic debris in the waste feed, such as paper and wood, provided size requirements are met (eg. through shredding). Large objects (>2cm) such as rocks need to be removed by pre-screening. Sediments must be dewatered prior to treatment.
Configuration: Modular; transportable and fixed. Most applications appear to be at fixed installations, including the H D Meyers plant, which was originally developed as a mobile unit but is now operated as a stationary facility.
Capacity/Throughput: The continuous feed solids units range from 100kg/hr to 20 tonnes/hr, and are intended for 24-hr/7-day operation. Two units are sometimes used in tandem to improve waste flows in large processing operations. The batch processing units for solids are typically rated at 1 to 5 tonnes per batch, with a throughput of 2 to 4 batches per day.

Capacities of the liquid reactors are typically 1000 to 2000 gallons (4500-9000 litres), with a throughput of 2 to 4 batches per day, depending on PCB concentrations (higher concentrations require longer reaction times). Smaller units are also available.
Efficacy: High destruction efficiencies (4 to 6 nines) have been demonstrated for DDT, PCBs and dioxins/furans in treatability trials.
Applicability: DDT, PCBs, dioxins/furans. Also demonstrated for most other POPs.
Emissions: Measureable discharges of dioxins and organochlorines to air on older plants, but these have apparently been addressed by the process changes noted above.

By-products: Solid residues may be captured for assay and reprocessing if needed. The systems can be used for cleaning up contaminated transformer oils for reuse. Disposal of hydrocarbon residues may need careful assessment after treatment of mixed pesticide wastes.

Practical Issues: Solid residues not fully defined. Potential for emissions through pressure relief valve. A fire in unit operating in Melbourne in 1995. Process difficulties in unit operating in Sydney, Australia.

The report on the Melbourne fire indicates that the process is operated with a nitrogen blanket. This could prove difficult in developing countries.

The catalyst materials are described as "extremely low cost", and are used in very small quantities (0.1 to 5%). Sodium hydroxide requirements would be significant however (200-800 kg/tonne of PCB).

Licensing: Commercially licensed in US A, Australia, Mexico, Japan and Spain.

Vendor(s): Patent holder: BCD Group Inc., Cincinnati, OH 45208, USA, (kornel_a@bcdinternational.com; www.bcdinternational.com). Numerous licensed operators around the world.

Reason for category: This technology has been demonstrated to treat high strength POP wastes although further evidence of the performance at this level and with respect to emissions should be sought.

2.1.3 Solvated Electron Technology

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

Reason for category: This is a proven technology although some proof of applicability to high strength POP wastes is necessary.

2.2 Applicable technologies on the stage of a 'breaking through and/or start of commercialisation'

2.2.1 Molten Salt Oxidation

Info Sources: UNEP, 2003
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.
Applications
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
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 Super-Critical Water Oxidation (SCWO)

Info Sources: General Atomics literature and Vijgen, 2002.
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*
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 (23/6 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)
Reason for category: Proof is required of this technology's ability to treat high strength organic POP wastes.

2.2.3 Sodium Reduction

Info Sources: Powertech literature
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 polybiphenyl, 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. ploybiphenyls), 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)
Reason for category: Although used for PCBs, this technology has not been applied to treat high strength POPs.

2.2.4 Mediated electrochemical oxidation (CerOx)

Info Sources: Cerox literature and Vijgen, 2002.
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 (90-95C) and near atmospheric pressure. A core component is the so-called T-CELL, which utilizes 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. ie. 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)

Reason for category: Only lab scale at this point for treating high strength POP wastes.

2.2.5 GeoMelt™ Process

Info Sources: Vijgen, 2002.
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).
Reason for category: Proof is needed to ensure this technology can effectively treat high strength POP wastes.

2.3 Technologies that given the right financial circumstances could be full scale within approximately five years

2.3.1 Mediated electrochemical oxidation (AEA Silver II Process)

Info Sources: AEA product literature and Vijgen, 2002.
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°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)
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.

2.3.2 Ball milling

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

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

Reason for category: Research on DE and applicability to treat high strength wastes is necessary.

2.3.3 TiO_2-based V_2O_5/WO_3 Catalysis

Info Sources: 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*
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*
Process: From Weber and Sakurai, 2001:
'In this study, PCB were destroyed on a V2O5/WO3 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.'
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°C
Applicability: PCBs, potentially all POPs, including high strength wastes.
Emissions: potential formation of dioxins and furans if temperature should drop below 250°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):
Reason for category: This technology has significant potential but further research is required to prove its applicability to high strength organic wastes, define a practical process and set up a pilot plant.

2.3.4 Photochemically enhanced microbial degradation

Info Sources: Patent application database esp@cenet
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. A 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 liter 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 liter 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):

Reason for category: Further research is required to test and prove the application of this technology to high strength wastes and design, test and construct a pilot plant.

2.3.5 Molten Metal

Info Sources: UNEP, 2003, Costner, Luscombe and Simpson, 1998

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 NOx 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.141 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):

Reason for category: Significant problems with this technology have been identified and its application to high strength POP wastes needs to be researched and proven.

2.4 Technologies in the stage of laboratory scale testing

2.4.1 Microemulsion Electrolysis

Info Sources: 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*
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: Highly promising technology for destruction of POPs
Licensing:
Vendor(s):
Reason for category: Further research is required to confirm the suitability of this process to treat high strength organic wastes and design, test and construct a pilot plant. Cost may be a significant issue.

2.4.2 $MnO_x/TiO_2–Al_2O_3$ Catalyst Degradation

Info Sources: 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*

Process: From Liu et al, 2001:

'A highly active catalyst, Mn*O*x/$TiO_2–Al_2O_3$, was prepared by impregnating Mn*Ox* species on TiO-modified Al_2O_3. The TiO species in $TiO_2–Al_2O_3$ support is in a monolayer dispersion, and the Mn*Ox* species is again highly dispersed on $TiO_2–Al_2O_3$ support. The total oxidation of chlorobenzene and o-dichlorobenzene on Mn*O*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 Mn*O*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: Highly promising research but still requires assessment for destruction of POPs

Licensing:

Vendor(s):

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.

2.4.3 Catalytic Hydrogenation

Info Sources: Costner, Luscombe and Simpson, 1998

Process: PCBs in transformer oils are hydrogenated by robust sulphide based catalysts, yielding hydrochloric acid and light hydrocarbons.

Pre-treatment: N/A

Configuration: Pilot scale – used for a commercial treatment of 3000 litres of PCB oil with concentration < 1000 ppm.

Capacity/Throughput:

Efficacy: >99.9996% for 1300ppm PCB; >99.99999% for 40,000ppm PCB

Applicability: PCBs; potentially all POPs

Emissions: Unknown if all process streams can be contained for testing/further reprocessing.

By-products: HCl, light hydrocarbons

Practical Issues: Lack of detailed or corroborating information on all process streams and residues.

Licensing: Commonwealth Industrial Research Organisation (CSIRO), Australia

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

2.4.4 Self-Propagating High Temperature Dehalagenation (SPHTG)

Info Sources: Vijgen, 2002.
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 Fact Sheet
'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 favorable. 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 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 CO2 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
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.

2.4.5 Ultrasonic irradiation

Info Sources:
Jennifer D. Schramm and Inez Hua, Ultrasonic Irradiation of Dichlorvos: Decomposition Mechanism, *Water Research, Volume 35, Issue 3, February 2001, Pages 665-674*
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*
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*
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; CO2; 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:
Vendor(s):
Reason for category: This technology is highly promising but significant research is required to determine its suitability to treat high strength wastes at acceptable levels.

2.4.6 Photocatalytic degradation using TiO_2

Info Sources:

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*

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

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*

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*

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;*

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*

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.*

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 283-290.*

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*

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.*

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 TiO2; a fluoro surfactant assisted the TiO2 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:
Vendor(s):
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.

2.4.7 Fe(III) Photocatalyst Degradation

Info Sources: 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*
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*
Process: Degradation of pesticides in water at solubility levels using FeIII/H2O2/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)/H2 O2 /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 =25.08C, 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.'
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 25.020.28C. 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% melathion; 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:
Vendor(s):
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 and to improve its treatment efficacy.

2.4.8 Electron Beam Injection

Info Sources: 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*
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; CO2; 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):
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 and the efficacy of the treatment.

2.4.9 Ozonation

Info Sources: 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*
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*
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*
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*
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):
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, the efficacy of the treatment and the formation of breakdown products.

2.4.10 Biodegradation/Fenton's reaction

Info Sources: 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*
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:
Vendor(s):
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 and the efficacy of the treatment.

2.4.11 White rot fungi biodegradation

Info Sources: 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*
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*
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*
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*

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*

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; Bollag et al., 1988; Call and MuÈcke, 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 orgaic 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):
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, the efficacy of the treatment and assess the formation of breakdown products.
Enzyme Degradation
Info Sources: 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.*
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*
Process:
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):
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, the efficacy of the treatment and assess the formation of breakdown products.

2.4.12 Ozonation/Electrical Discharge Destruction

Info Sources: Haiyan Sun, H. Felix, A. Nasciuti, Y Herieti and W. Hoffelner, Reduction of NO/NO2 & SO2 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*
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/NO2 and SO2 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/NO2, SO2 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?, CO2
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:
Vendor(s):
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 and to improve its treatment efficacy.

2.4.13 In situ bioremediation of soils

Info Sources: 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*
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 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.'

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:
Vendor(s):
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.

2.4.14 DARAMEND bioremediation

Info Sources: 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.
US EPA http://www.epa.gov/ORD/SITE/reports/0029a.html
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: CO2; 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
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.

2.4.15 Fly Ash Destruction

Info Sources: 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*
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*
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*
Process: From Weber et al., 2002:
'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.'

Gupta et al (2002) used fly ash to remove lindane and DDT from wastewaters but ascribed the results as due to adsorption. Further research is necessary to determine if destruction was also occurring.

Pre-treatment: N/A
Configuration: N/A
Capacity/Throughput: N/A
Efficacy: 100% destruction of dioxins/furans, PCB
Applicability: gas at 2ppm or liquid streams (2ppb)
Emissions: N/A
By-products: fly ash can be regenerated; regeneration water requires disposal
Practical Issues: Significant research still required to determine the basic function of this process.
Licensing:
Vendor(s):
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.

2.4.16 Molten Slag Process

Info Sources: UNEP, 2003
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:
Vendor(s): Ausmelt, Australia. (www.ausmelt.com.au)
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 could exist with emissions, formation of toxic daughter products and with disposal of the final product.

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

2.5.1 Phytoremediation

Info Sources: Siegfried Johne, Roland Watzke, Konstantin Terytze, Phytoremediation on HCH-contaminated soils *6th International HCH and Pesticides Forum*, 20-22 March 2001, Poznan, Poland, http://www.6thhchforum.com/forum_book/
Wim H. Rulkens, 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/
Process: 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.
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
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.

Table 1: List of Technologies and Information Sources

Technology	Vendor	Information Sources
6. Direct applicable 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
Solvated Electron Technology (SET)	Teledyne Commodore LLC, USA	www.commodore.com and www.teledyne.com
7. Applicable technologies on the stage of a 'breaking through and/or start of commercialisation'		
Molten Salt Oxidation	Lawrence Livermore National Laboratory, and Los Alamos National Laboratory, USA	www-cms.llnl.gov, www-emtd.lanl.gov/ASTF-NM/MSO
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
Mediated Electrochemical Oxidation – Ce (MEO-Ce)	CerOx Corporation, USA (G. Anthony Steward, CEO & President)	www.cerox.com and other information supplied by Cerox
GeoMelt^{TM} Process	GeoMelt, USA (licensed globally to AMEC, USA)	www.geomelt.com and www.amec.com
3. Technologies that given the right financial circumstances could be full scale within approximately five years		
Mediated Electrochemical Oxidation – Ag (MEO-Ag)	AEA Technologies, UK	www.accentus.co.uk
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
TiO_2-based V_2O_5/WO_3 Catalysis		Weber and Sakurai, 2001
Photochemically enhanced microbial degradation		UNIV CALIFORNIA (US) Patent US5342779, date 1994-08-30
Molten Metal Process	Molten Metal Technologies, USA	(no longer operating)
4. Technologies in the stage of laboratory scale testing		
Microemulsion Electrolysis		Rusling, Schweizer, Zhang and

Technology	Vendor	Information Sources
		Kamau, 1994
$MnO_x/TiO_2–Al_2O_3$ Catalyst Degradation		Liu et al, 2001
Catalytic hydrogenation	Commonwealth Industrial Research Organisation (CSIRO), Australia	Costner, Luscombe and Simpson, 1998
Self-Propagating High Temperature Dehalogenation (SPHTG)	Centro Studi sulle Reazioni Autopropaganti, Italy	Vijgen, 2002
Ultrasonic irradiation		Schramm and Hua, 2001; Zhang and Hua, 1999; Hoffman, Hua and Höchemer, 1996
Photocatalytic degradation using TiO_2		Konstantinou and Triantafyllos, 2003; Higarashi and Jardim, 2000; Bandala et al., 2002; Huang and Hong, 2002; Zaleska et al., 2000; Vidal et al. 1999a, b; Hema et al., 1997; Prevot and Pramauro, 1999;
Fe(III) Photocatalyst Degradation		Huston and Pignatello, 1999; Catastini et al., 2002
Electron Beam Injection		Cooper et al., 2002
Ozonation		Ormad et al., 1997; Kearney, Muldoon and Somich, 1987; Hayashi et al., 1993; Chiron et al., 2000
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

Technology	Vendor	Information Sources
Enzyme Degradation		Köller, Möder and Czihal, 2000; Torres, Bustos-Jaimes and Le Borgne, 2003
Ozonation/Electrical Discharge Destruction		Sun et al., 1998
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
Fly Ash Destruction		Weber et al., 2001; Gupta et al., 2002; Gupta and Ali, 2002.
Molten Slag Process	Ausmelt, Australia[1]	www.ausmelt.com.au
5. Technologies which are unlikely to be applicable for destruction of POPs stockpiles		
Phytoremediation		Johne, Watzke, Terytze, 2001; Rulkens, 2001

Table 2: Process Summaries

Technology	Process Description	Configuration	Applicability	Scale
1. Direct applicable 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 (eg. 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 6.	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.
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 (eg. oil or soil) are removed from the cell	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

Technology	Process Description	Configuration	Applicability	Scale
	and disposed.			
2. Applicable technologies on the stage of a 'breaking through and/or start of commercialisation'				
Molten Salt Oxidation	POPs wastes are injected into a bath of a molten salt (eg. sodium carbonate) at 900-950 °C, yielding carbon dioxide, sodium chloride, water and nitrogen.	Fixed/transportable	Tested for a few pesticides	Full scale under construction
SCWO	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 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
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	Modular system design which indicates potential for set-up as a transportable system (but really	Demonstrated for most POPs. Optimum performance for organic content >15%. Aqueous	The base unit (2 cell-packs) has a capacity of 25 gals/day for 50% organics liquid input (ca. 2kg/hr

Technology	Process Description	Configuration	Applicability	Scale
	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.	only applicable for small units)	process with solids or sludges homogenised and pumped in as a liquid. Liquid organic wastes are pre-treated by sonication to emulsify the mixture.	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
GeoMelt™	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
3. Technologies that given the right financial circumstances could be full scale within approximately five years				
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
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)
TiO_2-based V_2O_5/WO_3 Catalysis	Contaminant dissolved in toluene, heated to 300°C 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

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
Molten Metal Process	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)
4. Technologies in the stage of laboratory scale testing				
Micro-emulsion Electrolysis	Dehalogenation of organohalide pollutants by electrochemical catalysis in bicontinuous microemulsions of didodecyldimethylammonium bromide (DDAB)-water-dodecane. Complete conversion of 100 mg of a 60% chlorine industrial PCB mixture in a 20 ml	Concept not developed	PCBs, DDT, potentially all POPs at high strength but further research required	Bench scale

Technology	Process Description	Configuration	Applicability	Scale
	microemulsion could be carried out overnight using an activated lead cathode, zinc phthalocyanine as catalyst, and ultrasonic mass transport.			
MNO_x/TiO_2 $–Al_2O_3$ Catalyst Degradation	A highly active catalyst, Mn*O*x/TiO_2–Al_2O_3, with TiO species in a monolayer dispersion, and the Mn*Ox* species highly dispersed on the TiO_2–Al_2O_3 support. The total oxidation of chlorobenzene and o-dichlorobenzene on Mn*O*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 Mn*O*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}.	N/A	Potentially all POPs but tested on chlorobenzene and dichlorobenzene	Laboratory
Catalytic hydrogen-ation	PCBs in transformer oils are hydrogenated by robust sulphide based catalysts, yielding hydrochloric acid and light hydrocarbons	N/A	PCBs	Laboratory
SPHTG	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 The reaction of many chlorinated organic compounds with strongly reductive substrates, such as alkaline	N/A	Potentially all POPs at high strengths	Laboratory

Technology	Process Description	Configuration	Applicability	Scale
	metals or their hydrides, is very exothermic with typical adiabatic temperature of these processes as high as 4000 K.			
Ultrasonic irradiation	The contaminanted water is irradiated with 500 kHz ultrasound at input powers ranging from 86 to 161 W, using an Argon/Oxygen (60/40% v/v) sparge gas mixture . 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}.	N/A	Dichlorvos, trichloroaceto-nitrile, chloropicrin and bromobenzene; chlorinated hydrocarbons, pesticides, phenols, explosives, and esters	Laboratory
Photo-catalytic degradation using TiO_2	Use of UV, TiO2 and H2O2 to improve degradation of organic pollutants	N/A	Low strength contaminated soils and water; further research required to determine suitability to treat high strength wastes	Laboratory only
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	N/A	Low strength contaminated waters: alachlor, aldicarb, atrazine, azinphos-	Laboratory scale; used for treatment of low strength wastes in the field

Technology	Process Description	Configuration	Applicability	Scale
	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 25.020.28C. 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		methyl, captan, carbofuran, dicamba, disulfoton, glyphosate, malathion, ethoxylchlor, metolachlor, picloram and simazine	
Electron Beam Injection	A mobile 20-kW electron accelerator is used to inject accelerated electrons into a contaminated aqueous solution	N/A	Low levels of of halogenated solvents (chlorination), disinfection by-products, pesticides, and nitrosodimethylamine	Laboratory
Ozonation	This oxidation process was carried out using ozone (O_3) in basic medium (pH 9.4) at low dosage (0-1.5 g O_3 g^{-1} initial	N/A	Low levels of chlorobenzenes, DDTs and its	Laboratory

Technology	Process Description	Configuration	Applicability	Scale
	TOC) and in the presence of hydrogen peroxide (H_2O_2), with a 0.5 H_2O_2/O_3 molar ratio		metabolites and other organochloride compounds	
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
Ozonation/ Electrical Discharge	Gas containing the contaminant is either treated directly with an electrical discharge or with ozone produced by a	N/A	Dioxins/furans; other POPs in a gas form	Laboratory

Technology	Process Description	Configuration	Applicability	Scale
Destruction	discharge; the latter appears to be more effective			
In situ bioremediation of soils	Enhancement of soil biodegradation using surfactants and reducing agents	N/A	2500ppm DDT	Laboratory
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
Fly Ash Destruction	Use of fly ash to destroy chlorinated organics in wastewaters	N/A	Dioxin/furan, PCB; potentially other organochlorines	Laboratory
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
5. Technologies which are unlikely to be applicable for destruction of POPs stockpiles				
Phyto-	Use of plants to enhance bioremediation	Growth of plants	aldrin, dieldrin	Laboratory

Technology	Process Description	Configuration	Applicability	Scale
remediation	by improved soil aeration and release of plant enzymes and exudates, phytodegredation and phytovolatilisation; enhanced by compost and fungi addition	on contaminated soils	(spikerush), PCBs (plant cells, enzymes)	

Table 3: Process Performance

Technology	Performance Data	Emissions	Byproducts
1. Direct applicable 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
SET	Typically >99.9% on PCB-contaminated soil	Potential ammonia releases	Sodium salts, hydrocarbons/oils, treatment residues
2. Applicable technologies on the stage of a 'breaking through and/or start of commercialisation'			
Molten Salt Oxidation	High DRE reported for chlordane	Carbon dioxide	Salt residues from bath need to be disposed (may be recycled).
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
(MEO-Ce)	>99.995% DRE for chlorinated pesticides	Carbon dioxide gas	Caustic scrubber liquor. Reagent liquor will gradually accumulate metals and other contaminants
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.
3. Technologies that given the right financial circumstances could be full scale within approximately five years			
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 metals and other contaminants. Solids removed from treatment liquor by

Technology	Performance Data	Emissions	Byproducts
			filtration
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
TiO_2-based V_2O_5/WO_3 Catalysis	>99.9% destruction of PCBs	HCl; water; CO_2	Reaction liquid with contaminants
Photo-chemically enhanced microbial degradation	99-100% removal of PCB	N/A	Cl^-, CO_2; organic acids?
Molten Metal Process	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
4. Technologies in the stage of laboratory scale testing			
Microemulsion Electrolysis	>99.9% dechlorination of PCB	N/A	Declorination products – phenols in the case of PCBs; Cl- in solution
MnO_x/TiO_2–Al_2O_3 Catalyst Degradation	100% degradation of 1300ppmv chlorinated benzene gas	HCl, H_2O, carbon oxides	N/A
Catalytic hydrogenation	>99.9996% for 1300ppm PCB; >99.99999% for 40,000ppm PCB	Not known	HCl, light hydrocarbons in oil
SPHTG	>99.999% destruction for hexachlorobenzene and the herbicide	CO, CO_2; potential other gases	Hydrogen and methane (with CO and CO_2 in the case of 2,4-

Technology	Performance Data	Emissions	Byproducts
	Dichlorprop		DP) were the main gaseous compounds. Traces of benzene, mono-, di- and tri-chlorobenzene, dichloroetylene, dichloro-methane, xylene and trimethylbenzene were also found.
Ultrasonic irradiation	Complete degradation of chlorinated hydrocarbons, pesticides, phenols, explosives such as TNT, and esters	CO_2	carbon dioxide, short-chain organic acids, and inorganic ions.
Photocatalytic degradation using TiO_2	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)	CO_2	Cl^-, CO_2; some toxic breakdown products may occur
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
Electron Beam Injection	68 – 99.8% removal of MTBE, pesticides etc. at low levels	CO_2	Inorganic acids; other breakdown products not known but possibly short chain organic acids
Ozonation	99.93-99.99% removal of low level contamination of dichlorobenzophenone, tetradifon, chlorobenzene, trichlorobenzene; no effect on DDT	CO_2	Short chain organic acids including *o*-Chlorophenol, *p*-chlorophenol, benzenemethanol, *n*-chlorohydroxibenzaldehyde, *n*-chlorobenzenemethanol,

Technology	Performance Data	Emissions	Byproducts
			chlorobenzoic acid
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
Ozonation/ Electrical Discharge Destruction	88% for indirect ozone treatmentof VOCs and dioxins/furans	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
Fly Ash Destruction	100% destruction of dioxins/furans, PCB at 2ppb in liquid stream or 2ppm in gas stream	CO_2	regeneration water requires disposal; may contain inorganic and organic acids
Molten Slag Process	N/A	N/A – could include dust and other contaminants	N/A
5. Technologies which are unlikely to be applicable for destruction of POPs stockpiles			
Phytoremediation	N/A	N/A	N/A; may include runoff problems

Table 4: Practical Aspects

Technology	Infrastructure Needs	Operational Needs	Practical Issues	Safety Issues
1. Direct applicable 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	Batch process	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
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.
2. Applicable technologies on the stage of a 'breaking through and/or start of commercialisation'				
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
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

Technology	Infrastructure Needs	Operational Needs	Practical Issues	Safety Issues
				hazards
(MEO-Ce)	Significant electricity requirements	Continuous process	Not clear how solids build-up is prevented in the treatment liquor	No major issues
GeoMelt™ Process	Significant electricity requirements	Batch process	Highly saturated soils need to be dewatered before treatment	No major issues
3. Technologies that given the right financial circumstances could be full scale within approximately five years				
MEO– Ag	Significant electricity requirements	Continuous process	No major issues	No major issues
Ball Milling	Moderate electricity demand	Batch operation	Supplies of base metal. Disposal of treated residues.	No major safety issues, but possible noise/vibration
TiO_2-based V_2O_5/WO_3 Catalysis	Moderate temperature requirement (300°C)	Batch or continuous process	Supply of catalyst; disposal of spent catalyst	No major issues identified at this stage
Photo-chemically enhanced microbial degradation	Moderate electricity and sunlight requirement	Batch operation	None identified at this design level	Disposal of wastewater
Molten Metal 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.
4. Technologies in the stage of laboratory scale testing				
Microemulsion Electrolysis	Moderate electricity requirement	Not clear at this stage of design	Supply of didodecyldimethyl-ammonium bromide (DDAB)-water-	Disposal of lead cathodes and spent catalysts

Technology	Infrastructure Needs	Operational Needs	Practical Issues	Safety Issues
			dodecane and metal phthalocyanine tetrasulfonates catalysts	
MnO_x/TiO_2–Al_2O_3 Catalyst Degradation	Moderate temperature requirement (300°C)	Batch or continuous process	Supply of catalyst; disposal of spent catalyst	No major issues identified at this stage
Catalytic hydrogenation	N/A	Batch operation	Supply of sulphide catalyst	Disposal of acid; spent catalyst; further design details needed
SPHTG	Moderate electricity requirements	Batch operation	Supply of calcium hydride or calcium metal; argon	Release of H_2, CH_4 and traces of benzene, mono-, di- and tri-chlorobenzene, dichloroetylene, dichloro-methane, xylene and trimethylbenzene
Ultrasonic irradiation	Moderate electricity requirements Production of salts and localised high temperatures and pressures due to cavitation may result in pitting and corrosion	Batch or continuous process	Argon/O2 sparge gas	Disposal of salt bearing wastewaters
Photocatalytic degradation using TiO_2	Moderate electricity/sunlight requirements	Not clear at this stage of development	Supply of TiO_2	Not clear at this stage of development
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
Electron Beam	High electricity requirement	Batch or continuous	Not clear at this stage	No major issues

Technology	Infrastructure Needs	Operational Needs	Practical Issues	Safety Issues
Injection		process	of development	identified at this stage of development
Ozonation	Moderate electricity/sunlight requirements	Not clear at this stage of development	Supply of O_3 and H_2O_2	Handling of O_3 and H_2O_2
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
Ozonation/ Electrical Discharge Destruction	High electricity requirement	Batch or continuous process	Batch or continuous process	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
Fly Ash Destruction	Not clear at this stage of development	Not clear at this stage of development	Disposal of fly ash	Potential for formation of toxic breakdown products
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.

Technology	Infrastructure Needs	Operational Needs	Practical Issues	Safety Issues
5. Technologies which are unlikely to be applicable for destruction of POPs stockpiles				
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 - Draft

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 should 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 technologies for stockpile destruction is different to the non-combustion technology required for soil decontamination.

The authors of this review have extensive experience with POPs projects in developing countries or countries in transition as well as developed countries that go back more than fifteen years. This experience started with PCB projects in the late 1980s and continued onto POPs in the 1990s. Such projects ranged from small quantity storage of PCB to projects involving thousands of tonnes of mixed obsolete pesticides, POPs and PCBs. The authors have been fortunate in that they have been personally involved over many years with the project design and the day to day project management of large scale POPs projects around the planet. The authors between them have been responsible for the removal, transportation and decontamination or destruction (not including contaminated soils) of more than one million tonnes of POPs.

Several of these projects involved vast quantities of miscellaneous POPs in thousands on non uniform containers and located in dozens of sites within developing countries. We have been involved with site technology such as autoclaving, desorption, bio remediation (of contaminated soils only) phytoremediation, sodium reduction, BCD and others. Obviously over time we have gained a significant knowledge of what works and what does not and many principles have emerged.

It is with this experience that we discuss the criteria, ramifications and implications of the application of technology in developing countries to treat and destroy POPs.

The first requirement of an obsolete pesticide disposal technology is a destruction efficiency greater than 99.99% (Rahuman, Pistone 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 et al. 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, Pistone 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. 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, Pistone et al. 2000).

Recent POPs projects (involving the authors)

During a recent project in Venezuela (2001) where some 8000 tonnes of obsolete pesticide waste were recovered from jungle and urban storage approximately 40% of the waste was Lead Arsenate. There was no possibility, on the part of the local people, that all of the waste would not be recovered from the sites. In addition there were thousands of containers that also had to be removed. All waste was shipped to Europe for destruction.

A project in Argentina (2002) involved 60 tones of buried lindane at a site 1000 km north of Buenos Aires. It was impracticable to bring a technology of any kind to the site and effect destruction. Waste included the original lindane, soil, water and other materials. All waste was shipped to Europe for Destruction

The South Pacific Islands POPs project (2000) involves several hundred tonnes of POPs and other non POPs waste scattered over 14 islands states. This waste is being collected and shipped to Australia for destruction using desorption and Plasma Arc. Initially it was thought that a technology could be transported to each of the islands and the destruction done in situ. Due to the variability of the waste this was not an option.

The 2000 project in Mozambique involved 1000 tones of mixed POPs and non POPs over four storage facilities. The variability of the waste meant that an in situ treatment technology was not feasible and the waste was packed and transported to Europe for destruction.

In 2000 a project was established in Australia to destroy PCB in oil using the sodium reduction process. Some 1000 tonnes were in situ treated.

The 2003 project in Senegal involved many small POPs storage and large quantities of unknown as well as non POPs and POPs mix. All waste was shipped to Europe for destruction.

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 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) 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 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 POP waste management. In our experience the possibilities for application of the 3R's 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. 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 is 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 both ex and in situ. In this case this can be done by using a simple algorithm within the spread sheet but it can also be performed on each element. 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 say 25 KW this would attract a rating of say 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 judgement 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. This simple application of comparative values is not cross linked in that one or more criteria elements is worth more or less than others. In other words we have not said that the issue of environmental impact is of higher importance than the issue of energy requirements. All the criteria areas are treated equally. In doing this while it is recognised that some may debate this approach it does allow for a clean, simple relative comparative analysis to be made.

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 kicks in and the technology is discounted. These criteria

have been developed from the authors on site experience as well as from other individuals 'in the business' so to speak and also from academics who are involved with developing countries and their economics.
The assignment of the values is an exercise in judgement and is something that engineers have to do all the time when evaluation the application of technologies. Within the final table summaries for the technologies there will be two columns that resolve out the issue of in situ versus ex situ.

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 criterium 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

4.5.8 SUSTAINABILITY

4.6 Adaptation of the developing country to the non-incineration technology

4.6.1 RESOURCE NEEDS

This criterium 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 & telecoms 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 criterium 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-
Discharges to water
Discharges to land
Social Impact (noise etc)

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 say 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 (eg. pH and leachable metals)	(Scale 0-5) Units TCLP

4.6.7 SUSTAINABILITY

5.0 PROMISING TECHNOLOGY FOR USE IN DEVELOPING COUNTRIES

[This section to be completed post workshop – Washington 3 October 2003]
When the criteria are completed and the matrices loaded then an output table is generated. The outline of this table is shown below and subsequently the promising non-combustion technologies emerge. See Table 5. below.

5.0 Promising Technologies (Not Completed)

Destruction efficiency	DE		(Scale 0-100) Units
Capability to treat all POPs	Cap		(Scale Binary 0-1) N/Y NotFF
Secondary waste streams volumes < primary stream		SW	(Scale binary 01-) N/Y NotFF
Off gas treatment	OGT		(Scale linear 0-100)
Containment	Con		(Scale binary 0-1) N/Y NotFF
New POPs formation	NPF		(Scale binary 0-1) N/Y
Uncontrolled releases	UR		(Scale binary 0-1) N/Y
Minimum pretreatment		MP	(Scale binary 0-1) N/Y
Toxic reaction byproducts		TRB	(Scale binary 0-1) N/Y
Complete elimination	CE		(Scale binary 0-1) N/Y
Waste/ tonne	W/t		(Scale linear 0-24) Units hrs /tonne
Quantity per day/month		Q/d	(Scale linear 0-5) Units tonne /day

UK - Unknown
P - Possible
UL – Unlikely

Technology	DE	Cap	SW	OGT	Con	NPF	UR	MP	TRB	CE	W/t	Q/d
1. Direct applicable technologies with considerable experience												
GPCR												
BCD												
SET												
2. Applicable technologies on the stage of a 'breaking through and/or start of commercialisation'												
Molten Salt Oxidation												
SCWO												
Sodium Reduction												
(MEO-Ce)												
GeoMelt™ Process												
3. Technologies that given the right financial circumstances could be full scale within approximately five years												
MEO– Ag												
Ball Milling												
TiO_2-based V_2O_5/WO_3 Catalysis												
Photo-chemically enhanced microbial degradation												
Molten Metal Process												
4. Technologies in the stage of laboratory scale testing												
Microemulsion												

Technology	DE	Cap	SW	OGT	Con	NPF	UR	MP	TRB	CE	W/t	Q/d
Electrolysis												
MNO_x/TiO_2–Al_2O_3 Catalyst Degradation												
Catalytic hydrogenation												
SPHTG												
Ultrasonic irradiation												
Photocatalytic degradation using TiO_2												
Fe(III) Photocatalyst Degradation												
Electron Beam Injection												
Ozonation												
Biodegradation/ Fenton's reaction												
White rot fungi biodegradation												
Enzyme Degradation												
Ozonation/ Electrical Discharge Destruction												
In situ												

Technology	DE	Cap	SW	OGT	Con	NPF	UR	MP	TRB	CE	W/t	Q/d
bioremediation of soils												
DARAMEND bioremediation												
Fly Ash Destruction												
Molten Slag Process												
5. Technologies which are unlikely to be applicable for destruction of POPs stockpiles												
Phyto-remediation												

6.0 CONCLUSIONS AND RECOMMENDATIONS

[This section to be completed post workshop – Washington 3 October 2003]

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TECHNOLOGY LIT REVIEW (Annotated)
DDT Pesticide - still widely used in southern countries for malaria control.
PCBs - Coolant in electrical transformers; heat exchange fluid; additive in paints, plastics and paper.
Dieldrin - Insecticide.
Endrin - Insecticide.
Aldrin - Insecticide.
Chlordane - Insecticide.
Mirex - Insecticide; fire retardant.
Toxaphene - Insecticide.
Dioxins - Unintentional by-product of combustion; pesticide. manufacture.
Furans - Unintentional by-product of combustion; PCB manufacture; pesticide manufacture.
Heptachlor - Insecticide.
Hexachlorobenzene - Fungicide; industrial solvent; by-product.

GPCR
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=90oC; 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 TiO2 photocatalysis together with ozonation are the most promising; TiO2 is effective in large scale wastewaters with available sunlight and concentrations <50ppm Ozonation more easily controlled, can be implemented with UV/H2O2 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 TiO2 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 identi®cation 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 e†ciency 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 usinga 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.Usingfundamental 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, Mn*O*x/Ti**O2** –A**l2 O3**, was prepared by mpregnating Mn*Ox* species on Ti**O2** -modified A**l2 O3**. The Ti**O** species in Ti**O2** –A**l2 O3** support is in a monolayer dispersion, and the Mn*Ox* species is again highly dispersed on Ti**O2** –A**l2 O3** support. The total oxidation of chlorobenzene and o-dichlorobenzene on Mn*O*x/Ti**O2** –A**l2 O3** catalyst can be achieved at 300±C and 250±C respectively, at the space velocity of 8000 h¡ **1** . The activity of Mn*O*x/Ti**O2** –A**l2 O3** 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 Ti**O2** -modified A**l2 O3** 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 TCPproducing 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
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.

Photodegration

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*
Abdul J. Chaudhary, Susan M. Grimes and Mukhtar-ul-Hassan
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 TiO2 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 TiO2 with a surfactant at a pH of 3 and T=25oC after 90 minutes

Martha M. Higarashi a , Wilson F. Jardim Remediation of pesticide contaminated soil using TiO2 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 TiO2 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 TiO2 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/TiO2/O2 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 – still requires research
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 ug/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 TiO2 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 TIO2

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 (TiO2). 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 H2O2 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 (H2O2) during irradiation. When photocatalysis was performed with TiO2 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 TiO2 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: S2O 2ÿ 8 > Oxone > H2O2. 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 FeIII/H2O2/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)/H2 O2 /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 =25.08C, 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, ala-
chlor) 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 H2O2 and scwo at 30Mpa and 673oC to a level of 99.999% releasing HCl and CO2
Hawthorne, Steven B; Lagadec, Arnaud JM; Kalderis, Dimitrios; Lilke, Alan V; Miller, David J
Pilot-scale **destruction** of TNT, RDX, and HMX on contaminated soils using subcritical water Environmental Science & Technology [ENVIRON SCI TECHNOL]. Vol. 34, no. 15, pp. 3224-3228. Aug 2000.
Use of subcritical water to degrade explosives at up to 12% contamination at 275oC 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 *(23*).
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, CO2, 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/NO2 & SO2 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/NO2 and SO2 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/NO2, SO2 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 V2O5/WO3 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 _ After 30 min at 340 _ less than 1%of the spiked OCDD and OCDF was recovered as T4CDD/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 _ which was considerably increased at 340 _

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 _ In contrast, FA1 type fly ash was found to effect both dechlorination and destruction of these compounds already at temperature settings of 260 _ 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 .y ash at 380 _ 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 – 250 m 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 200–250 um 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 H2O2, 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 HCmolecules

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

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*

Biodegradation of DDT

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 2,20 ,5,50 -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 [12].Biobed matrix was prepared by mixing together on a w/w basis 50% barley straw, 25%topsoil (Wick series sandy loam,1% organic C [13])and 25%compost,according to Fogg
[14].
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 .8ug/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 fo P. ostreatus able to degrade 40% Delor 103 in 2 months; efficiency decreased with increasing no 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
di•erent 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.

Table 1

Examples of environmental pollutants oxidized by lignin degrading fungi

Environmental pollutants oxidized by white rot fungi References

Chlorinated compounds 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;

Bollag et al., 1988; Call and MuÈcke, 1997.

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 _ ersicolo*r, *Phanerochaete chrysosporium* and *Lentinus edode*s, respectively, in 10-day incubation tests. The highest PCB transformation 70% was obtained with *T. _ ersicolor* 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. _ ersicolor* 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 synergistically 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.

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

Phytoremediation

Phytoremediation on HCH-contaminated soils - 187
Siegfried Johne, Roland Watzke, Konstantin Terytze
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

Perspectives of phytoremediation for soil contaminated with pesticides - 191
Wim H. Rulkens
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

DARAMEND technology for in situ bioremediation of soil containing organochlorine pesticides - 487
Theresa Phillips, G. Bell, D. Raymond, K. Shaw, Alan Seech
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