Non-combustion Technologies
for POPs Destruction
Review and Evaluation

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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Preface

This publication has been developed within the framework of the programme of the International Centre for Science and High Technology of the United Nations Industrial Organization (ICS-UNIDO).

For more than five years the Area of Chemistry of ICS-UNIDO has conducted activities related to Persistent Organic Pollutants (POPs) within the subprogrammes of Catalysis and Sustainable Chemistry and Remediation, with a specific focus on the survey, assessment and promotion of technologies for POPs destruction and transfer of knowledge of these technologies to developing and transition-economy countries.

The problem of POPs has been recognized in the last 20 years as one of the priorities of the world community to be addressed. POPs and some other halogenated organic compounds represent a class of chemicals which are harmful to humans and the environment. One of the concerns is that most of these chemicals have been formerly produced on an industrial scale to be used in agriculture (chlorinated pesticides) and other applications (e.g. PCBs). Enormous quantities of these chemicals have accumulated worldwide. Measures should be taken, first in the developing world to prevent further contamination resulting from POP stockpiles, given that the conditions of storage of these chemicals in these countries are often inadequate.

POP issues have become of concern to many national and international bodies, including the UN (POP programmes of UNIDO, UNEP, UNDP, WHO, FAO, etc.). The Stockholm Convention on POPs requires that for 12 priority chemicals production and use be stopped and that existing stockpiles be eliminated by safe destruction. This task should be addressed through consideration of the relevant technologies, and the more environmentally safe options should be applied. However, there is overcapacity of incineration technologies on the market, which are sometimes considered as undesired for destruction of chlorinated waste due to the risk of secondary contamination.

For this reason ICS-UNIDO has elaborated a review and evaluation process of alternative POP destruction technologies. It is imperative that innovative and emerging technologies be considered and their advantages be evaluated and compared before common options, so that cleaner options become available on the market and better technologies are offered to developing countries.

This review does not only aim to divulgate and transfer knowledge of these technologies but also to provide guidance for evaluation and selection of technologies. The technologies considered in this review have been quantitatively assessed against numerous criteria related to their performance, risk, experience, configurations, etc. Based on the results of this evaluation, the concept for creation of a decision-support tool was also developed. The proposed tool will extend the scope of DARTS, DAWTS, and other software based expert systems already developed at ICS-UNIDO. These tools can assist decision makers in the choice of the most appropriate technologies or be used for educational purposes.

The authors would like to stress that any critical opinion expressed in this review regarding evaluation of technologies, synthesis of criteria for evaluation and theoretical considerations that were adopted for this evaluation, should be referred to only as an independent and individual viewpoint. Such opinions are based on the available information obtained from open sources and on authors’ expertise. The authors and UNIDO do not take
any responsibility if the data presented in this review or data to which reference is made which appear incorrect, incomplete, or not up-to-date. Any prioritization of technologies that can be derived based on the data presented herein in no case can be considered as the opinion of authors or UNIDO.

Trieste, March 2007

Stanislav Miertus
Chief of Area
Pure and Applied Chemistry
ICS-UNIDO
Introduction to the Programmes of the ICS-UNIDO
Area of Pure and Applied Chemistry

The United Nations Industrial Development Organization (UNIDO) is a specialized agency of the United Nations dedicated to promoting sustainable industrial development in developing and transition-economy countries. It harnesses the joint forces of the government and private sector to foster competitive industrial production and international industrial partnership and promote socially equitable and environmentally friendly industrial development.

UNIDO is the only worldwide organization dealing exclusively with industry from a development perspective. UNIDO’s services are non-profit making, neutral and specialized. UNIDO acts as a catalyst to help generate national economic wealth and raise industrial capacity through its role of a worldwide forum for industrial development and by providing technical cooperation services. UNIDO’s ultimate goal is to create a better life for people by laying industrial foundations for long-term prosperity and economic strength.

The International Centre for Science and High Technology (ICS) is an institution within the legal framework of UNIDO, with headquarters at the AREA Science Park in Trieste, Italy. The Centre’s mandate is the transfer of know-how and technology in favour of developing countries and is based on the premise that competitive industrial technological capability cannot be built-up without adequate scientific knowledge and commitment to a sustainable development approach based on new and environmentally friendly technologies. It serves the UNIDO global programmes as a centre of technological expertise in selected sectors.

The ICS work programme focuses on activities in specific sectors within the Areas of:

- Pure and applied chemistry
- Earth, environmental and marine sciences and technologies
- High technology and new materials.

The main tools for the implementation of the work programme in the ICS Area of Pure and Applied Chemistry are: organization of events for capacity and awareness building (expert group meetings, training courses and workshops); evaluation and development of project proposals; networking and participation in international projects and initiatives; creation of databases and preparation of publications; fellowships and on-the-job training schemes.

Particular attention is paid to the development of in-house ICS-UNIDO expertise focused on assessment technologies. Information tools such as molecular modelling, process simulation and decision-support tools are extensively used.

In selecting the specific subprogrammes of each Area and the related activities, special consideration was given to their relevance in relation to the scientific and technological development of developing and transition-economy countries.

In acknowledging that sustainable development depends upon the harmonization of economic growth and environmental conservation and protection, the ICS Area of Pure and Applied Chemistry has identified as priority fields in its work programme the following themes, which are of key relevance to economic and industrial development as well as the safeguarding of the environment:

- environmentally degradable plastics
- remediation technologies
- combinatorial chemistry and technologies
- catalysis and sustainable chemistry.
Environmentally Degradable Plastics

The expanding global production and consumption of polymeric materials coupled with increasing public awareness of environmental issues have created serious concern for problems related to the disposal of plastic waste generated by various sectors of human activity. Besides recycling, re-use, incineration and composting, new technological developments of environmental degradable plastics contribute dramatically to the tackling of the environmental issue in specific sectors of plastics use.

Remediation Technologies

One of the most urgent problems to be faced at a global level is the decontamination of soils and waters that have become polluted through domestic and industrial activities. Large polluted areas, in addition to having lost their eco-functionality, often represent a serious risk for human health. Policy for the restoration of natural resources is thus a priority in developing as well as industrialized countries. In recent years, several remediation technologies have been developed for the decontamination of polluted sites, and many have proved to be very promising for the clean-up of contaminated water and soil.

Combinatorial Chemistry and Technologies

These technologies have a strong impact on the development of new chemicals (pharmaceutical industries, agro-chemicals, new materials). Developing countries need to become acquainted with and gain expertise in combinatorial technologies to help local enterprises remain competitive and economically viable in the coming decades. Combinatorial chemistry and technologies have a potential influence not only on industrial growth but also on environmental protection. In fact, by optimizing industrial processes and production, with the lowering of relevant costs, less waste and fewer by-products are created.

Catalysis and Sustainable Chemistry

This is an important scientific and technological programme for the development of environmentally friendly chemical processes, which are the basis for cleaner industrial production and the key elements for an industrial pollution prevention approach. New, less polluting processes together with the optimization of existing processes depend to a great extent upon the improvement of catalyst performance in heavy and fine chemical production lines, with direct impact on the by-products or waste generated.

An important part of this programme is dedicated to technologies for safe destruction of hazardous compounds, including POPs.

For further information see, http://www.ics.trieste.it
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>(Na-, K-)PEG</td>
<td>Sodium, Potassium Polyethylene Glycolate</td>
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<tr>
<td>(US) EPA</td>
<td>United States Environmental Protection Agency</td>
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<td>ACWA</td>
<td>Assembled Chemical Weapons Assessment</td>
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<td>AHO</td>
<td>Assisted Hydrothermal Oxidation</td>
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<td>APEG</td>
<td>Alkaline Polyethylene Glycol</td>
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<tr>
<td>BDS</td>
<td>Bilger Dispersed Sodium</td>
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<tr>
<td>BCD</td>
<td>Base Catalyzed Decomposition (or Dechlorination – old version)</td>
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<tr>
<td>BCDP</td>
<td>Base Catalyzed Decomposition Process</td>
</tr>
<tr>
<td>CEE</td>
<td>Central and Eastern Europe</td>
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<td>CEO</td>
<td>Catalyzed Electrochemical Oxidation</td>
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<td>CerOx</td>
<td>Cerium Oxidation</td>
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<tr>
<td>CFC</td>
<td>Chlorofluorocarbons</td>
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<tr>
<td>CHD</td>
<td>Catalytic Hydrodechlorination</td>
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<tr>
<td>CPEO</td>
<td>Center for Public Environmental Oversight</td>
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<td>CSIRO</td>
<td>Commonwealth Scientific and Industrial Research Organisation (Australia)</td>
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<td>CESF</td>
<td>Commonwealth Environmental Security Facility</td>
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<tr>
<td>CHT</td>
<td>Combined Heat and Power</td>
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<tr>
<td>CIP</td>
<td>Critical Infrastructure Protection</td>
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<td>CIPM</td>
<td>Critical Infrastructure Protection Management</td>
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<td>CMAP</td>
<td>Critical Infrastructure Management Program</td>
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<td>CMT</td>
<td>Critical-Medium Temperature</td>
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<td>CPU</td>
<td>Computer Programmes Unit</td>
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<td>CWA</td>
<td>Clean Water Act</td>
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<td>CWC</td>
<td>Clean Water Coalition</td>
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<td>CWS</td>
<td>Clean Water Service</td>
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<td>CWSS</td>
<td>Clean Water Services Support System</td>
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<td>DEC</td>
<td>Department of Energy of USA</td>
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<tr>
<td>DRE</td>
<td>Destruction and Removal Efficiency</td>
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<td>DST</td>
<td>Decision-support Tools</td>
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<tr>
<td>EDL</td>
<td>Environmental Decontamination Ltd.</td>
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<td>ESM</td>
<td>Environmentally Sound Management</td>
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<td>ESTCP</td>
<td>Environmental Security Technology Certification Program</td>
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<td>FAO</td>
<td>Food and Agricultural Organization</td>
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<td>FRTR</td>
<td>Federal Remediation Technologies Roundtable</td>
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<td>GEC</td>
<td>Global Environment Centre</td>
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<td>GEF</td>
<td>Global Environmental Facility</td>
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<td>GPCR</td>
<td>Gas Phase Chemical Reduction</td>
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<tr>
<td>HCB</td>
<td>Hexachlorobenzene</td>
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<tr>
<td>HCC</td>
<td>Hexachlorocyclohexane</td>
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<tr>
<td>HEP</td>
<td>High Efficiency Particulate Air</td>
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<tr>
<td>HTO</td>
<td>Hydrothermal Oxidation</td>
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<tr>
<td>HydroDec</td>
<td>Hydrodechlorination (technology)</td>
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<tr>
<td>ICV</td>
<td>In-Container Vitrification</td>
</tr>
<tr>
<td>IFAD</td>
<td>International Fund for Agriculture</td>
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<tr>
<td>IP</td>
<td>Intentionally Produced</td>
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<tr>
<td>ISV</td>
<td>In-Situ Vitrification</td>
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<tr>
<td>ITD</td>
<td>Indirect Thermal Desorption</td>
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<tr>
<td>LANL</td>
<td>Los Alamos National Laboratory</td>
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<tr>
<td>LLNL</td>
<td>Lawrence Livermore National Laboratory</td>
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<tr>
<td>LRTAP</td>
<td>Long-Range Transboundary Air Pollution</td>
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<td>LWPS</td>
<td>Liquid Waste Pre-Heater System</td>
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<tr>
<td>MCA</td>
<td>Multicriteria Analysis</td>
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<tr>
<td>MCD</td>
<td>Mechanochemical Dehalogenation</td>
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<tr>
<td>MCDM</td>
<td>Multiple Criteria Decision-Making</td>
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<tr>
<td>MEO</td>
<td>Mediated Electrochemical Oxidation</td>
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<tr>
<td>MSO</td>
<td>Molten Salt Oxidation</td>
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<tr>
<td>NIP</td>
<td>National Implementation Plan</td>
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<td>NFESC</td>
<td>National Facilities Engineering Services Center</td>
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<td>NSW(C)</td>
<td>Naval Surface Warfare (Center)</td>
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<tr>
<td>OCPs</td>
<td>Organochlorine Pesticides</td>
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<td>ODS</td>
<td>Ozone Depleting Substances</td>
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<tr>
<td>OECD</td>
<td>Organization for Economic Cooperation and Development</td>
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<tr>
<td>OGTS</td>
<td>Off-Gas Treatment System</td>
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<tr>
<td>PACT</td>
<td>Plasma Arc Centrifugal Treatment</td>
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<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbon</td>
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<tr>
<td>PAHWTS</td>
<td>Plasma Arc Hazardous Waste Treatment System</td>
</tr>
<tr>
<td>PAT</td>
<td>Plasma Arc Technologies</td>
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<tr>
<td>PCBs</td>
<td>Polychlorinated Biphenyls</td>
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<tr>
<td>PCDD(s)</td>
<td>Polychlorinated Dibeno-p-dioxins</td>
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PCDF(s) Polychlorinated Dibenzofurans
PCF Plasma Centrifugal Furnace
PCP Pentachlorophenol
PLASCON Plasma Conversion
PlasmOx Plasma Oxidation
PNNL Pacific Northwest National Laboratory
POP Persistent Organic Pollutant
POTW Publicly Owned Treatment Works
PPC Primary Processing Chamber
PWC Plasma Waste Converter
RKR Rotary Kiln Reactor
ROK Republic of Korea
SBC Secretariat of Basel Convention
SBV Sequencing Batch Vaporiser
SCWO Supercritical Water Oxidation
SET Solvated Electron Technology
SITE Superfund Innovative Technology Evaluation (Programme)
SPHTD Self-Propagating High-Temperature Dehalogenation
SR Sodium Reduction
STAP Scientific and Technical Advisory Panel
STC Secondary Treatment Chamber
STR Stirred Tank Reactor
TAG Technical Advisory Group
TRBP Thermal Reduction Batch Processor
TRM Thermal Reduction Mill
TSCA Toxic Substances Control Act
UNDP United Nations Development Programme
UNECE United Nations Economic Commission for Europe
UNEP United Nations Environmental Programme
UP Unintentionally Produced
UNITAR United Nations Institute for Training and Research
VOC(s) Volatile Organic Compound(s)
WHO World Health Organization

Units of measurement

£ UK Pound
°C Degree Centigrade
atm 1 atmosphere pressure
AUSD Australian dollar (rate of 1AUSD = 0.714 USD was applied)
cm Centimetre
g Gram
gallon = 3.785 L
hr (h) Hour
K Kelvin
kg Kilogram
kJ Kilojoule
kW(h) Kilowatt(hour)
L Litre
lb Pounds
m² Square metre
m³ Cubic metre
mL Millilitre
mm Millimetre
ms Millisecond
MW Megawatt
ng Nanogram
ppb Part per billion (microgram per kilogram)
ppm Part per million (milligram per kilogram)
ppt Part per trillion (nanogram per kilogram)
psi Pound on square inch
ton(s) (t) Ton in SI units
USD ($) US dollar
W Watt
wt% Percent by weight
µm Micrometre
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1. Introduction

Background

The problem of environmental pollution has received urgent concern worldwide. Removing and preventing pollution by toxic substances is one of the fundamental milestones on the way towards building sustainable industry and promoting future socio-economic development, which is among the priorities of the world community.

Nowadays particular attention has been drawn to the so-called POPs (Persistent Organic Pollutants). According to the definition of the UN Environmental Programme (UNEP), Persistent Organic Pollutants are chemical substances that persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment. Some POPs have been known for a long time, some have been used only recently as pesticides, and some, unfortunately, are still being produced and used in several countries.

These substances if present in very small concentrations can produce mutagenic and carcinogenic effects, reproducibility and immune system disorders, etc. Unlike other pollutants, POPs are very stable in the environment and accumulate when passing through the nutrition chains. There is evidence of long-range transport of these substances to regions where they have never been used or produced and the consequent threats they pose to the environment of the whole globe. Because they are so long-lived and toxic, POPs are inherently impossible to manage. The question is no longer whether action should be taken but rather how the regulation and restriction of these POPs should proceed.

For example, dioxin,\(^1\) which is usually the worst POP, can persist in soils and tissues for decades to then accumulate in human milk. Mothers and children are the main risk group, because the dioxin first of all affects the reproductive function. Dioxin is not an immediate poison, its action is felt after decades and results in a general health deterioration; because of this, journalists call dioxin a “chemical AIDS” and, though the mechanism is very different, this comparison is very accurate.

In addition to dioxins and furans, many other chlorinated and halogenated organic compounds exhibit similar toxicity. Even though the other POPs are less toxic than dioxins and furans, their broad distribution poses a serious concern. More than a half of chemical industries produced these substances intentionally or still produces them unintentionally.

Stockholm Convention on POPs

In 2001, representatives of 92 countries agreed to sign the Stockholm Convention on POPs to reduce or eliminate releases of 12 specific POP substances, the so-called “dirty

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\(^1\) This common name of “dioxin” usually applies to the group of 17 polychlorinated dibenzo-p-dioxins and dibenzofurans which are produced unintentionally, often in the combustion processes, and representing extreme toxicity (the so-called dioxin-like toxicity).

dozen”. All 12 priority POPs outlined by the Stockholm Convention are polychlorinated organic compounds, which are:

1. Polychlorinated dibenzo-\(p\)-dioxins (PCDD)
2. Polychlorinated dibenzofurans (PCDF)
3. Polychlorinated biphenyls (PCBs)\(^2\)
4. Hexachlorobenzene (HCB)
5. DDT
6. Toxaphenes
7. Mirex
8. Chlordane
9. Heptachlor
10. Aldrin
11. Dieldrin
12. Endrin

The first four POPs are called unintentionally produced (UP) POPs, formed in combustion processes and as by-products of chemical industries. PCB and HCB were also produced on purpose, as well as the following eight POPs on the list and are therefore considered as intentionally produced (IP) POPs. These last ten POPs on the list were all produced on a large scale worldwide to be used mainly in electrical equipment (PCBs), as pesticides, herbicides, or fungicides. PCDD, PCDF, PCB, and toxaphenes represent groups of compounds, while the others are singular chemical formulations.

The Convention requires that production and use of the above-mentioned 12 POPs be stopped and their stockpiles destroyed so that the resulting products are no longer POP. Article 6 of the Convention text addresses the identification and management of POPs waste, nine of which are pesticides, which for the most part are now obsolete. The Convention requires that such wastes be managed in a safe, efficient, and environmentally sound manner and that the disposal be done that the POP content destroyed or irreversibly transformed so it is no longer a POP.

The Stockholm Convention states that Parties are to take measures so that POPs wastes are:

“Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of persistent organic pollutants or otherwise disposed of in an environmentally sound manner when destruction of irreversible transformation does not represent the environmentally preferable option …” (Article 6, L (d) (ii))

Further, measures are to be taken so that POPs wastes are:

“Not permitted to be subject to disposal operations that may lead to recovery, recycling, reclamation, direct reuse or alternative uses of persistent organic pollutants.” (Article 6 (d) (iii))

Detailed information on the state of the art of POPs and the Stockholm Convention can be found on the UNEP website, www.chem.unep.ch/pops and on www.pops.int.

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\(^2\) PCBs represent a wide class of toxic compounds which are still used widely as transformer and condenser oils. Some PCBs (dioxin-like PCBs) are also known to possess the same type of toxicity as dioxins and furans.
The Interim Secretariat of the Stockholm Convention was established by UNEP Chemicals. UNEP also provides the Secretariat to the Basel Convention on the transboundary movements of hazardous waste and their disposal and, in collaboration with the UN Food and Agricultural Organisation (FAO), to the Rotterdam Convention on the prior informed consent procedure for certain hazardous chemicals and pesticides in international trade. The interests of the Stockholm Convention intercept with the above-mentioned conventions as regards the management of PCB and some chlorinated pesticides. The three conventions collaborate and together provide the international framework for the environmentally sound management of hazardous chemicals and wastes through their whole life cycle, including production, use, trade and disposal. 12 POPs of the Stockholm Convention are all among the 16 POPs subject to the Geneva Convention on Long-Range Transboundary Air Pollution (LRTAP) under the auspices of the United Nations Economic Commission for Europe (UNECE).

A special body of experts established under UNEP (POP Review Committee) work on the criteria for adding further chemicals to the POPs protocol in the future. Negotiations are currently underway to include in the Convention other four substances, namely pentabromodiphenyl ether, chlordecone, hexabromobiphenyl and hexachlorocyclohexane. Some other chemicals are under considerations.

The Global Environmental Facility (GEF) is the designated interim financial mechanism for the Stockholm Convention. The three implementing agencies of GEF are UNEP, UNDP, and World Bank. Four regional development banks, UNIDO, and FAO, and the International Fund for Agriculture (IFAD) are the Executing Agencies with Expanded Opportunities which, together with the implementation agencies, assist countries in developing all projects and programmes that receive GEF co-financing.

On the country level the Stockholm Convention is implemented starting from the development of the National Implementation Plan (NIP) and going through a series of actions and projects aimed at pollution inventory, development of national waste management strategy, technology transfer and demonstration projects, training, etc. These activities can be coordinated by the national focal points of the Stockholm Convention, regional centres of the Basel Convention, in cooperation with other stakeholders, including local NGOs, industries, and environmental organizations.

For more than thirty years POP related issues have been of concern to many international organizations, whose targeted programmes have been elaborated in order to manage the problem in different territorial and technical areas. The UNEP Chemicals was the main catalytic force in the UN system for concerted global action on the environmentally sound management (ESM) of POPs. Many other international organizations, including UNIDO, UNDP, FAO, UNITAR, OECD, US EPA, WHO, and others now actively collaborate with countries on POP issues connected to disposal, prevention, health issues, etc.

In the early seventies UNIDO started its POP activities and since then has actively participated in intergovernmental negotiations on POPs. With the support of GEF it has been providing services assistance in introduction of best available techniques for waste minimization in developing countries. UNIDO has been instrumental in the promotion of non-combustion technologies for the destruction of POPs. It is currently implementing the global project “Demonstration of Viability and Removal of Barriers that Impede Adoption and Effective Implementation of Available, Non-combustion Technologies for Destroying Persistent Organic Pollutants” in cooperation with GEF and UNDP, and several other projects are in preparation. Local activities on POPs destruction related to knowledge and technology transfer and instrumental support are carried out in numerous affiliated centres of UNIDO.
**INTRODUCTION**

**POPs in the general context: definition and focus**

It is known that many other chlorinated and halogenated substances manifest POP-like toxicity. In addition to the 12 POPs, some organohalogen compounds are on the list of persistent toxic substances (PTS), e.g. polybrominated biphenyls (PBB) and diphenylethers, chlorinated naphthalenes and paraffins, pentachlorophenol (PCP), lindane, etc. Halogenated Cl-C3 hydrocarbons, CFCs, and chlorinated solvents are also known to be toxic or environmental hazards (ODS). A number of halogenated compounds belong to the EPA list of 188 hazardous air pollutants.

The presence of a contaminant on the list represents a strategy to reduce historically increased risks connected to the exposure to this contaminant. In some countries there are local regulations on the disposal of certain chemicals or groups of chemicals (e.g. scheduled wastes in Australia). In a more general case, such as that of the POP list of Stockholm Convention, the major risk of international dimension is recognized for a group of chemicals. Usually, the risk is especially relevant for developing and transition economy countries. However, it is understood that such general regulations do not always address situations of particular countries, and are limited to available inventory data, which are usually scarce.

In practice, there is a large number of chemicals which possess toxicity similar to that of the 12 POPs and which have been produced on an industrial scale. It can be envisaged that many of such chemicals will appear to be halogenated ones, owing to their intrinsic toxicity, persistence and high production volumes in the past. Many other halogenated chemicals will probably be subject to future regulations.

In connection with this, when addressing the technical feasibility of POP destruction, a more general definition of the object can be given. For the scope of this review, the definition of POP will be extended to *any halogenated organic substance manifesting toxicity*. For most physical chemical technologies, which are considered suitable to POP destruction and are included in this review, this applicability and related performance data can be considered as common for any halogenated chemical.

**Stockpiled POPs**

Stockpiles of POPs can be generally defined as a POP waste with medium to high content of POP chemical(s). These are, first of all, pure or concentrated POPs present as bulk solid or liquid organics containing one or more individual chemicals. Organic POP matter can be dissolved in a solvent or mixed with some inorganic or inert materials, like soil or debris. Stockpiled chemicals can be stored in containers, landfills, or piles; in the latter case, the piles can be stored in dedicated buildings or be simply dumped on open land. PCBs can be often found inside electrical equipment.

Typical examples of stockpiled POPs are obsolete pesticides, PCBs discarded from use (PCB oils and liquids), heavily contaminated soil (e.g. soil surrounding landfills and deep wells containing POP). Substantial concentration of POPs can be found in the waste streams of various chemical industries. These wastes or any other obsolete POP chemical, stored or disposed in a way that does not lead to chemical decomposition of the POP content can also account for POP stockpiles.

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3 For more information see [www.chem.unep.ch/pts](http://www.chem.unep.ch/pts).
The stockpiled POPs are particularly dangerous because they pose a high risk of secondary POP contamination. Many stockpiled POPs are present in developing countries and are usually stored in improper conditions, causing continuous contamination of surrounding territories. POP stockpiles represent a time bomb for human health and the environment not only in these countries, given that it is well known that POPs can ‘travel’ great distances.

Considerable stockpiles of POPs exist in many countries. It is estimated (FAO) that the global obsolete pesticide stock is over 500,000 tons and that several hundred thousand tons are located in CEE, but the real amounts are certainly higher. The PCB stock probably exceeds 1,000,000 tons. The European Environmental Agency has concluded in 1998 that over 300,000 potentially contaminated sites have been identified in Western Europe alone, and the estimated total number in Europe is much larger.

It is imperative that the action be taken on stockpiled POPs so that concentrated POP sources are secured and consecutively eliminated. The correct and timely disposal of POP stockpiles appears often to be more economically justified than costly and time-consuming remediation activities that would otherwise be necessary to remove secondary contamination of the surrounding land. In addition, the correct planning of POP disposal requires the thorough analysis of consequences that these operations can bring across.

It is therefore the main objective of the current review, as well as of numerous publications, programmes and activities related to POP disposal, to spread awareness and to provide a critical and independent review of available options (technologies) for safe and effective management of POP stockpiles.

**POP destruction technology**

According to the Stockholm Convention on POPs, the irreversible destruction of POPs or their transformation into other non-POP molecules is the preferred action. There are a restricted number of technologies that can be effectively applicable to concentrated chlorinated chemicals. Three principal requirements for the choice of the most appropriate destruction technology for concentrated POPs apply.

1) It should be applicable to concentrated POPs (stockpiles).
2) It should guarantee complete and efficient destruction of POPs. Only chemical physical technologies can provide fast and efficient decomposition of the POP molecule. Biotreatment options are not suitable for destruction of concentrated chemicals.
3) It should guarantee that no new POPs are formed and released.

Generally speaking, the destruction of POP should be complete in the sense of the complete elimination of organic chlorine (mineralization). In the case of non-complete dechlorination, the residual chlorinated organics can still appear toxic or new chlorinated toxicants can be formed out of it (e.g. de novo synthesis of dioxins and furans).

The destruction technologies that are suitable for destruction of POP stockpiles (POP destruction technologies) are usually divided into two groups: 1) combustion technologies, and 2) non-combustion technologies, which are also called alternative technologies.

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4 Since 1929, the beginning of their commercial use, until 1989, world production, excluding the Soviet Union, totaled 1.5 million tons (UNEP 1999 report).
5 Both direct and indirect applicability are implied. The indirect applicability can require additional waste pretreatment for certain waste types. For a more detailed description of direct and indirect applicability see Chapter 3: Technology options.
Combustion technologies

Definition of combustion:
A chemical reaction in which a substance reacts rapidly with oxygen with the production of heat and light. Such reactions are often free-radical chain reactions, which can usually be summarized as the oxidation of carbon to form its oxides and the oxidation of hydrogen to form water.

A Dictionary of Science (Oxford University Press, © Market House Books Ltd 1999)

The combustion technologies (hazardous waste incinerators, rotary kilns, furnaces, boilers, IR incinerators, etc.) are usually believed to be the most economically appropriate way for concentrated POP waste treatment. Many of them are fully developed and are commercialized technologies.Lots of vendors offer incineration technologies in many countries and there is a tight market competition between different vendors, as these technologies have been on the market for decades. This is why in industrialized nations POP wastes are routinely burnt in incinerators and for most countries combustion technologies still remain the most economically acceptable way to treat POP waste on the macro scale.

Modern waste incinerators are designed to satisfy the required emissions levels. Development of new and safer and improvement of existing combustion techniques should not be disregarded a priori. However, care should be taken about safety aspects and proper equipment operation, especially when it is planned to install a combustion plant in a developing country. There is concern that improperly operated or obsolete combustion technologies could generate rich levels of incomplete or secondary combustion products, whose formation is intrinsic in combustion processes. For this reason combustion approach often encounters strong public opposition.

Non-combustion or alternative technologies

Over the last 15 years, a number of non-combustion technologies have been demonstrated to effectively treat POPs wastes in countries such as Canada, USA, Australia, and Japan. Some methods, particularly for PCBs, are outlined by UNEP. However, even developed non-combustion technologies can hardly be competitive with incineration ones, as there is an overcapacity of the latter on the market. Other non-combustion technologies lack in research or technical development, and most of them have a scarce commercial operation history. It is recognized that external funding and promotion is required to demonstrate viability of non-combustion technologies. Such support can be provided by governmental and international organizations.

Thus, the current review focuses on non-combustion technologies, which can be called alternative technologies for stockpiled waste treatment. This is a limited number of technologies, including both technologies in development phase and some more developed

6 Regarding waste incineration and other combustion technologies with potential of formation of UP POPs, The Stockholm convention requires that the parties promote and require the use of the Best Available Techniques (BAT) for new and existing sources of UP POPs formation. In addition, the parties should promote the use of Best Environmental Practices (BEP) for identified source categories [UNEP, 2004d]. Regarding the general guidance on BAT and BEP we read “When considering proposals to construct new facilities or sign modify existing facilities using processes that release ... [dioxins/furans] ... priority consideration should be given to alternative processes, techniques or practices that have similar usefulness but which avoid the formation and release of such chemicals” (Annex C, Part V, B. (b)).

7 See webpage: www.chem.unep.ch/pops/newlayout/repdocs.html
technologies. On one hand, such an attempt of evaluation and comparison of emerging technologies provides a useful background for their wider acceptance by promoting the related transfer of knowledge and outlining particular expectations, advantages and drawbacks. On the other hand, this evaluation invites the reader to gain insight into the diversity of existing chemical and technological ways of solving the problem, beyond their commercial and technical advancement status and original application scope.

First of all, the alternative technologies include technologies based on the so-called reductive processes. These are usually low temperature processes that involve the reduction of organochlorine compound with hydrogen, hydrogen transfer agents, or other reductants. The advantage of such processes is that dioxins and furans are not formed in the reductive atmosphere.

This review also considers alternative non-thermal oxidation technologies (without oxygen) and oxidation technologies with oxygen in the dense phase (non-flame). These processes include mediated electrochemical oxidation processes (MEO), and oxidation with oxygen in water or in melts.

The definition of non-thermal technologies proposed by US DOE\(^8\) is as follows:

"Non-thermal treatment means the destruction of hazardous organic waste in a device which uses chemical or electrochemical oxidants other than oxygen or air as the primary means to change the chemical, physical, or biological character or composition of the hazardous waste. Moderate increases in temperature may be used to accelerate the rates of the organic destruction reactions but gas phase oxidation or pyrolytic degradation with or without combustion flames or plasma arcs is not included in these systems."

In addition to the true non-combustion technologies above, this review also includes the so-called plasma arc technologies (PAT). Even though these technologies are usually assimilated to incinerators,\(^9\) they can be considered as alternative as they involve significantly different chemical and physical conditions which allow to substantially reduce the levels of toxic combustion products in emissions. PAT range from pyrolysis to combustion. For example the PWC technology uses oxygen deficient atmosphere to convert waste into syngas (pyrolysis) which can then be burnt or otherwise utilized. The PLASCON technology also involves pyrolysis in a plasma arc at the first step to break up organics, and the produced pyrolysis products are then burnt at the second step. The PACT technology involves plasma arc treatment of waste together with a reduced amount of oxygen which makes the process similar to combustion; however the amount of off-gas is reduced and the heat produced from plasma arc allows a more extensive breaking and ionization of organic molecules than in an open combustion system.

It can be argued if the demand of the Stockholm Convention regarding POP destruction, as to transform POPs into chemicals which are no longer POPs, is formulated properly and explicitly. For example, the removal of one chlorine atom from the POP molecule, e.g. from the most toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin, would give 2,3,7-trichlorodibenzo-p-dioxin, which is no longer “official” POP; however, the latter has more or less the same toxicity as strychnine. Toxic secondary products can also arise in the processes where a profound decomposition of organic molecules takes place. For example, the light chlorinated C1-C3 hydrocarbons are also considered toxic. Therefore, the safe destruction of POPs

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\(^8\) Schwinkendorf, 1997.

should be carried out preferably via complete dechlorination (mineralization) of organic chlorine. From this viewpoint, the technologies based on reduction represent an eco-friendly option.

The 15 technologies selected for evaluation in this review are listed in chapter 2. Some of the technologies are represented by two or more of different processes (e.g. Ball Milling, SCWO, and SR processes) which are offered by different vendors, but save some minor differences they can be considered within the same technology types. We again stress that this choice was done with the aim to perform a more general comparison of approaches of diverse chemical natures rather than to deal with a more specific and narrow evaluation of a limited class of technologies. Thus, more different chemical processes were included, even though some of the technologies are not fully commercialized or are still in the development phase.

One of the goals of the current review and evaluation was to lay a basis for creation of a decision-support tool for technology evaluation and selection. This set of technologies can be viewed as an attempt to validate the conceptual DST model in this field. It is envisaged that this model can be updated by including more options in the future, e.g. also by considering combustion processes, or by separating general technology classes in specific ones, or by extending the definition of application.

**Justification**

The Stockholm Convention, along with the measures for UP POPs, foresees elimination of existing stocks of IP POPs (mainly PCBs and organochlorine pesticides). The countries that signed the Convention are required to develop their national implementation plans (NIP) which include the general phases of inventory and destruction of POP stockpiles. Between these phases, a strategy should be selected, rationalized and appropriate technologies for particular sites selected.

The right choice of technology to address a particular stockpile is a very important and responsible task, as it requires a good knowledge of the state of the art and market of available technologies. UNEP, UNIDO and other organizations offer services to countries to develop their NIP and make independent decisions regarding the choice of treatment strategy and technologies, which requires consideration of numerous parameters, from economic aspects to environmental impact and public opinion.

It is very important that up-to-date knowledge on existing technologies be available and that capacity related to sustainable POP treatment be built worldwide, especially in developing countries. The problem of POPs in developing countries arises from the lack of knowledge of sustainable POPs treatment options. Incorrect handling and disposal of these chemicals could lead to serious local and interregional environmental problems.

It is recognized that the combustion approach has a series of drawbacks and difficulties, first of all connected to the formation of toxic secondary combustion products or the measures to avoid this. This is of special concern to the developing world where uncontrolled POP combustion is practised. It is therefore very important to promote development and spin-off of alternative non-combustion technologies as they can represent an alternative environmentally safe way to treat POP waste.
Decision making and decision-support systems

The choice of technology for a particular application is a complex task because a great variety of contamination problems are being defined and innovative technologies are becoming available. Alternative non-combustion technologies for POP treatment are basically innovative technologies, which usually lack a long history of full-scale applications and/or do not have the extensive documentation necessary to take them into consideration when a decision is to be made. However, some innovative technologies have been successfully used for remediation and destruction of POP stockpiles in New Zealand, Australia, United States, Mexico, Europe, Japan, etc.

Decision-support tools are designed to help decision makers (DMs) (site owners, local community representatives, environmentalists, regulators, etc.) assess technologies and preliminarily select preferred options. The demand for DST in selecting the most appropriate technology for specific contaminated sites and stockpiles has consequently increased and several tools have been developed recently.10

To use a decision-support tool it is not necessary that the DM be acquainted with all the specific technical aspects of the considered technologies. In its database the DST already comprises the most important relevant information for the DM. It also provides a tool to manipulate this information thereby allowing the DM to compare certain aspects of the technologies, or to perform a complex comparison taking into consideration more than one aspect or to use this tool for educational purposes.

The DST can address situations when the DM has to balance information on technology performance with limited budgetary resources and regulatory constraints. In addition, information on the concerns of stakeholders, as well as their meaningful involvement in the larger decision process, influences the ultimate technology selection and deployment decision. Therefore, all involved parties (environmentalists, policy makers, local community representatives, site owners and other stakeholders) need tools to help them to assemble and synthesize information to respond to these challenges and at times conflicting issues.

The plan is to develop a decision-support tool based on the this review and evaluation of technologies. The DST could be useful to attain the following general goals11:

- Enable users to identify and systematically compare information on technologies to meet specific goals, highlighting their strengths and weaknesses;
- Establish a structure of technology evaluation and selection process, which simplifies decision-making and organizes the variety of factors involved in the process of technology selection;
- Define consistent, qualitative and quantitative indicators for key technical, environmental, economic, legal and social criteria that influence selection and deployment of technologies;
- Provide documented, reproducible evaluation which can be updated as the required information becomes available;
- Provide flexible, multicriteria optimization approach allowing trade-offs among criteria on the basis of waste type and site-specific needs;
- Enhance communications and help focus dialogue between the local community,

10 E.g. Remediation technologies screening matrix and reference guide by FRTR, Remediation and Characterization Innovative Technologies (REACHIT) by EPA, TechTree by CPEO, DARTs by ICS-UNIDO, etc.
environmental managers and stakeholders, including regulators and policy makers;
• Enable explanation and justification of the choice by offering evidence of the advantages and disadvantage of the possible choices in a concise and consistent way;
• Speed-up development of feasibility studies for emerging technologies;
• Provide site owners, environmental managers and other stakeholders with the opportunity to explore alternative options, etc.

It is believed that a relevant DST could be very helpful in accomplishing the goals of the Stockholm Convention and other POP treaties. This review of technologies not only provides useful information on technologies, organized according to the essential technical and chemical aspects, but also proposes a system for evaluation of these technologies. This system, including a database of technology evaluation results and a selection algorithm, represents the concept of the first DST for selection and evaluation of alternative/non-combustion technologies for destruction of POP stockpiles. This review could be used as a guide to alternative POP destruction technology selection, or for educational purposes.

Objectives

1. Provide the most up-to-date information on the status and availability of non-incineration technologies suitable to address the destruction of POP stockpiles.

2. Independently review existing facts and provide a comprehensive description of 15 selected technologies, outlining their basic data on history, chemistry and technological arrangement, etc. To resume drawbacks and advantages of the selected technologies.

3. Develop a system for evaluation of technologies for POP destruction, including evaluation criteria and scoring policies

4. Perform the evaluation of technologies according to the system developed and based on available data and independent considerations

5. Formulate the concept and structure of a DST for technology evaluation and selection to be developed, which will use the database of technology evaluation results

6. Foster the transfer of knowledge and capacity building in developing countries in the field of POP destruction in order to better implement the requirements of the Stockholm Convention.
2. **Technology sheets**

Technologies included in the review:

1. Ball Milling
   a) MCD™ (Mechanochemical Dehalogenation)
   b) DMCR (Dehalogenation by Mechanochemical Reaction)
2. BCD (Base Catalyzed Decomposition)
3. CerOx™ (Mediated electrochemical oxidation by Ce IV)
4. GeoMelt™ (Destruction in the soil melt)
5. GPCR™ (Gas-Phase Chemical Reduction)
6. HydroDec™ (Hydrodechlorination)
7. MSO (Molten Salt Oxidation)
8. PACT (Plasma Arc Centrifugal Treatment)
9. PLASCON™ (Plasma Conversion)
10. PWC™ (Plasma waste converter)
11. SCWO (Supercritical Water Oxidation)
12. SET™ (Solvated Electron Technology)
13. Silver II™ (Mediated electrochemical oxidation by Ag II)
14. SPHTD (Self-Propagating High-Temperature Dehalogenation)
15. SR (Sodium reduction)

In this chapter a brief review of the above technologies is presented. In this part the accent is placed on the basic introduction to the nature of related chemical processes and their technological arrangement, including post- and pre-treatment, referring also to the history of technology development and its developers and vendors. Some illustrative information such as technology charts and photos of existing plants are included. Basic advantages and drawbacks are outlined for each technology.

This chapter includes mainly qualitative information in order to help the reader to understand principles of operation of each technology before going into quantitative details, which are then described in Chapter 3, Technology evaluation.

**A sample technology sheet**

Each technology sheet is composed of the following sections:

- Commercial and development history
- Technology description and chemistry of related processes (including pre- and post-treatments and other options)
- Process schemes and pictures
- Advantages
- Limitations, disadvantages, and concerns
- Principal information sources
Sheet 1. Ball Milling

Commercial and development history

This type of technology is represented by two similar processes, that is the MCD process by Environmental Decontamination Ltd (EDL), New Zealand and the DMCR process by Tribochem, Germany. These two technologies have been developed independently and have different development statuses: MCD is a patented process,12 which is currently being demonstrated on the full scale in a national remediation project. DMCR has been operating on the pilot scale only, and even though the technology seems to have a developed design for commercial operation, no full scale experience has been acquired as yet. The chemical nature of the related processes and technical arrangement of both technologies are the same or very similar which made it easy to consider them under the same technology name within this review.

Over the last ten years, scientists around the world have conducted laboratory and pilot plant experiments using the fundamental principles of ball milling to achieve destruction of toxic chemicals,13 which created a favourable base for the engineering implementation of this knowledge.

EDL was established in 1998 to specifically develop non-incineration technology for the remediation of persistent organic pesticides in soils. The shareholders and directors of EDL carried out their research through the use of in-house chemical engineers and chemists, and with a technology exchange agreement with the Auckland University of Technology. For its process EDL uses a patented purpose built reactor, in lieu of a proprietary fine grinding mill. The history of the EDL’s processes is relatively short: following the agreement in 2001 on the remediation of the Mapua (New Zealand) site and various improvements, the full scale operation was scheduled for late 2004.

The DMCR technology has been applied successfully to the detoxification of contaminated soils and contaminated oils in cooperation with several European companies in pilot projects (feasibility scope) over the last 5 years. Tribochem’s process is also very recent and focuses on the concept of PCB destruction and only consists of the reactor module, while the EDL process is designed for contaminated soil treatment and includes different treatment steps of pollutant extraction, drying, etc. Developers of DMCR have a very rich research history and a number of pilot projects completed, however the process is not based on patented technological concepts and currently represents a technology in the early development phase.

Technology description and chemistry of related processes

The Ball milling process employs the mechanochemical energy for the initiation of a reduction reaction between a chlorinated substrate (PCBs, pesticides) and a reagent. The reagent (CaO, Mg, sodium, or other metals or their oxides) can play a role of the reductant and a base. Therefore, the products of Wurtz coupling, hydrodechlorination, if a hydrogen donor (e.g. alcohol, polyethers, amines) is present, dehydrochlorination, and hydrolysis can arise. As a result, the metal always binds the organic chlorine giving

12 NZ Patent 504341/510521/510752/510824; NZ Patent 510522/511602/511603/511604; NZ Pat Apps 520676 and 520677; Aus Pat Apps 60817/01 and 60816/01; PCT/NZ01/00068 and PCT/NZ01/00069
rise to a mixture of products of coupling, saturated or unsaturated hydrocarbons, etc. depending on conditions. The true process chemistry is very complex as it is based on radical transformations involving metal-organic radical species, e.g. the process using Mg is likely to involve Grignard-like catalytic reactions. The following simplistic processes can roughly illustrate the nature of occurring reactions between the chlorinated substrate and reagent ([H] is the hydrogen donor):

\[
RCl + Mg + RCl \rightarrow R-R + MgCl_2
\]

\[
RCl + Na + [H] \rightarrow R-H + NaCl
\]

\[
2C_xH_yCl + CaO \rightarrow CaCl_2 + H_2O + C_{2x}H_{2y-2}
\]

The reaction between a solid reagent and a solid or liquid substrate in the ball mill (a closed vessel where the reagent(s) are placed together with the rigid balls), takes place under mechanical agitation produced by rigorous shaking. The reagents may not react, or such reaction could be very slow, under normal conditions, especially if both reagents are solids. The mechanochemical assistance relies on the generation of the so-called tribo-plasma, lasting a fraction of a millisecond in the moment of collision between the balls, which is localized in the point of collision and where the active radical species appear, giving rise to the reaction. Moreover, the grinding of solid reagents in the ball mill assists the reaction by augmenting the contact surface between reagents.

The process streams include dechlorinated hydrocarbons, chloride salt, and residual metal, or its hydroxides. In full scale applications air emissions would also probably arise, which are expected to be substantially higher for soil treatment as the latter should be dried. Seemingly for soil separation the latter is treated with water to solubilise remaining metals/oxides and to dissolve hydroxides and salts, and heated to volatize the organic reaction products (if such are many, otherwise they can remain in soil). In these case basic water stream arise. Separated organic residuals should then be disposed of. The soil can be returned to the site or be disposed of in landfills.

**Pre-treatment**

Solid powdered contaminants or organic liquids can be treated without pre-treatment. Humid waste requires dewatering. Contaminated solids, such as soils, sludge, debris, etc. are normally dried and then treated directly. Crushing may be required for big pieces of solids.

**Post-treatment**

Gaseous effluents are normally scrubbed. The decontaminated soil can disposed on site. There is no mention of any post-treatment system and way of products disposal after the treatment of bulk organics.
Process schemes and pictures

Sketch and photo of the DMCR vibratory mill (mobile design)

Flow diagram for treating contaminated soils by the DMCR process

Sketch of the DMCR process containing three ball mills

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14 All figures are reproduced from Tribochem and EDL websites.
Outline of an off site Tribochem’s vibratory mill plant capable of treating solid materials principally (throughput approximately up to 1 ton per hour) and a photo of a pilot vibratory mill plant

Full scale MCD plant, EDL, New Zealand

General scheme of EDL MCD process
Advantages

- Very low risk of forming new contaminants, such as dioxins because of low temperature and reductive environment.
- Low risk of the release of contaminants because of good containment. The process can also be readily shutdown in a short period of time.
- Increased safety because of ambient conditions and absence of vigorous reactions that can go out of control.
- Little gaseous emissions are produced.

Limitations, disadvantages and concerns

- Noise and vibration.
- Relatively long reaction times.
- High electricity requirements.
- Limited to dry, solid, and non-concentrated POP waste.

Principal information sources

1. Birke, 2001
2. CMPS&F Environmental, 1997
3. UNEP, 2004a
4. UNIDO, 2001
5. US-EPA, 2005
7. Vijgen, 2002
Sheet 2. BCD

Commercial and development history

The BCD technology\textsuperscript{15} and formerly named “Base Catalyzed Dechlorination”, was developed on the basis of earlier APEG dechlorination methodologies (KPEG, NaPEG, APEG-PLUS)\textsuperscript{16} by EPA’s Risk Reduction Engineering Laboratory from 1988 to 1993, in cooperation with the National Facilities Engineering Services Center (NFESC) of US Navy to remediate liquids, soils, sludge and sediments contaminated with chlorinated organic compounds, especially PCBs, dioxins, and furans. The BCD process has received approval by EPA’s Office of Toxic Substances under the TSCA for PCB treatment.

The EPA patents\textsuperscript{17} on the first BCD processes then passed to the developers, and all worldwide rights for all patents are now owned by BCD Group, USA who began licensing these processes to private environmental companies in 1993. The BCD process has been licensed in USA, Australia, New Zealand, Mexico, Japan, Spain, and Czech Republic.

In 2006, BCD group Australia was acquired by DoloMatrix International Limited. As a result, DoloMatrix also gained access to a licensed treatment facility located in Queensland, Australia, which comprised BCD, thermal desorption, and plasma arc treatment (PLASCON) processes.

Technology description and chemistry of related processes

The applications of BCD technology range from treatment of PCB liquids to organochlorine pesticides. Depending on the type of the feed the treatment can be direct or by 2 separate steps, where the first step is the indirect thermal desorption (in case of solids and contaminated matrices), which is a continuous flow process, and the second step is the intrinsic BCD reaction of POPs (condensates from the first step or liquid POPs which can be fed directly), which is a batch process.

In the typical direct BCD application for treating pure or high level liquid PCB, the PCB material is pumped into the reactor heated to 350°C, called also Stirred Tank Reactor (STR), containing high boiling point hydrocarbon oil, a base (alkali or alkaline earth metal carbonate, bicarbonate, or hydroxide; sodium hydroxide is more often used), and a proprietary BCD catalyst. The hydrocarbon oil acts as solvent and hydrogen donor at the same time. Other donors of hydrogen, such as aliphatic alcohols, amines, or other compounds can also be used, in addition to the oil, as well as other reactants (no mention which kind, probably proprietary).

Bulk organic solids can be fed as slurries in water as well as organic liquids can also be fed as water emulsions. Wastes containing up to 90-95% inorganics, e.g. POP waste mixed with soil, can also be fed directly in the reactor. During the BCD treatment halogen is removed from the target compound producing NaCl, and the rest of organic

\textsuperscript{15} Whereas BCD name originally refers to the core chemical destruction process based on dechlorination or other reductive decomposition of organic molecules, the frequently occurring BCDP specification refers to the general treatment scheme, which can exclude the chemical BCD module, e.g. in the case of thermal desorption of contaminated soils.

\textsuperscript{16} US patent 5,019,175.

\textsuperscript{17} US patent 5,064,526.
molecule is converted into a carbon-like material ranging from carbon black to asphalt. The other products of reaction include water and small quantities of cracked hydrocarbons. The reaction times are normally short (several hours) and must be longer for higher chlorine content in the feed. As the reaction is exothermic the high chlorine content POPs (over 50%) should be fed over periods of time.

The BCD chemistry involves the generation of highly active atomic hydrogen, which is formed by the dehydrogenation of the oil, which is promoted in the presence of the base and a catalyst. The proprietary catalyst probably involves a source of carbon, like sucrose or another carbohydrate which can produce carbon upon heating. In situ formed carbon particles provide active sites for dehydrogenation of hydrogen donors. The presence of other or additional catalytic species is possible, such as some PAH (phenanthrene, anthracene, or alkyl naphthalenes), hexagonal forms of carbon (graphite or carbon black as present in scrap latex) or transition metals (zero-valent iron and stainless steel). These catalysts are able to accumulate active hydrogen after it is formed, e.g. via hydrogenation of aromatic catalysts or via its adsorption on carbon or metals. The adsorbed hydrogen atoms then react promptly with the organochlorine waste giving rise to reduced saturated hydrocarbons and hydrochloric acid, the latter then is converted to the chloride salt in the presence of base. The developers suggest BCD reactions to be either free radical and/or ionic decomposition with further evidence of catalytic transfer hydrogenation occurring.

\[
\text{RCl} + \text{NaOH} + [\text{H}] \rightarrow \text{RH} + \text{NaCl} + \text{H}_2\text{O} \\
(\text{catalyst, } T = 350^\circ\text{C}, \text{nitrogen blanketing})
\]

[H] is the source of hydrogen

Inert solids containing low concentration of POPs or the types of waste not suitable for loading in the STR directly (contaminated soils, sludges, debris, transformers, etc.), after the pre-treatment, if any applied, are fed into a heated Indirect Thermal Desorption (ITD) unit having either batch or continuous flow design and allowing treatment of a range of throughputs. The ITD unit represents a rotary reactor, called also Rotary Kiln Reactor (RKR), where the mixture is heated at 200-400 °C. In the ITD unit the halogenated compounds volatilize and undergo partial or complete decomposition (sodium bicarbonate promotes lower temperature desorption) and partial destruction of chlorinated organics, via reaction with sodium oxide (it forms from sodium bicarbonate decomposition at heating together with CO\(_2\), the latter also contributes to the inert atmosphere). Steam is used to maintain an inert atmosphere above the hot soil in order to avoid open combustion and prevent oxidative processes leading to the formation of dioxins/furans. Taking into account the presence of steam it seems that the formation of sodium oxide would be suppressed and that decomposition would rather take place because of the base-hydrolysis reaction. The percent of decomposition depends on the material type and the concentration level. The residual PCB, if any, is collected in the ITD resulting condensate. If PCB decomposition is not complete, then the resulting condensate is treated in the main liquid phase BCD reactor with oil, as described above.

**Pre-treatment**

For contaminated soil, or sediment treatment, before feeding in the ITD, the contaminated material is screened to remove debris and large particles and premixed with sodium bicarbonate (one part sodium bicarbonate to ten parts soil). Unlike the direct treatment case described above, which can address POPs treatment in aqueous media,
water would need to be evaporated from moist inert matrices containing POPs (sludges, soils, etc.) before treatment of such. Volatile solvents would also need to be removed by evaporation, whether when treating inert matrices or bulk organic POPs (direct treatment).

Post-treatment

BCD plants are equipped with charcoal filters which capture organic emissions. The resultant salt/water can be carbon filtered and recycled or disposed. The oil and catalyst can also be recovered for reuse or be disposed of, e.g. in a cement kiln. A new option allows recovery of up to 95% of oil by refining it. Heavy oils cannot be recycled and are disposed of in the incinerator.

Options

ADI Services, a BCD licensee in Australia, has developed a variation of the BCD reaction (called the ‘ADOX’ reaction) in which an ‘accelerator’ replaces the patented BCD catalyst. In the ADOX reaction the nature of the reaction changes dramatically in that organochlorines are decomposed completely to carbon. The reaction, which takes place rapidly, can be applied to much higher concentrations of organochlorines than the conventional BCD process and without the requirement for the addition of oil.

The BCDP technology refers to the soil treatment as the only step. As reported by US Navy Naval Facilities Engineering Command on Guam site,19 during the demonstration of BCDP the dechlorination step in the STR was not used. During the desorption step, the PCB contaminated soil was heated with sodium bicarbonate and steam, which caused partial decomposition of PCBs, thereafter the effluent gases underwent several purification steps and the condensates containing PCB were disposed in landfill.

The technology name was changed from Base Catalyzed Dechlorination to Base Catalyzed Decomposition. In fact, the process can also treat other than chlorinated pollutants. Moreover the new name was more relevant to the chemical nature of the whole process, because in the case of soil treatment most organic contaminants, like PCB, could be efficiently destroyed already during the thermal desorption step with base in the rotary kiln reactor. The new process formulation also suggests that the soil thermal desorption step can be considered as principal or the only step (unless the pollutant content is high). This option is not considered for evaluation being not relevant to the scope of the present review, which is the applicability of the process to the POP waste with high organic content.

19 Terres, 1997.
Process schemes and pictures

BCD process diagram of PCB oil treatment\textsuperscript{20}

Simplified flow diagram of the Homebush Bay NSW BCD plant\textsuperscript{21}

\textsuperscript{20} Reproduced from the BCD presentation at the South American regional workshop on the environmentally sound destruction of POPs and the decontamination of POP containing waste in the framework of Basel and Stockholm conventions.

\textsuperscript{21} Reproduced from [Vijgen, 2002].
NON-COMBUSTION TECHNOLOGIES FOR POPS DESTRUCTION

General BCD process scheme of soil treatment

BCD plant in Spolana, Czech Republic

22 Reproduced from Remediation Technologies by NFESC.
23 Reproduced from the BCD presentation at the South American regional workshop on the environmentally sound destruction of POPs and the decontamination of POP containing waste in the framework of Basel and Stockholm conventions.
Advantages

- The technology is robust, contained, and environmentally safe as it does not involve oxidation processes leading to the formation of dioxins/furans.
- Mobile concepts and different capacities are available to satisfy different scale and on-site projects, so hazardous wastes do not need to be transported.
- The technology can address a wide class of waste types, including PCBs, chlorinated dioxins, pesticides in soil, organic solutions, aqueous waste, etc.
- The technology has a long history of operation in different countries

Limitations, disadvantages, and concerns

- Factors limiting throughput can be high contents of water, clay, other organics, and increased acidity. Therefore, costs are higher for organic solutions and aqueous waste treatment. Also not cost effective for very high volumes of contaminated soils.
- Salt, carbonaceous residuals, solid organics and used oils and carbon filters should be disposed of. Such residuals can potentially contain chlorinated hydrocarbons and PAH.
- The process is complex and labour intensive, qualified and trained personnel are required.
- High temperatures and flammable liquids present a potential danger of ignition; however, it this risk was reduced in the modern plant designs.

Principal information sources

1. CMPS&F Environmental, 1997
2. Danish EPA, 2004
3. Costner, 1998
4. Rahuman, 2000
5. Remediation technologies by NFESC, and references therein
6. Remediation technologies screening matrix and reference guide, version 4.0 by FRTR
7. SITE technology profiles
8. South American regional workshop on the environmentally sound destruction of POPs and decontamination of POP containing waste in the framework of Basel and Stockholm conventions
9. TechTree, Decision-making tool by CPEO
11. UNEP, 2004a
12. UNEP, 2004b
13. UNIDO, 2001
14. US-EPA, 2005
15. Terres, 1997
16. Vendor website: www.bcdinternational.com
17. Vijgen, 2002
Sheet 3. CerOx

Commercial and development history

The CerOx technology is an electrochemical process able to destroy hazardous organic waste, derived from industrial processes and laboratory wastes, such as biogenic wastes, toxic chemicals, pesticides, herbicides, PCBs, dilute organics in water, etc. by converting them into CO₂ and water.

The technology was commercialized by CerOx Corporation, founded in 1992, who designed the specialized equipment for operating the process. The fundamentals of the process chemistry, based on cerium electrochemistry, were developed at the Pacific Northwest National Laboratory (PNNL) over the past 2 decades. At present, CerOx Corporation has a worldwide, exclusive license for this proprietary technology including the cerium process chemistry and specialized equipment (T-CELL™) for its practice.

CerOx Corporation designs and manufactures its systems in a facility located in CA, USA. These systems are then transported as modules to be installed on-site. The available data reports that at least two commercial systems have been sold or installed up to now, namely at the University of California Irvine and in Merck, New Jersey. However, the technology can be considered sufficiently developed and technically concluded to meet full scale applications. The commercial plants of different scales are right available.

Technology description and chemistry of related processes

The CerOx (Cerium Oxidation) process is a variation of the Mediated Electrochemical Oxidation (MEO) technology, also termed Catalyzed Electrochemical Oxidation (CEO), which also includes the Silver II process. It is based on the oxidation of organic compounds with the use of cerium +4 ions, which is defined as catalyst or mediator.

According to the principle of MEO, an electrochemical mediator is being brought to its higher oxidation state via electrochemical reaction, and is then being put in contact with an organic compound to be oxidized; the mediator, now in a lower oxidation state, is brought back to the electrochemical cell. Cerium ions, formed as a result of dissolution of metallic cerium in a strong acid, maintain a stable Ce³⁺ form. When oxidized to Ce⁴⁺, cerium appears deep amber in colour and becomes a very strong oxidizing agent. Ce⁴⁺ then vigorously reacts with any kind of organic substance oxidizing it to CO₂ and water and being itself reduced to Ce³⁺. After the cerium is reduced to Ce³⁺ by taking an electron from an organic compound, the cerium is brought to the electrochemical cell and reoxidized to Ce⁴⁺ which is then again introduced in the reaction with an organic compound thereby closing the cycle. This cycle only seems to be catalytic, as cerium participates and is not consumed in the reaction, every time being recovered for a new transformation. However, this process should not be confused with true catalysis since the recovery of the mediator takes place artificially and separately.

An example of destruction process in the reactor is given in the equation below:

\[
\text{C}_6\text{H}_5\text{Cl} + 29 \text{Ce(IV)} + 12\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 29 \text{H}^+ 1/2 \text{Cl}_2 + 29 \text{Ce(III)}
\]


The processes that take place in the T-CELL are the following:

\[
\text{Ce(III)} \rightarrow \text{Ce(IV)} + e^- \quad E^o \approx 1.6V \\
\text{HNO}_3 + 2\text{H}^+ \rightarrow \text{HNO}_2 + \text{H}_2\text{O}
\]

Nitrous acid formed as result of the cathode reaction then disproportionates giving nitric acid and nitric oxide, NO. The latter is oxidized with atmospheric oxygen to NO\(_2\) which is then dissolved in water giving nitric acid. Therefore, the bigger part of nitrogen is recovered into the original HNO\(_3\).

Electrochemical oxidation of cerium takes place in the T-CELL which never comes in contact with the original waste streams. The T-CELL plus the external modules for electrolyte circulation and storage, hazardous waste injection, mixing and holding, off-gas handling and processing, electrolyte (aqueous solution of cerium salts) regeneration, and electronic monitoring and reporting are balanced into a single system called the CerOx System, which represents an automated plant built into a small steel cabinet.

The majority of waste is treated in the liquid phase reactor. These include water soluble compounds, emulsified or suspended organic substances or inert particles (soil), given that the waste components boil at higher point than 100° C. Concentration of Ce\(^{4+}\) of 70% in the anolyte is maintained by constantly circulating through the T-CELL to the anolyte inventory tank. Wastes and anolyte are pumped together and pass then through a sonicator, where the mixture is emulsified to increase the contact area of water immiscible solids or liquids with the aqueous phase containing Ce\(^{4+}\). The homogenized mixture then flows into the liquid phase reactor where the reaction of organic waste with cerium takes place.

Measuring the concentration of Ce\(^{4+}\) on the exit from the reactor, the reaction rate is determined thereby the system automatically adjusts the organic cerium ratio to reach optimal efficiencies.

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26 Reproduced from the vendor website.
As a result all organics are oxidized to CO₂, gaseous products, and water. Gaseous products can be vented into the gas phase reactor for further oxidation, and the accumulated water is pulled into the catholyte through the membrane, for removal. Inorganics are tolerated by the chemistry and are removed by replacing the electrolyte and regenerating the old electrolyte in small systems (done by CerOx). In larger systems, the removal process is done continuously, via a bleed stream to inorganic removal modules.

The gas phase reactor uses a countercurrent flow of Ce⁴⁺ over packing to effect a liquid to gas interface, allowing the Ce⁴⁺ to oxidize organics. This reactor will process small amounts of VOCs and can be sized to handle large quantities of compounds that transform into gas phase at lower than 95° C. Following this reactor is a condenser, designed to condense potentially emitted VOCs and send them back into the reactor loop.

**Pre-treatment**

The technology can process only liquid or liquidized waste. Solids and sludges should be homogenized and pumped as slurries in water. No special pre-treatment equipment is provided other than sonicator mentioned above, the latter needed to further break up the particles of solids in the sludge or emulsify the organic liquids.

**Post-treatment**

The gas phase system involves two separate scrubbers. The first scrubber is designed to “capture” volatile organics - passing the CO₂ and chlorine to the second scrubber, designed to remove chlorine. The system’s two effluents come from the chlorine scrubber, CO₂ is passed into the atmosphere; water containing NaOCl (bleach) and NaCl (salt) are sent to the sewer (CerOx systems). Chlorine arises from reaction of any chlorine contained organics, i.e. from all POPs. The scrubber removes the chlorine by dissolution in water and subsequent neutralization with sodium hydroxide. The scrubber also is used to neutralize the small amount of nitric acid in the reject water from the evaporator used on smaller on-site units before this stream is sent to the POTW (publicly owned treatment works).

**Process schemes and pictures**

All figures are reproduced from the vendor website.
Advantages

- Low potential of dioxin formation
- Mild operation conditions: temperature below 100°C and atmospheric pressure
- CerOx can treat a variety of wastes, including low-level radioactive, pharmaceutical, biotech, and power industry wastes
- The technology does not pose thermal runaway danger and is easy to shut down
- Compact, mobile and easy to install units
Limitations, disadvantages, and concerns

- Some uncertainty about efficiency of POP treatment remains, as there is no commercial scale experience with POPs wastes
- The issue was raised on the obstruction of the electrolytic cell membrane by the remaining solid particles present in electrolyte, e.g. after treatment of organics containing inorganic matter
- The technology can be not suitable for waste with high POP content, which is poorly soluble in water,
- High electricity requirement can be not justified for treatment of bulk organics with low content of POPs

Principal information sources

1. Norvell, 2001
2. UNEP, 2004a
3. UNIDO, 2001
4. US-EPA, 2005
5. Vendor website: www.cerox.com
6. Vijgen, 2002
Sheet 4. GeoMelt

Commercial and development history

The GeoMelt technology by AMEC belongs to the family of vitrification remediation technologies, which can treat a range of contaminants in soil, from radioactive to POPs. GeoMelt can be applied in a variety of in situ modes and above ground, ex situ modes. In the latter case, which is of interest for stockpiled POP treatment, it appears suitable for the destruction of matrices with high content of POPs, namely soil mixed with POPs such as land filled pesticides and bulk POPs (e.g. PCBs and liquids) if premixed with soil.

GeoMelt is a registered trademark and the technologies are the patented property Geosafe Corporation, a subsidiary of the Battelle Memorial Institute of Columbus Ohio. AMEC has an exclusive license to develop, market, and implement the technologies globally. AMEC is implementing the GeoMelt technology from three business centres located in the United Kingdom, North America and Australia to provide worldwide coverage. AMEC also has a licensee in Japan.

The GeoMelt technology has been in commercial use since the early nineties. GeoMelt has been used to process more than 25,000 tons of soil and waste, mostly radioactive waste. GeoMelt has been evaluated by the US EPA under the SITE Program and has been granted a National TSCA Operating Permit by EPA for the nationwide treatment of PCBs at concentrations approaching 18,000 ppm, which is the only vitrification technology so permitted in the U.S.

A series of GeoMelt In-Container Vitrification (ICV™) demonstrations were performed in Australia on soils contaminated with 33 wt% hexachlorobenzene (HCB) wastes. The successful results obtained from these tests have led to the design and construction of a facility to process the 16,000 208-L drums of HCB wastes present at a chemical processing plant there. This facility was scheduled for operation in 2004.

Technology description and chemistry of related processes

The GeoMelt technologies use electric current to convert contaminated soil and wastes into a stable glass and crystalline product. Graphite electrodes are inserted into the contaminated material and a flow of electric current is applied. As the molten zone grows it incorporates hazardous inorganic elements while the high processing temperatures destroy organic components thermally. When electrical power is shut off, the molten mass cools and ultimately solidifies into a vitreous and crystalline, rock-like monolith. Organic contaminants are destroyed and undestroyed contaminants, e.g. residual organic and inorganic, are immobilized within the resulting vitreous product.

The chemistry of the process is that of pyrolysis, i.e. the organic content is thermally decomposed in the presence of limited amount of oxygen. A number of reactions can take place, giving, as result, a wide range of products, namely mono- and dioxide of carbon, elementary carbon, methane, water, hydrogen, etc. All types of organics are equally destroyed at such high temperatures, including polychlorinated POPs. In this case, chlorine would mostly transform into hydrochloric acid.

The GeoMelt technology can be employed in a number of application configurations that may best suit varying site conditions. There are four basic application configurations, including: 1) in situ, 2) deep GeoMelt planar-ISV (in situ vitrification), 3) staged in situ, and 4) ICV or ex-situ vitrification. Herein we consider only the ICV configuration of GeoMelt.

The ICV system involves batch treatment of contaminated wastes in a refractory-lined, steel container. Commercially available containers can be used including drums, standard waste boxes and roll-off boxes. Contaminated soil and wastes are placed in the lined container, an off-gas collection hood fitted to the container and the waste treated. After treatment, the hood is removed and a lid installed. When the melt has solidified, the container of vitrified waste is transported to the disposal site. Capital and operating expenses are small because the ICV container and its simple lining system serve as the melter vessel, the shipping container and the disposal container. The ICV container can be reused or disposed of after use.

Typical waste streams generated by the GeoMelt process include scrub solution, particulate and carbon filter media, and personal protective equipment. Solid secondary waste materials are typically staged in subsequent melts.

Liquid wastes can be treated with the ICV process by first absorbing them on soil or other suitable materials. Solid wastes or bulky contaminated items can be treated by placing them in the ICV container and surrounding them with soil. The soil added around the wastes could be contaminated soil.

**Pre-treatment**

As already mentioned, bulk organic waste would need to be mixed with soil before treatment. Humid waste should be dewatered and dried.

**Post-treatment**

The off-gases are collected under a stainless steel hood and are then sent to the Off-Gas Treatment System (OGTS). The OGTS consists of a combination of filtration, dry & wet scrubbing, and thermal treatment stages. Thermal oxidation is used as a final polishing step in the off-gas treatment. The small quantity of secondary wastes generated by the OGTS (e.g. filters, scrubber liquids, and personal protective equipment) can be loaded into subsequent GeoMelt applications for processing.

**Process schemes and pictures**

The system consists of an electrical power transformer, off-gas collection hood, off-gas treatment system, and process control system. All equipment is mobile (trailer mounted).

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29 Reproduced from the vendor website.
Advantages

- Mobility (all equipment easily transported on site)
- Low cost
- Simple in operation, no other reagents/materials are required than soil
- Vitrified product from ICV is easily transported by truck and the container itself can be re-used or disposed of after treatment
- Efficiency does not depend much on the waste type
- Able to simultaneously process mixtures of organic, inorganic and radioactive contaminants
- The process can accommodate large items of debris, which minimizes the need for size reduction and other handling steps

Limitations, disadvantages, and concerns

- Need to dispose of large volumes of the vitrified slag
- Only limited to soils, no bulk chemicals can be processed without mixing with soil
- Not applicable to humid soil, dewatering increases costs
- Does not seem safe and effective for destruction of volatile waste
- High electricity requirements
- Formation of dioxins/furans seems very probable. Very efficient off-gas treatment is needed.
- No sufficient data to prove feasibility and economic reasonability of the application to POPs, especially at high concentrations
- Relatively low destruction efficiency

Principal information sources

1. UNEP, 2000
2. UNEP, 2004a
3. US-EPA, 2005
4. Vendor website: www.geomelt.com and additional information from vendor
5. Vijgen, 2002
Sheet 5. GPCR

Commercial and development history

The GPCR technology, previously known as ELI Eco Logic process, is one of the vanguard commercial non-combustion technologies for POP destruction. The technology was developed and commercialized by ELI Eco Logic International Inc. in Canada. Since the eighties ELI Eco Logic has been conducting research starting from the laboratory and bench scale tests. The full scale plant operated for more than 5 years in Kwinana, Australia (now shut down). Other full and pilot scale plants and demonstration projects ran in Canada, USA, and Japan.

The GPCR technology is now provided by Hallett Environmental & Technology Group Inc. of Ontario, Canada.

Technology description and chemistry of related processes

The Eco Logic’s GPCR technology is based on the gas-phase thermochemical reduction of organic compounds by hydrogen at temperatures of 875°C and low (atmospheric) pressures. The process can treat all types of chlorinated waste in different forms, namely bulk organic solids and liquids, high-strength PCB oils and mixed solid materials, aqueous waste, contaminated soils and sediments.

The reaction between waste and hydrogen occurs only in the gaseous phase, therefore solid and liquid materials need to be pretreated (see pre-treatment). Pure organic liquid waste streams, as well as organic gases (if oxygen free) can be fed directly to the reactor through atomizing nozzles, where the recirculation product gas is used to atomize the liquid waste. The reducing power is enhanced by the presence of water, which acts as a heat transfer agent as well as a source of hydrogen. Therefore, the process requires electricity, hydrogen, water, and caustic for scrubbing.

The process provides in excess the 2 seconds residence time for gases in the reactor at 875°C needed for efficient destruction of organic wastes. Emissions include mainly hydrogen chloride, methane and other low molecular weight hydrocarbons. The gases exiting the reactor are going through the scrubber where hydrogen chloride is removed (see post-treatment). To assure the complete dechlorination an on-line mass spectrometer is provided which can divert all gases into the recirculation mode. Following the scrubbing step the resulting mixture of gases, which is rich of methane, propane and hydrogen can be recirculated entirely or partially, where the other part can be used as fuel in the boiler.

Residues from the GPCR process include used scrubber liquor and water (require disposal). Solid residues can also be generated from solid waste inputs and should be suitable for disposal in a landfill. Since the GPCR process takes place in a reducing atmosphere the possibility of PCDD and PCDF formation does not seem to be an issue.

The general chemistry of conversion of a hydrocarbon structure containing chlorine and possibly oxygen can be expressed in the following way:

\[ C_xH_yCl_\text{x}O_\text{z} + H_2 \rightarrow CH_4 + H_2O + HCl \text{ (thermal)} \]

Methane is converted into hydrogen via the steam reforming and gas-water shift reactions, which are expressed as follows:

\[ CH_4 + H_2O \rightarrow H_2 + CO \text{ (steam reforming, catalytic)} \]
\[ CO + H_2O \rightarrow CO_2 + H_2 \text{ (water-gas shift, catalytic)} \]

30 US Patents 4819571; US Patents 5050511.
The same processes occurring in the reactor to a certain degree via a non-catalytic (thermal) mechanism can also contribute to the hydrogen amount and to the reducing power.

**Pre-treatment**

Depending on the waste type, one of the following three pre-treatment units can be used to volatilize wastes prior to treatment in the GPCR reactor:

1. The liquid waste pre-heater system (LWPS) is used for homogeneous liquids with low suspended solids content (up to 0.5%), like PCB oil, oily waste, and watery waste. The vaporized liquids are then injected directly in the reactor.
2. The TORBED™ reactor, developed by Torftech Limited (UK), Torftech (Canada) Inc., is designed for contaminated soils and sediments, but can also be adapted for liquids and sludges.
3. Thermal reduction batch processor (TRBP) is used for bulk solids, including those in drums, such as electrical equipment, drummed waste, wood pallets, concrete, rubble, miscellaneous solids. The treatment involves the high temperature desorption of the organic waste content from solid in an oxygen free atmosphere (heated in presence of hydrogen to appx. 600°C). The volatized organic compounds are mixed with hydrogen and water and swept into the reactor. The TBRP has been recently adapted to process the liquid wastes, as well.

In addition, other pre-processing is required for large capacitors and building rubble. Large capacitors are punctured and drained, while rubble and concrete must be reduced in size to less than one square metre.

**Post-treatment**

Gases leaving the reactor are scrubbed to remove water, heat, and acid. A caustic scrubbing agent is used to maintain the scrubber water pH at between 7 and 9. Scrubber residue and particulate require disposal off-site.

In place of the boiler, the methane rich gas after scrubber can also be sent in the catalytic steam reforming and water shift units to produce hydrogen (and carbon dioxide) from methane and water, thereby generating more hydrogen for reuse in the system. This is particularly useful when a hydrogen source for plant operations is not immediately available. Only small amount of hydrogen would be required to start the process. However, it was reported that the hydrogen production unit has been plagued by reliability problems in the past.

Side-streams may also go to a Thermal Reduction Mill (TRM) and Sequencing Batch Vaporiser (SBV) as a sweep gas. Excess gas is directed to the compressor and product gas stage tank, where the gas is stored temporarily and analysed on a continuous basis. The compressed product gas may then be used to fuel the boiler, steam reformer, SBV or TRM.

**Options**

Three configurations are available: full scale, semi-mobile, and portable.

The semi-mobile GPCR plant (footprint is 1,000 m², throughput 70 t/month bulk solid or liquid material) is designed for use at sites or in regions with smaller waste stockpiles, or where mobility is important.

Small size portable units are available and can suit commercial applications on-site, in-process treatment of manufacturing wastes and carbon filter material. The unit fits into single sea container or gooseneck trailer (100 m² footprint) and can treat from 5 to 50 tons organics per year, depending on reactor configuration, chemical concentration and waste matrix.
Process schemes and pictures

General organizational diagram of the GPCR process

Flow diagram of the GPCR process (liquid waste treatment configuration)

31 Reproduced from the GPCR presentation at South American regional workshop on the environmentally sound destruction of POPs and the decontamination of POP containing waste in the framework of Basel and Stockholm conventions.

32 Reproduced from [US Congress, 1991]
Thermal Reduction Batch Processor (TRBP) in Australia\textsuperscript{33}

TORBED Facility at Heijmans Asphalt Plant, Holland (left) and a 5 tph TORBED Plant (right)\textsuperscript{33}

GPCR reactor: photo\textsuperscript{34} and a sketch of the reactor\textsuperscript{35}

\textsuperscript{33} Reproduced from Eco Logic presentation.
\textsuperscript{34} Reproduced from the GPCR presentation at South American regional workshop on the environmentally sound destruction of POPs and the decontamination of POP containing waste in the framework of Basel and Stockholm conventions.
\textsuperscript{35} Reproduced from [US Congress, 1991].
Advantages

- Excellent destruction efficiencies and generally low environmental impact
- Long and documented history of commercial operation, including POPs
- Relatively low amounts of solid residuals produced
- Product gases can be reused
- The technology can handle practically all types of wastes
- Different scale fixed, mobile, and semi-mobile units are available

Limitations, disadvantages, and concerns

- Use of hydrogen raises a safety issue, both related to its transportation and handling
- Liquor from caustic scrubber needs to be treated and disposed
- Power consuming as the waste needs to be evaporated at heated to high temperatures
- The process is complex and labor intensive, highly qualified and trained personnel is required
- The process may appear not cost-effective for low concentrated waste or small scale applications

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36 Reproduced from Eco Logic presentation.
37 Reproduced from the GPCR presentation at South American regional workshop on the environmentally sound destruction of POPs and the decontamination of POP containing waste in the framework of Basel and Stockholm conventions.
Principal information sources

1. CMPS&F Environmental, 1997
2. Costner, 1998
3. Danish EPA, 2004
4. Documentation from former vendor (ELI EcoLogic)
5. Information from vendor (Hallet Environmental)
7. SITE technology profiles
9. UNEP, 2000
10. UNEP, 2004a
11. UNEP, 2004b
12. UNIDO, 2001
13. US-EPA, 2005
14. Vijgen, 2002
Sheet 6. HydroDec

Commercial and development history

The HydroDec technology (named as “catalytic hydrogenation” or “catalytic treatment” processes before commercialization) is a technology for the refurbishment of dielectric fluids (in particular used transformer oil) through dechlorination of chlorinated hydrocarbons.

The development of HydroDec started in 1992 by the Commonwealth Scientific and Industrial Research Organisation of Australia (CSIRO), Division of Coal and Energy Technology in conjunction with TransGrid. HydroDec Development Corporation Pty Ltd was incorporated in 2000 as a wholly owned subsidiary of Virotec International Ltd to commercialize the HydroDec Technology. In 2002 HydroDec has entered into an exclusive global license with CSIRO for the marketing and distribution of the HydroDec Technology.

Shortly after the commercialization of the technology in 2004 Virotec announced the sale of the HydroDec Technology to Vert-eco Group plc that has been approved and completed in the late 2004. Successfully in 2004, the new owner of the technology Vert-eco changed its name to HydroDec Group plc. At the current time, HydroDec operates one small plant in Australia under the Joint Venture Agreement with Oil Treatment Services Pty Ltd.

Another catalytic hydrodechlorination technology (CHD technology) is being developed by Japanese Kansai Electric Power Co and Kanden-Engineering Co., which started to treat capacitors containing or contaminated with PCBs in 2004. A commercial scale CHD plant with capacity of 2 t PCB per day is being designed and is expected to operate very soon in Japan. The patent for this technology is held by Kansai Electric Power Co and Kanden-Engineering Co. There is very limited information on this technology, which is still in the development phase. There are a number of research/pilot studies related to the use of catalytic hydrodechlorination for destruction of POPs. However, these projects are not considered here as individual technologies, also because a lack of technical data does not enable to individuate significant differences between them that need to be used for their comparison and evaluation.

As far as almost no data available on the Japanese technology, only HydroDec technology is evaluated and considered in the review.

Technology description and chemistry of related processes

The HydroDec (hydrodechlorination) process is based on substitution of the organic chlorine with hydrogen. The reaction of a chlorinated chemical with hydrogen gas occurs in the liquid phase on the surface of a heterogeneous catalyst. It gives rise to hydrogen chloride and reduced hydrocarbon.

Destruction of chlorinated wastes via reductive catalytic dechlorination with hydrogen over a metal catalyst has been known for many years. This reaction is probably the most alluring possibility of sustainable disposal of polyhalogenated waste and is at present the focus of many scientific findings. CSIRO’s hydrodechlorination technology was

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38 The technology former name “catalytic hydrogenation” was not accurate chemically if referred to the treatment of PCB or other POPs.
probably the first successful attempt to push this methodology towards commercialization. Unlike the GPCR process the hydrodechlorination reaction with hydrogen in the presence of a catalyst (usually noble metals or nickel) can take place at relatively low temperatures and pressures. The common problem connected to the development of this technology lies in the catalyst poisoning by a range of elements. Prominent among these poisons are the sulphur compounds found in petroleum products such as transformer oils. These compounds are the known poisons for the noble catalysts which are of the choice for hydrodechlorination. According to some sources\textsuperscript{39} the CSIRO process used hydrogenation catalysts based on metal sulphides, which are tolerant of most catalyst poisons. They are considerably less active than noble metal catalysts, so that at the harsh conditions required for hydrodechlorination, the hydrogen chloride formed causes extensive cracking and rearrangement of hydrocarbons. This results in excessive hydrogen consumption and unacceptable changes in transformer oil composition. This problem was overcome by using a proprietary additive which scavenges the hydrogen chloride and ensures that the hydrochloric acid produced does not lead to degradation of the catalyst and side cracking reactions. More recent data from HydroDec report that a supported nickel-molybdenum catalyst is used in their process.

The general chemistry of related processes is simple and is similar to other reduction processes considered in this review, for example to the BCD and GPCR processes.

\[
\begin{align*}
RCl + H_2 & \rightarrow RH + HCl \text{ (catalyzed by metal sulphides)} \\
ROH + H_2 & \rightarrow RH + H_2O \text{ (catalyzed by metal sulphides)} \\
HCl + NaOH & \rightarrow NaCl 
\end{align*}
\]

As the result of the reaction with hydrogen chlorinated molecules are converted into their dechlorinated analogues. Oxygen present in compounds resulting from aging of the oil in service is converted to water, while any chlorinated species are converted to hydrogen chloride. Hydrogen chloride, as formed is neutralized by the proprietary aqueous acid scavenger. Its nature is not disclosed, however it is well known that hydrodechlorination reaction requires just simple base to proceed, which can be a caustic soda solution, potassium carbonate, or the like.

The treatment involves the following steps:

1. Feedstock is pumped into the process at the system operating pressure.
2. The acid scavenger and top up hydrogen is pumped into the process at system operating pressure.
3. The combined feed is heated to the reaction temperature.
4. The feed is gravity fed across a catalyst bed.
5. The gas component of the product is separated and captured for recycling into the process.
6. The product oil is collected and washed.
7. The wash water is collected and separated from the product oil.
8. The product oil is recovered for recycling into the process or for sale as a refined product

The process operates semi-continuously. Liquid feed (PCB oils) is introduced in the system together with aqueous scavenger under a circulating hydrogen flow under

\textsuperscript{39} UNEP, 2004a; Costner, 1998.
pressure. After being heated, all the system components a pushed in a single pass through the reactor, which contains the catalyst bed. The reaction takes place at above 300°C and 3 MPa pressure. Recent data report that the present Virotec’s HydroDec technology uses the hydrogenation reactor which is a patented modification of a known oil refining technology.

Downstream processing involves separation of the gases and light hydrocarbons from the regenerated oil, and washing stages for the product oil to remove chlorides formed as a reaction product of organochlorine destruction. Aqueous and organic phases are then separated. In the prototype most of the gases leaving the reactor are recycled, with a small purge gas stream passing to a catalytic combustor.

Hydrogen required for the process is produced on site by electrolysis of water. The developers claim that most gaseous effluents are recycled through the reactor. Purge gases are discharged through a catalytic combustor supplied. Chlorine containing effluents are scrubbed with caustic solution. Therefore, another process stream is the aqueous waste containing metal chlorides (as result of the neutralization of HCl formed). Such wastewater from the process is collected and disposed but in the immediate future it is proposed that wastewater will be treated within an on-site wastewater treatment plant by ozomolysis and ion exchange, which will allow treated water to be recycled in the process.

Following the treatment of PCBs the resulting dechlorinated oil, free of other oxidation products can be used as a dielectric fluid.

**Process schemes and pictures**

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*Fig. 40* Reproduced from the HydroDec website.
Advantages
- The process by its nature excludes the risk of formation of dioxins and furans
- Low emissions (high containment), the primary reaction occurs in a closed loop
- The process allows to reuse the treated material (PCBs)
- Catalytic nature: potential of improvement
- High DE demonstrated

Limitations, disadvantages, and concerns
- Limited to liquid and low concentrated POP solutions (solid and pure POPs require dilution in organic solvent)
- Relatively high cost, especially for other POPs than PCB
- The use of hydrogen gas requires adequate controls and safeguards to ensure that explosive air-hydrogen mixtures are not formed
- Catalysts are poisoned/deactivated with time, especially if the wastes contains impurities
- No full scale operation experience

Principal information sources
1. Costner, 1998
2. CMPS&F Environmental, 1997
3. UNEP, 2004a
4. UNIDO, 2001
Sheet 7. MSO

Commercial and development history

Molten Salt Oxidation (MSO) is a thermal, non-flame process that has the inherent capability of completely destroying organic constituents of mixed wastes, hazardous wastes, and explosives, including POPs.

In the mid-1950s Rockwell, Inc. conducted extensive tests of molten salts for the purpose of destroying chemical weapons. Since then there have been several projects to develop the MSO technology. Usually, the MSO technology applied to organic waste streams is referred to as a process by LLNL, which did an extensive research on it with a variety of waste streams including POPs.

Lawrence Livermore National Laboratory (LLNL) constructed an integrated pilot scale MSO system in 1997 to demonstrate the technology, following a period of laboratory development. 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 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.

As reported by DOE in 1997, following an old MSO project by DOE of 1992 which involved NSWC, LLNL, and several other organizations terminated in 1994, another MSO project was started by Naval Surface Warfare Center (NSWC) in consortium with several companies in order to develop the MSO technology. In 1997, the NSWC MSO system was approved for energetic operation, and development of mobile and modular scalable units was underway. Another DOE project on the use of MSO for stabilization of $^{238}$Pu wastes is run by the Los Alamos National Laboratory (LANL).\(^4\)

Most of applications of the MSO technology dealt with military or radioactive wastes and not with POPs (only several trial tests with POPs have been performed). However, this technology is potentially suitable for POP destruction and was included in several recent surveys on the topic.

Technology description and chemistry of related processes

The technology can treat a wide variety of solid, liquid, and gaseous waste streams. Organic wastes are oxidized with air under a pool of molten carbonate salts (usually either sodium carbonate or a eutectic of alkali carbonates) at temperatures between 700-950 °C and converted into CO$_2$, N$_2$, and water. HCl formed is scrubbed within the salt melt to form chloride salts and carbon dioxide.

MSO has several advantages over incineration. The molten mass provides a heat-transfer medium that ensures temperature uniformity. Flame-outs are avoided, since MSO is a non-flame process that is based on the catalytic liquid-phase oxidation reactions. MSO generates less off-gas than incineration, since it does not require supplemental fuel to

\(^{41}\) http://www-emtd.lanl.gov/ASTD-NM/MSO.html
sustain a flame. Operation of the MSO system is at temperatures hundreds of degrees lower than flame combustion temperatures.

The integrated MSO system consists of several subsystems, including a reaction vessel, an off-gas treatment system, a salt recycle system, feed preparation equipment, and a ceramic final waste forms immobilization system.

The waste is injected in the reaction vessel along with oxidant air from side penetrating nozzles. Solids should be crushed to a small particle size to permit their feeding. Gases can be injected directly into the air stream before it enters the vessel. Product off-gas exiting the vessel is then treated in the off-gas system. As waste is injected into the MSO vessel, residues of inorganic components build up in the salt bed which necessitates periodic removal of salt and replenishment with fresh salt to maintain process efficiency. A salt recycle system is needed to segregate inorganic inert materials and to reduce the consumption of fresh salt.

The unit would normally not require an auxiliary fuel except for start up, stand by, or shutdown because of heat generated by oxidation of the waste. This is even true for low energy content wastes such as hexachlorobenzene.

**Pre-treatment**

The feed preparation area includes waste receiving drums, a centrifuge for solid liquid separation, a shredder for size-reducing solid wastes.

**Post-treatment**

The off-gas system is aimed to remove entrained salt particulates, moisture, and traces of CO and NOx. It comprises a piping section with a gas-to-air cooler, an air cylinder and salt trap, a ceramic filter, a heat exchanger and condenser, an electrical heater, a HEPA (HEPA means high efficiency particulate air) filter, and a catalytic converter.

Spent salt from the MSO reactor is extracted, cooled, and sent to the salt recycle subsystem where the metals, radionuclides, and other mineral residues are removed from the salt. The cleaned salt will then be either disposed of as a brine or dried for reuse in the MSO vessel.
Process schemes and pictures

Integrated MSO system diagram

Unit to be used for demilitarization of obsolete U.S. munitions in Korea (on the left) and an integrated system including a salt recycle system (on the right)

Advantages

- Non-expensive alternative to incineration
- Simple in operation

42 Reproduced from [Hsu, 2001].
43 Reproduced from the LLNL website.
• Satisfies a wide range of waste types, including solids, liquids, gases, high strength organic waste, inorganic/radioactive, mixed waste, etc.
• Complete destruction of any organic waste

Limitations, disadvantages, and concerns
• Large volume of salts is generated in the process and requires disposal
• High potential of dioxin formation
• Formation of NaCl in the event of POPs treatment would require more frequent salt replacement and would lower the reactor lifetime
• Lack of detailed analytical data and experience on POP treatment
• Danger of superheated-vapour explosion if liquid wastes are introduced

Principal information sources
1. Adamson, no date.
Sheet 8. PACT

Commercial and development history

Generally, the plasma arc technologies (PACT, PLASCON, and PWC) can be classified as thermal destruction process ranging from pyrolysis to combustion that use heat generated by a plasma arc to destroy the organic waste content and to melt and vitrify the inorganic material.

The PACT process was developed by Retech and is now offered under different names by the other licensees; it also known in Europe as PlasmOx (Plasma Oxidation) by MGC Plasma AG, or PAHWTS (Plasma Arc Hazardous Waste Treatment System). A plant installed by Retech under a contract from the Naval Research Laboratory of the US Dept of Defense) operates commercially in the USA since around 1997 (as the demonstration tests finished). There are also commercial scale PACT plants in Europe (Switzerland, Germany) and Japan (Toyo Engineering Corporation) – total of 6 full scale units installed worldwide up to now and 5 system operating on pilot/lab scale.

Technology description and chemistry of related processes

PACT technology is a vitrification technology that utilizes the heat produced by the plasma arc to melt the inorganic content and destroy the organic content of waste. The process operates in the presence of limited amount of oxygen, therefore in can be defined as pyrolysis in relation to the organic waste destruction process involved. It can also involve a flameless waste oxidation similar to the technologies utilizing molten media (e.g. GeoMelt and MSO) if the organic waste is mixed with inorganic content. Compared to other PAT technologies, the PACT process more resembles combustion, because the waste is treated in the presence of more oxygen than PWC, and at lower temperatures and with lower degree of dissociation of organics than PLASCON.

In a PACT system, there is a rotating centrifuge inside of the primary processing chamber (PPC) which mixes the molten slag during processing. The system is designed to accept both liquids and bulk solids, which are conveyed into the PPC. Once in the PPC, the waste is heated by a transferred arc plasma torch. The rotating system with oxygen introduction constitutes the patented concept of the technology.44

The plasma torch provides temperatures of up to 6,000°C causing the ionization of gases such as oxygen or nitrogen (plasma gas). The plasma gas then imparts heat into waste resulting in the complete destruction of organic molecules. Most metals and other inorganic materials are reduced to molten slag, which ends in the slag collection chamber. A part of the heavy metals are expected to vaporize and end up in the gas/particulate scrubber system. Water and organics in the feed are volatilized, as are most chlorides and sulfates. The organics are partially oxidized in the PPC, and the off-gas is maintained at approximately a 45% CO\textsubscript{2}/(CO+CO\textsubscript{2}) ratio. The off-gas is also rich in hydrogen and is flammable.

The off-gas passes to the secondary treatment chamber (STC), which is designed to fully oxidize the combustible gas species with air and provide a 2-second residence time for the products of combustion at temperatures above 980°C. If necessary, supplementary heat is added to the system by a non-transferred plasma arc torch to maintain the temperature inside the STC in the range of 980°C to 1315°C.

44 US patent 4,770,109; US patent 5,005,494; US patent 5,136,137.
When the centrifuge is full of slag, feeding is interrupted, and the molten mass is held at temperature for a specified period of time in order to drive off the volatile components. It ensures that all solids are melted and all organics in the region are volatilized and transferred to the STC. The melt is then cooled and the vitrified product is dumped into the slag collection chamber.

**Pre-treatment**

Bulk solids are dumped directly into the feed screw which conveys the material into the PPC. Solids up to the size of the pails should be processed through a shredder. Liquid waste from drums is pumped into a liquid transfer vessel. The combined liquid waste in the liquid transfer vessel is then pumped in a metered fashion to the PPC.

**Post-treatment**

The off-gas treatment system removes particulates, acid gases, and volatilized metals. The design of the off-gas treatment system depends on the waste material.

**Process schemes and pictures**

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45 Reproduced from [Womack, 1999].
Schematic of a PACT-8 system

Flow diagram of PACT

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46-47 Reproduced from [ESTCP, 2003].
Advantages

- Complete and rapid destruction of any kind of organic waste
- Developed commercial technology
- The process does not need reagents
- The process can treat a variety of waste streams.
- The process requires minimal waste pre-treatment

Limitations, disadvantages, and concerns

- Potential dioxin formation
- High emissions
- Limited experience of POP treatment
- High electricity requirements
- Costly equipment and qualified staff needed

Principal information sources

1. CMPS&F Environmental, 1997
2. Costner, 1998
3. ESTCP, 2003
4. Joint service P2 opportunity handbook by NFESC
5. Rahuman, 2000
6. SITE technology profiles
7. US-EPA, 2005
8. Vendor website: www.retechsystemsllc.com
9. Womack, 1999
Sheet 9. PLASCON

Commercial and development history

This technology uses the argon plasma arc process and is designed to process CFC and organic liquids, such as PCBs. The process was in development in Australia in cooperation between Siddons Ramset Ltd and CSIRO starting from the mid eighties and was commercialized in 1992. In 1993 Siddons established a new wholly owned division, SRL Plasma Limited which has been granted an exclusive worldwide license to commercialize and further develop the technology. PLASCON is patented in most major countries. The three patents for PLASCON\(^{48}\) are jointly owned by Siddons Ramset Ltd and CSIRO, which also hold a number of other plasma related patents.

Since 1993 extensive pilot tests for destruction of halon compounds, herbicides, and PCBs were conducted. The first pilot plant was installed in 1992 at Nufarm Ltd., a herbicide manufacturing works in Laverton, Victoria; in 1995, the second Nufarm PLASCON of higher throughput was installed. Another plant was commissioned at Australia’s National Halon Bank in 1996 and since then about 1,000 tons of Halon 1011 and about 100 MT of CFCs have been destroyed. BCD Technologies purchased a license for PLASCON from SRL Plasma in 1997 to treat a range of concentrated chlorinated wastes including PCB’s and organochlorine pesticides, which could not be treated with the same efficiency by the BCD technology. BCD Technologies operated two plasma plants in Australia: one in Brisbane for PCBs and POPs; and another in Melbourne for treating CFCs and halons. Mitsubishi Chemical Corporation has installed a PLASCON plant in Japan to treat wastes consisting of, containing or contaminated with PCBs. Nine installed commercial PLASCON plants are still in operation. Four plants operate in Japan, one in United Kingdom, and four in Australia. Over 3,000 t of POPs have been treated.

In 2000, the SRL Plasma (subsidiary of Siddons Ramset Ltd), which licensed users of the PLASCON technology and built PLASCON plants to order, was acquired by BCD Holdings Pty. Ltd. and became SRL Plasma Pty. Ltd. BCD Holdings Pty Ltd owned both BCD Technologies and SRL Plasma Pty Ltd. Successfully in 2006, DoloMatrix International Ltd acquired BCD group and thereby also gained the rights for manufacturing, selling, and licensing the PLASCON process.

Technology description and chemistry of related processes

PLASCON is an “in flight” plasma process, which means that the waste mixes directly with the argon plasma column. Argon is used as the plasma gas since it is inert and does not react with the torch components.

The waste is fed directly into the plasma torch within the current of argon, where it is rapidly heated (one millisecond) up to 12,000°C and then passes into the flight tube where its pyrolysis occurs in nearly 20 ms at temperature of about 3,000°C. In the beginning of the flight tube oxygen is also added (limited amount) to ensure that any carbon formed during pyrolysis is then converted to carbon monoxide. The high temperature generated by plasma causes compounds to dissociate into their elemental ions and atoms. Recombination occurs in a cooler area of the reaction chamber, followed by rapid (2 ms) alkaline quenching from 1,500°C to less than 100°C. Such rapid quenching prevents the formation of dioxins and furans.

\(^{48}\) Patents: TW4523, TW2169, TW2653.
The cool gas from the quench is further scrubbed with alkaline liquor in a counter-current packed column to neutralize HCl and other acid gases. The off-gas from the column, which consists mainly of CO, H₂, Ar and some CO₂, then passes to a small ground flare that converts CO to CO₂ and H₂ to H₂O. The halide salt solution from the scrubbing system is stored and discharged to the municipal wastewater treatment system.

PLASCON has been demonstrated with PCB oils containing 60% PCBs. Recently, a PLASCON plant in Australia has been configured to destroy pesticide wastes.

The process requires electricity (requires 1,000 to 3,000 kWh of electricity per ton of waste) argon gas, oxygen gas, caustic and cooling water. Emissions include gases consisting of argon, carbon dioxide and water vapour. Residues include an aqueous solution of inorganic sodium salts.

**Pre-treatment**

Pre-treatment is not required for most liquids. Solids and very viscous liquids or sludges thicker than 30 to 40 weight motor oil cannot be processed without pre-treatment. Solid organic matter should be crushed and dispersed in organic liquid and treated in a form of pumpable slurry or be evaporated via thermal desorption. Solids such as contaminated soils, capacitors and transformers can also be pre-treated using thermal desorption or solvent extraction.

**Post-treatment**

No other post-treatment than that applied to the effluent gases (see process scheme) is provided/required.

**Process schemes and pictures**

![Basic scheme of the PLASCON plasma torch system](image-url)

49 Figures are reproduced from vendor website and [Bridle, 2003].
Simplified process schematics

A PLASCON plant at BCD Technologies (Australia) unit (left) and a 150kW PLASCON unit for ODS treatment (right)
Flow chart of a PLASCON unit
Advantages

- High destruction efficiencies
- Relatively low cost, especially for concentrated waste (efficiency and consumption do not depend on the concentration of pollutant)
- Easy in operation
- Compact and easy to transport
- Low process inventory; the process does not use reagents; it is electrically powered and can be shut down or started up in seconds

Limitations, disadvantages, and concerns

- High electricity requirements and the need of infrastructure
- Not cost effective if waste is low contaminated
- Cannot treat solids directly (only applicable to gases, liquids and slurries)
- Risk of dioxin formation, which is relatively low comparing to other high temperature oxidation processes

Principal information sources

1. UNEP, 2004c
2. CMPS&F Environmental, 1997
3. Costner, 1998
4. Rahuman, 2000
5. UNEP, 2000
6. UNEP, 2004a
7. UNEP, 2004b
8. US-EPA, 2005
Sheet 10. PWC

Commercial and development history

The Plasma Waste Converter (PWC) process, which is sometimes called Pyrolysis process in other reviews, belongs to a family of PAT as it uses heat generated by plasma to destroy the waste.

PWC process was developed by the Startech Environmental Corporation, USA. The system was designed to treat a range of organic wastes. It is claimed that the PWC systems can be suited for the treatment of POPs, such as PCBs and hexachlorobenzene (HCB). However, the commercial experience of POP treatment has net been documented by now.

PWC is commercially available in the USA since 1996. The technology is also marketed in Japan, China and Australia. The process has been in demonstration in Canada since 1989.

Technology description and chemistry of related processes

The PWC process is more similar to PACT than to PLASCON but operates in the oxygen deficient or reductive atmosphere and is therefore involves more pyrolysis than combustion processes. Similarly to PACT, wastes are reduced to their metallic components, a slag, and a gas that can be used as a fuel.

As the other plasma arc technologies considered above, the Plasma Waste Converter uses the energy of a gas (air, argon, CO2 or nitrogen) which is ionized in the plasma torch. The plasma gas heated at temperatures in the order of 3,000 to 5,000°C (according to some sources up to 15,000°C) is introduced in the reaction chamber. The waste and steam are introduced from the side and the off-gases are removed from the top.

Organic and inorganic wastes can be introduced into the plasma chamber (e.g. solid and liquid bulk organics, solids, liquids, and sludges, as well as gases). The inorganic content melts and is removed as vitrified slug. The organic matter dissociates into its elemental atomic components that in the presence of limited amount of oxygen are then assemble in partial oxidation products and pyrolytic gases, such as CO, H2, HCl, H2O, light molecular weight hydrocarbons, including chlorinated ones and other functionalized, e.g. methanol, etc.

Solids and bulk wastes can be fed into the system without pre-conditioning or shredding. Feeding is automatic and is normally on a continuous basis, but can be batch. Liquids, gases and sludges can be pumped directly into the chamber.

Pre-treatment
No special pre-treatment is required, except that humid waste may need to be dewatered.

Post-treatment
Off-gases (Plasma Converted Gas, similar to synthesis gas) after passing through scrubbers and filters can be reused as chemical feedstock or fuel gas to recuperate energy.
Molten vitrified solids are removed from the bottom of the chamber and can be reused or may need to be disposed of.

**Process schemes and pictures**

*Materials previously regarded as wastes are recycled and processed as feed stocks to make commodities...*

**Advantages**

- All waste types including solids, liquids, sludges and gases can be treated
- Products can be useful
- The process does not use reagents
- Applicable to pure POPs
- High throughput

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50 Figures are reproduced from the vendor website.
Limitations, disadvantages, and concerns

- Experience on POP application is missing
- Potential of dioxin formation
- High electricity requirements and need of infrastructure
- Solid slug requires special disposal

Principal information sources

1. Vendor website: http://www.startech.net
2. CMPS&F Environmental, 1997
3. UNEP, 2004a
4. US-EPA, 2005
Sheet 11. SCWO

Commercial and development history

The SCWO technology (other names include Hydrothermal oxidation (HTO), Assisted Hydrothermal Oxidation (AHO), Hydrothermal Decomposition, Aqua Critox®, etc.) has been in development by many companies for more than two decades. There have been a number of projects, from pilot to neo-commercial, on the use of the SCWO for treatment of chemical weapons and other organic wastes, including POPs. The companies that commercialized and operated SCWO are summarized in a table below.51

<table>
<thead>
<tr>
<th>Company</th>
<th>Year of establishment or first involvement</th>
<th>Licensees or partners</th>
</tr>
</thead>
<tbody>
<tr>
<td>MODAR, Inc.</td>
<td>1980</td>
<td>Organo</td>
</tr>
<tr>
<td>MODEC (Modell Environmental Corp.)</td>
<td>1986</td>
<td>Organo, Hitachi, NGK, NORAM</td>
</tr>
<tr>
<td>Oxidyne Corp.</td>
<td>1986</td>
<td></td>
</tr>
<tr>
<td>EcoWaste Technologies, Inc.</td>
<td>1990</td>
<td>Chematur, Shinko Pantec</td>
</tr>
<tr>
<td>Abitibi-Price, Inc.</td>
<td>1991</td>
<td></td>
</tr>
<tr>
<td>General Atomics</td>
<td>1991</td>
<td>Komatsu, Kurita</td>
</tr>
<tr>
<td>Foster Wheeler Development Corp.</td>
<td>1993</td>
<td></td>
</tr>
<tr>
<td><strong>SRI International</strong></td>
<td><strong>1993</strong></td>
<td><strong>Mitsubishi</strong></td>
</tr>
<tr>
<td>KemShredder, Ltd</td>
<td>1993</td>
<td></td>
</tr>
<tr>
<td>Chematur Engineering AB</td>
<td>1995</td>
<td>Johnson Matthey, WS Atkins, Stora-Enso, Feralco</td>
</tr>
<tr>
<td>HydroProcessing, L.L.C.</td>
<td>1996</td>
<td></td>
</tr>
<tr>
<td>ProchemTech, Inc.</td>
<td>1987</td>
<td></td>
</tr>
</tbody>
</table>

At present, the main vendors of the SCWO technology include Chematur Engineering AB, General Atomics, Foster Wheeler Development Corp., HydroProcessing, L.L.C., ORGANO Corp., and SRI International.

SCWO is especially efficient for treatment of aqueous waste, but can also address treatment of inorganic wastes, chemical weapons and a number of other applications. At present different plants/variations of the technology address treatment of oxygenated hydrocarbons, amines, semiconductor manufacture wastes, lab waste water and municipal/industrial wastewater sludges, smokes, dyes, etc. The SCWO process has been approved for full scale development and use in the chemical weapons programme of the United States of America.

The Japanese AHO plant for PCB and other chlorinated waste destruction operates from 2002. This technology developed by SRI International, USA was licensed to Mitsubishi Heavy Industries which received exclusive field-of-use license in Japan. Whereas other technologies may be also useful for POP waste reaction (e.g. the ORGANO’s SCWO technology was successfully tested for PCB treatment on the bench scale), it seems that only the SRI/Mitsubishi plant has had relevant commercial experience. Therefore, attention will be more focused on the data available on the SRI’s technology configuration when considering particular technical details.

Technology description and chemistry of related processes

A group of technologies with the general name of SCWO use a principle of oxidation of organics with an oxidant (such as oxygen, hydrogen peroxide, nitrite, nitrate, etc.) in the supercritical water, e.g. water near or above its critical point on the phase diagram, which is 374°C and 218 atm. Supercritical state of the water is achieved at heating and compressing water over the above indicated points of temperature and pressure. Some techniques utilize subcritical water, which corresponds to a state of water slightly below the critical point (e.g. 370 °C and 262 atmospheres).

In a typical SCWO system, the waste is injected, together with water and air or oxygen, in a column where the mixture is heated and compressed so that the water becomes supercritical. Most organic matter is highly soluble in SCW (solubility is near to that in alcohols or acetone). Moreover the viscosity and diffusivity of SCW are comparable with more like that of gas, while the density is comparable with liquid. Due to these physical properties, the SCW has high molecular kinematic energy and is considered as highly activated reaction phase. Therefore, in the presence of oxygen, the organic compounds are oxidized and completely destroyed to carbon dioxide, nitrogen and water. Chlorinated organics produce hydrochloric acid.

Most SCWO and subcritical water oxidation techniques are thought to be applicable to all POPs, which can be fed in the form of aqueous wastes, oils, solvents, slurries, and solids with a diameter less than 200 µm (depending on configuration). Normally, the organic (or polychlorinated) content of the waste is limited to less than 20%.

Energy requirements are expected to be relatively high because of the combinations of high temperatures and pressures. It has been claimed, however, that as long as relatively high hydrocarbon content is present in the feed, no energy input is required to heat up the feed to supercritical temperatures.

It is known that supercritical water represents a strong acidic environment in the presence of hydrochloric acid which is formed as result of oxidation of chlorinated organics. Therefore the SCWO reaction vessels must be constructed of materials capable of resisting corrosion. This problem can be overcome by using resistant titanium alloys or other advanced materials, engineering designs or additives.

For example, the SRI’s AHO technology is based on the use of sodium carbonate as an additive that allows operating at quite moderate temperature conditions (380°-420°C) while mitigating the corrosion problem. As reported by SRI, sodium carbonate is fully insoluble at the critical temperature of pure water (374°C). Under conventional SCWO conditions (450°-650°C and 3,600 psi), the density of water is very low (< 0.1 g/mL) and the destruction of organic material through ionic routes is negligible. At lower temperatures (380°-400°C and 3,600 psi), however, waste is pumped through a fluidized sodium carbonate bed maintaining a water density > 0,3 g/mL to promote both ionic and radical reactions. Halogenated organics hydrolyze rapidly on the heterogeneous surface of sodium carbonate to form easily oxidizable products. Air or oxygen then brings about rapid oxidation. The products are carbon dioxide, water, NaCl and other salts, depending on the feed waste.

AHO technology is developed mainly for corrosive and most difficult to decompose wastes such as polychlorinated biphenyls (PCBs) where formation of HCl at high temperature conditions result in critical corrosion problems. The concept thus directly avoids the production of acid gases, and encourages salts to separate out on the carbonate surfaces rather than on the metal components of the reactor system facilitating their removal.
Pre-treatment

Concentrated wastes may have to be diluted prior to treatment in order to reduce the organic content to less than 20%. If solids are present, they will have to be reduced to less than 200 µm in diameter.

Post-treatment

There is no specific information available regarding post-treatment requirements.

Process schemes and pictures

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52 Reproduced from [Jayaweera I., 2001].
53 Reproduced from the Database on Japanese Advanced Environmental Equipment.
Advantages

- Very low emissions to the environment
- Relatively low costs
- High DE and DRE
- Low process inventory and minimal need of facilities for remote applications

Limitations, disadvantages, and concerns

- Corrosion problem when treating chlorinated waste
- High temperatures and pressures require safety precautions
- Potential of dioxin/furan formation when treating polychlorinated waste
- Not applicable to bulk solid organics

Principal information sources

1. CMPS&F Environmental, 1997
2. Costner, 1998
3. Database on Japanese Advanced Environmental Equipment, by GEC
5. Rahuman, 2000
6. UNEP, 2004a
7. UNEP, 2004b
8. UNIDO, 2001
9. US-EPA, 2005

54 Reproduced from [Suzuki, 2001].
Sheet 12. SET

Commercial and development history

The SET technology was commercialized and patented by Commodore Solution Technologies, Inc., Marengo, Ohio. Through its wholly owned subsidiaries, Commodore Nuclear, Commodore Advanced Sciences, and Commodore Solution Technologies, Commodore provides proprietary remediation technologies, technical engineering services and facilities management to the public and private sectors.

The technology is based on the patented SET chemistry\textsuperscript{55} and is also known as the SOLV\textsuperscript{TM} process, which incorporates pre- and post-treatment modules in a single process concept.

The SET technology was in development since the late eighties. For many years the technology operated on the pilot scale in USA for soil treatment. In 1995-1995 SET was demonstrated to the EPA and received a national permit for on-site treatment of PCB contaminated soil, which was extended to the treatment of oils in 1998. Commodore’s medium scale S-4 units are available since 1997-1998. Later on bigger scale commercial S-10 units appeared, which were demonstrated for PCB treatment in soil in 2000 at a Pennsylvania Air National Guard facility.

Commodore systems are also applicable to mixed wastes, chemical weapons, explosives, CFC and halons. A number of field demonstration projects have been completed in the USA. The full scale experience of POP treatment is limited to the contaminated soils mainly.

Technology description and chemistry of related processes

The SET process is a method of reducing halogenated hydrocarbons in a mixture of sodium or other alkali metal in liquid ammonia. Anhydrous sodium or potassium is added to liquid ammonia at nearly 100°C that results in a blue coloured solution, due to the solvated electrons. As sodium dissolves in ammonia it disassociates into sodium ions (\(\text{Na}^+\)) and electrons (\(\text{e}^-\)) as follows:

\[
\text{Na}_0\text{ anhydrous} + \text{NH}_3\text{ liquid} \rightarrow \text{Na}^+ + \text{e}^- \text{ (blue color liquid)}
\]

The solvated electrons are powerful reducing agents that can strip chlorine atoms, giving rise to the dechlorinated hydrocarbons and sodium chloride, as described by the following simplified equation:

\[
\text{RCl} + \text{Na}^+ + \text{e}^- \rightarrow \text{R} + \text{Na}^+ + \text{Cl}^- \\
\text{R} + \text{R}^- \rightarrow \text{R-R}
\]

In practice the chemistry of involved processes is far more complicated and resembles chemistry of other processes based on the use of sodium and other alkali or earth alkali metals, e.g. Ball Milling, SR. The organic radicals and ions formed as result of electron and sodium attack can give rise to a variety of polymerization products. When treating concentrated solutions of chlorinated compounds, especially of polychlorinated

\textsuperscript{55} US Patent 5,110,364.
ones, the polymerization processes might lead to a decrease of efficiency of dechlorination. Therefore, the method is only applicable to low concentrations of chlorinated organics. Full strength POPs, such as concentrated liquids or bulk solid organochlorines should be added in corresponding amounts to reach necessary concentration.

The technology is configured for treating soils, sludges, PCB oils, pesticides, and other organics. The reduction of halogenated materials from soils, oily wastes, sludge, and sediments requires almost complete removal of moisture through pre-drying, because liquid ammonia reacts quickly with water to form ammonium hydroxide, which is not only exothermic, but also inhibits production of solvated electrons. The sodium metal also has affinity for water to form sodium hydroxide. Moreover, water within debris and other inert materials prevents penetration of ammonia.

The whole SOLV process has been developed as a modular transportable system, based around the central SET 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.

The contaminated materials are placed into a treatment cell, and ammonia is pumped from the ammonia receiver into the treatment cell. Stirring of the waste ammonia slurry at approximately 70°C proceeds for at least 15 minutes in order to extract the organic contaminant such as PCBs into the ammonia. Ammonia is added to the solvated solution tank and the tank agitator is turned on. Molten sodium (98 °C) is pumped into the tank from the sodium reservoir. The solvated solution tank is stirred for approximately 15 minutes to ensure complete dissolution of the sodium. The solvated electron solution is then pumped from the tank into the treatment cell containing ammonia waste slurry. The chemical reaction between the solvated electron and the contaminant takes place almost instantly. At the end of the reaction, ammonia is removed for reuse by heating, and the remaining treatment residues are removed from the cell and disposed of.

Pre-treatment
Debris and big pieces of inorganics greater than 60 mm in diameter typically must be removed prior to processing or be shredded/crushed. Soil, sediments, or other waste containing >30% water (according to more recent sources 40%) must be dewatered. Dewatering units can be provided as front-end modules.

Post-treatment
Back-end modules are available for pH adjustment (adding diluted acid solution to the residues to neutralize ammonia), ammonia recycle, and product concentration. Products emissions are minimal and mainly consist of ammonia which is scrubbed. Solid residues, such as salts and organic oils should be disposed, e.g. in a landfill or be returned to the environment, depending on the waste type treated. The treated soils can be disposed in a non-hazardous landfill.
Process schemes and pictures

Basic flow diagram of the SET process

Schematic of the SET process

56 Reproduced from [Getman, 2001].
57 Reproduced from [Orton, 2001].
Advantages

- Non-thermal reductive process, no dioxin formation
- Closed system - low emissions
- Modular scalable and mobile equipment exists
- A wide range of treatable waste types
- Relatively low cost
- Low-to-medium resource and electricity requirements

Limitations, disadvantages, and concerns

- Use of highly reactive and toxic sodium metal and ammonia
- Cannot be applied to aqueous or humid waste
- Use of elevated pressures, risk of ammonia and of other components emissions
- The solution is highly corrosive, which could impact structural integrity of the SET reactor and other components

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58 Reproduced from [Getman, 2001].
• Toxic amines can be formed
• Salts and solid residues require disposal

**Principal information sources**

1. CMPS&F Environmental, 1997
2. Costner, 1998
3. FRTR, 2001
5. NFESC, no date
6. Rahuman, 2000
7. Remediation technologies, NFESC
8. SITE Technologies profiles
9. UNEP, 2004a
10. UNIDO, 2001
11. US-EPA, 2005
12. Vendor website: [www.commodore.com](http://www.commodore.com)
13. Vijgen, 2002
Sheet 13. Silver II

Commercial and development history

The Silver II technology is a MEO process which is very similar to the CerOx process considered above, but where in place of Ce$^{4+}$ ion another active oxidant is used, which is the ion of Ag$^{2+}$.

The Silver II has been developed by the AEA Technology since the eighties. The technology is designed for the treatment of radioactive wastes and a wide range of organics. Together with a number of other alternative technologies, in 2000 Silver II participated in the ACWA program by the US Army where it was demonstrated for the treatment of military wastes.

The technology is around for more than 10 years and has been extensively demonstrated on pilot scale and using 4-12 kW full scale plants which operated in the ACWA program, USA and in UK. AEA Technologies claims to have developed mobile self/contained concepts, transportable modular plants, and large static plants. However, the documented experience is limited only to the plant operated in the ACWA program.

The applications of Silver II to POP are limited; however, the reported pilot/lab scale tests with several chlorinated organic substances (trichlorobenzene, chlorobenzene, chlorofluorobenzoic acid, methylene chloride, chloroform, chloroethylethyl sulphide) have been performed including several tests on the full scale plant. The results confirm the possibility of using the technology for destruction of polychlorinated POP waste, such as pesticides and PCBs, which is believed to become one of the future Silver II applications.

Technology description and chemistry of related processes

The basic process step is the oxidation of organic molecules by aqueous solution of Ag$^{ii}$ ion. Ag$^{ii}$ is an instable form of silver in solution that can be generated at the anode of an electrolytic cell from the stable Ag$^{i}$ form.

As Ag$^{ii}$ attacks the organic molecule the radical organic species are formed, that progressively degrade to CO$_2$ via further oxidation and reaction with water. Silver is reduced back to Ag$^{i}$. Other reaction products include protons, chlorine, and eventually other elements, such as sulphur, phosphorus, nitrogen, etc. depending on the feed. Ag$^{ii}$ can also react with water giving oxygen, which is considered a parasitic reaction and can be suppressed at high waste loads. Another lateral reaction is the reaction of chloride with water resulting in the precipitation of AgCl. It is stated that silver chloride is prevented from entering the cell by solid/liquid separation in a hydrocyclone and that it can be treated with acid to recover silver. Nitric acid is also added to the reaction vessel (anolyte tank) which also recovers the precipitated silver chloride in situ.

Ag$^{i}$ is returned to the electrolytic cell where it is again oxidized to Ag$^{ii}$. The protons generated in the reaction with waste then transfer in the counterpart of the electrolytic cell through a membrane, where they enter in the catholyte reaction with nitric acid, reducing it to water and nitrous acid. The latter decomposes to nitrogen oxides which are then converted to nitric acid by simple reaction with atmospheric oxygen and water, which is returned to the electrolytic cell.
It is not necessary that waste be soluble in water as the reaction can also proceed on the surface that was confirmed by the tests with oils and bulk organic solids and polymers. However, the wastes soluble or partially soluble in water are treated more easily, as well as finely dispersed organic wastes which have a higher area of contact with water. According to some sources\textsuperscript{59}, the optimum treatment efficiency is achieved at an organic concentration (as carbon) of 2-10 g/L (<1%), other sources\textsuperscript{60} say that the organic content of the feed can vary between 5 and 100% without affecting the process unduly.

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. The process operates at nearly 90°C and atmospheric pressure. The process streams mainly include CO\textsubscript{2}, O\textsubscript{2}, chloride, nitrate, or other salts, and water. Water is distilled and discharged. Other residues arise from heteroatoms in the feed.

**Pre-treatment**

Organic solids and water immiscible liquids may require strong emulsification and dispersion in water (it is not clear if the respective pre-treatment units are provided) in order to provide rapid reaction with silver, otherwise Ag\textsuperscript{II} is expected to react with water.

**Post-treatment**

Scrubbing of off-gases is required to remove chlorine. Silver chloride should also be treated and silver recovered. There is mention that these modules exist but probably their efficiency has to be verified for the full scale POP treatment, which is new for the technology, and where these options appear very important. Excess of water is distilled and discharged (neutralization may be done if it still contains traces of nitric acid). Chloride, phosphate, and sulphate salts resulting from silver recovery and scrubbers are then disposed in landfill. NO\textsubscript{x} are scrubbed to low levels.

**Process schemes and pictures**

\begin{center}
\includegraphics[width=\textwidth]{silver_ii_cell_reaction.png}
\end{center}

\textit{Silver II cell reaction}\textsuperscript{61}

\begin{flushleft}
\textsuperscript{59} UNEP, 2004a. \\
\textsuperscript{60} Rahuman, 2001; Costner, 1998. \\
\textsuperscript{61} Reproduced from [Judd, 2001].
\end{flushleft}
Schematic of the core Silver II process

Schematic of the integrated Silver II plant (reproduced from [Turner, 2001]).

62 Reproduced from [Judd, 2001].
63 Reproduced from [Turner, 2001].
Advantages

- The system is compact, easy to transport and low-inventory – can suite remote on site application
- Low potential of dioxin formation (low temperature alternative oxidation)
- Mild operation conditions (temperature below 100°C and atm. pressure) - safe to operate and easy to shut down
- Low emissions and solid residues

Limitations, disadvantages, and concerns

- Limited experience of POP treatment and limited commercial experience in general
- Silver should be recycled due to precipitation and other solids should not be allowed to enter in the electrolytic cell
- Low reaction rate and efficiency are expected for wastes which are poorly soluble in water, e.g. soils and bulk solid organics
- High electricity requirements, may not be justified for low strength POPs
- Cost details and performance data are missing

Principal information sources

1. Board on Army Science and Technology, 2002
2. Costner, 1998
3. Judd, 2001
5. Rahuman, 2000
6. Turner, 2001
7. UNEP, 2004a
8. US-EPA, 2005
9. Vijgen, 2002

64 Reproduced from [Judd, 2001].
Sheet 14. SPHTD

Commercial and development history

The Self-Propagating High-Temperature Dehalogenation (SPHTD) process represents an alternative promising approach of destruction of hazardous halogenated waste via the dehalogenation reaction that utilizes heat produced by the same reaction which is, in principle, similar to combustion, except that the reaction proceeds via reduction and not oxidation.

This methodology is still in a very early development phase and a pilot SPHTD plant has operated only on the lab scale in the University of Cagliari, Italy. However, a number of tests have already proven applicability of SPHTD to completely destroy chlorinated toxicants.

Notwithstanding the absence of commercial experience this technology (methodology) was considered a useful example for this review as it theoretically represents a more favourable approach of the treatment of concentrated organochlorine wastes than other methodologies in development.

Technology description and chemistry of related processes

The SPHTD method is based on the reaction of chlorinated organic compounds with strongly reductive substrates, such as alkaline metals or their hydrides.

In the self-propagating reaction the reaction takes place in the form of a wave (self-propagating front) where the localized reaction zone is moving through the reaction mixture from the point of its ignition. Similarly to the Ball Milling process considered above, the self-propagating reaction takes place between two solids, in our case waste and reductant that would not react under normal conditions. However these reagents react at high temperatures, because the solids melt, so the reagents come in a closer contact and are imparted enough energy to overcome the activation barrier. The reactions that proceed in a self propagating way should be very exothermic (typical reaction enthalpies are well above 1,000 kJ per mole), so that the heat produced by the reaction in the point of ignition could provoke the same reaction in the neighbouring zone and so on, making the reaction proceed in a spontaneous way. The adiabatic temperature of self-propagating processes can reach 4,000 K. Under these severe conditions, all organic molecules break into small pieces.

Generally, operating the process would require premixing the reagents and loading the mixture into the reactor, which is sealed and the mixture is ignited. After the vigorous reaction between the reagents is finished the mixtures stays for cooling, thereafter the reactor is unsealed and the products are unloaded and disposed or stored.

Laboratory tests have been performed with hexachlorobenzene and other organochlorine chemicals, using calcium hydride, or calcium, as a reductive agent. According to the reported experimental procedure, reactants premixed and pressed, where placed in the reaction chamber under argon and fired by a power pulse.

From reference data, a reaction enthalpy of 1,709,6 kJ/mole is foreseen for a direct and complete reduction of hexachlorobenzene as:

$$3\text{CaH}_2 + C_6\text{Cl}_6 \rightarrow 3\text{CaCl}_2 + 6C + 3\text{H}_2 (-1,709,6 \text{ kJ/mol})$$
which rises to 1,804.6 kJ/mole when an excess of CaH$_2$ is employed:

$$6\text{CaH}_2 + \text{C}_6\text{Cl}_6 \rightarrow 6\text{CaHCl} + 6\text{C} + 3\text{H}_2 (-1,804.6 \text{ kJ/mol})$$

The resulting reaction heats are large enough to maintain the self-sustaining character of the process within a range of CaH$_2$/organohalide molar ratios from about 2-3 up to 15-18.

Successful tests were carried out also with other chlorinated compounds and other reductants. In particular, the use of metallic calcium increased the reaction heat for the hexachlorobenzene, thereby creating still more effective reduction conditions.

**Advantages**

- Very high temperatures guarantee complete and fast destruction of any kind of organics
- Closed design exclude risk of fugitive emissions, only solid salts, low molecular weight hydrocarbons, and hydrogen are produced
- Low risk of dioxin formation due to reductive conditions
- Products can be useful
- Very low inventory, no infrastructure required, can easily suit remote applications
- Simple in operation

**Limitations, disadvantages, and concerns**

- Operated only on the lab (pilot) scale
- May be not cost effective due to high cost of CaH$_2$
- Only applicable to solids
- Not applicable to humid waste
- Process seems not to be applicable/justified for waste with low organic content

**Principal information sources**

1. Information from developer
2. Orrù, 2002
3. UNEP, 2004a
4. US-EPA, 2005
5. Vijgen, 2002
Sheet 15. SR

Commercial and development history

Sodium Reduction (SR) or alkali reduction technology is represented by a vast family of options for the treatment of PCBs in a number of countries, namely France, Germany, UK, Netherlands, South Africa, Australia, USA, Saudi Arabia, Japan, Italy, New Zealand, etc. All these technologies effectively utilize the same principle of reduction with sodium metal in the liquid phase and use similar technology design; therefore, they show very similar performance and parameters and can be grouped together within the group of SR technologies to be evaluated together in this review.

Application of SR technologies for PCB treatment started nearly almost 20 years ago. Now, the SR technology has a very firm experience of PCB treatment worldwide. Being very simple in operation, requiring almost no infrastructure, and easy to transport and install on site the SR was practically the first widely adopted alternative solution of PCB treatment. In particular, in North America, France, and in Germany most of the PCB oil above 50 ppm has been treated by the SR technology.

Technology description and chemistry of related processes

The use of dispersed sodium for the reduction of organic compounds is known since the 1850s, when it was found that metallic sodium removes the halide from the an alkyl halide molecule to produce a sodium halide and a saturated aliphatic hydrocarbon. This process is generally described by the Wurtz reaction:

\[ 2RX + 2Na \rightarrow R-R + 2NaX \]

where R is the alkyl radical and X is the halide. In the case of a chlorinated compound, X is the chlorine atom. Basic reaction products mainly include various dehalogenated hydrocarbons with higher molecular weight (polyphenyls), and sodium halide. The reaction can also give small quantities of hydrogen as byproduct and, eventually, nitrogen. The organic products can be reused as oil or combusted. The inorganic products are typically recovered as sludge and disposed of in an appropriate manner.

In most SR processes, organic liquids (better low vapour pressure ones), containing the contaminant, e.g. PCB oil is mixed with a fine sodium dispersion in hydrocarbon oil (use of potassium and sodium-potassium allows is also known but is not common). Some proprietary promoters/moderators can be used by some technologies to increase the rate or to reduce polymerization. Typically the reaction is run in a standard batch stirred reaction vessel, unless in situ treatment is applied. The technology operates at atmospheric pressure moderate temperatures (normally between 80 and 180°C, depending also on the substance treated). Nitrogen blanketing may be used for safety. Other process streams, besides mentioned basic reaction products also include sodium hydroxide, water, and solidified polymers. After the treatment is complete the oil fraction is separated from salts and polymerized product.

SR processes can be mobile or can be easily made such. For the in-situ treatment the sodium dispersion is placed directly in the transformer containing oil. SR can also be coupled with other technologies for post-/pre-treatment, such as solvent extraction (to
extract contaminants from matrices and electrical equipment). For example Shinko Pantec, Japan uses bio-treatment of liquid SR effluents.

**Pre-treatment**

PCB oils may need to be extracted from equipment and the latter washed with organic solvents. Similarly the POPs which are solid or in the adsorbed state would need to be dissolved to the required concentration or extracted from matrices. Water should be removed by phase separation, evaporation, or other method.

**Post-treatment**

No or minimal post-treatment is required. Depending on technology such can include off-gas treatment and neutralization or conservation of residuals. The excess of sodium, if not neutralized, may need to be recovered. Liquid products, if not reused, and solidified polymeric products should be usually burnt in incinerators and inorganic salts would require disposal. Minor quantities of volatile organics in emissions can be captured by activated carbon.

**Process schemes and pictures**

> In-situ SR treatment scheme

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65 All figures are reproduced from presentation “Alkaline Metal Reduction” at the South American regional workshop on the environmentally sound destruction of POPs and the decontamination of POP containing waste in the framework of Basel and Stockholm conventions.
Advantages

- Equipment is simple in operation and portable
- Reductive environment and low temperature prevents dioxin formation
- Very low emissions
- Low cost
- Treated PCBs can be reused
- A developed class of technologies, available in various configurations on the market

Limitations, disadvantages, and concerns

- Limited to PCBs and liquid organic waste
- Can treat efficiently only diluted POP solutions in order to reach high DE
- Waste should be dewatered
- Dispersed metallic sodium reacts violently with water and other substances to produce explosive hydrogen gas; increased safety precautions should be taken for sodium handling during storage, transportation, and process operation
Principal information sources

2. UNIDO, 2001
3. UNEP, 2004a
4. UNEP, 2004b
5. UNEP, 2000
3. **Technology evaluation**

Chapter 3 together with Annex 1, which summarizes its results, represent the key critical part of this review. This part deals with the first attempt to classify and evaluate the technologies for POP destruction, according to their performance and other specific parameters. This evaluation and any comparison of technologies that can be derived thereby should be considered only as a tentative exercise to propose and validate the basis for such technologies comparison. Authors express their understanding that the information collected at the moment and their own expertise in this evaluation may appear insufficient to provide the exhaustive evaluation, which could be recommended for use as guidelines or a decision-support system. Nor this exercise can be considered as the authors’ expression of a prevalence of one technological option over the other. The evaluation was performed in a strictly independent and unprejudiced way, and the information, which laid the base for this analysis, was obtained, for the most part, from open sources. Therefore, authors do not take any responsibility if such information is missing, incorrect, incomplete or not-up-to-date. Authors also reserve their right to freedom of opinion and expression, as regards the individual viewpoints whenever a qualitative or theoretical/presumed assessment of certain aspects related to technologies is performed. It should be noted that according to such aspects the technologies could be compared only or mostly based on the individual expertise, because the quantitative data are often missing or are not applicable to such aspects.

This preliminary evaluation for now should be considered as a preliminary step towards a more detailed and proven analysis of technologies, to be accomplished in the future. For the completion and validation of the final evaluation it is expected that the technology representatives more actively collaborate on the provision of the state of the art data on their technologies and revise/confirm the existing evaluation data. It is also encouraged that the readers of this publication communicate to ICS-UNIDO his/her critical opinion and recommendations regarding the evaluation of technologies.

**Technology evaluation system outline**

Evaluation of a group of technologies against their some common denominators or the so-called evaluation criteria is a process that lays the base for creation of the DST. The evaluation process is intended to bring into numbers the most important technologies parameters and characteristics. By comparing these numbers or their combinations with the help of DST the user is given a versatile tool for evaluating a variety of aspects in which the considered technologies are expected to operate and perform, so whether one or another technology may be suitable for a particular application.

In order to build the evaluation system it is first of all necessary to identify common parameters of more interest to technology user and consecutively formulate the criteria that can adequately assess these parameters. In this case it is proposed to divide the evaluation criteria into four groups:

1. Classification
2. Technology options
3. Technical and precise data
4. Approximated comparison

The first group implies a formal and qualitative division of technologies in several groups for simplicity (each technology is assigned a specific group). There are several possible types of classification; however it was not necessary to adopt several of them within the same DST, but the only one which is more essential and closer to the scope of the decision-support tool. Among the possible types of classification, it was therefore chosen to consider the technology development status as the basic classification. The development status classification is based on several particular parameters/data, such as experience on the market, scale, etc. These parameters are also evaluated numerically against separate criteria within the third group of evaluation criteria (Technical and precise data). Other possible classification types can reflect physical or chemical nature of the process involved, such as the type of chemical reaction, heat, catalysis, as well as engineering process characteristics, e.g. containment, localization, etc. Their brief overview is given in the end of the dedicated chapter.

The second group (Technology options) of evaluation criteria is similar to classification, but this evaluation is more flexible as each technology can appertain to one or more groups within the same evaluation criterion. Two such criteria are considered, namely waste type applicability and configuration (e.g. technology mobility/transportability and scalability options). As in the case of classification criteria, only binary numerical evaluation can be made, e.g. each technology can be scored either one or zero according to its belonging to one or another group. Notwithstanding their qualitative nature, these criteria constitute the primary evaluation stage as they allow the user to see which technologies can suit particular application project before any detailed assessment of technical parameters is made.

The third group of criteria comprises the true numerical criteria intended to assess various quantitative aspects of technology performance, efficiency, cost, etc. The evaluation of technologies against these criteria is usually performed on the 10-grade scale (e.g. each technology is assigned a number from 1 to 10). The technical criteria are based on precise numerical data, such as the destruction efficiency percent, cost values, years of operation, percent concentrations of compounds, etc. This group of criteria is principal in the DST (there is no need of computer support for the former two), however it is where there is more lack of data. In fact many criteria are given simplified scoring (e.g. 2, 4, 6, 10 or 2, 6,10) and many technologies cannot be assessed at all. The difficulty of technology scoring according to these criteria is that of defining, even approximately, the common conditions under which the numbers (parameters) should be considered, as usually the reported numbers correspond to other different conditions or are absent at all, or not applicable for some technologies at chosen common conditions.

The criteria considered within the fourth group are similar to the ones of the third group by structure of scoring. The difference is that these criteria aim at the evaluation of more complex technology characteristics, where a single criterion cannot be supported by a singular parameter but comprises a group of different parameters. Often, these criteria are not only based on numerical data but should account for various qualitative aspects, e.g. safety/risk, ease/difficulty, etc. Therefore the scoring cannot be linked to the reported precise data only, but should be based on expert evaluation.

A soon as every technology is rated according to all criteria foreseen in the system, the DST can be build by incorporating these ratings and providing an algorithm to manipulate them. The proposed structure of the selection algorithm is presented in chapter 4. The current chapter gives an insight into the evaluation structure and provides justification of the choice of all proposed criteria, also including explanation of the scoringscale and review of related original data.
Technology classification types

Technology development status and experience

In this review the technologies are grouped according to the four general categories, as follows:

1. **Established** – Technology is on the market with a long period of full scale experience

   This group is represented by the technologies which have been proven efficient in large scale application projects over several years and which are currently available on the market in the full scale configuration. These technologies therefore conform to the existing regulations, e.g. as regards DRE, and hold national licenses for POP waste treatment. The performance data and other related technical information should be adequately documented and available as regards cost, treatment efficiency, etc. For this category a technology may not have treated substantial quantities of POPs on a commercial scale, but there must be well documented evidence (e.g. demonstration projects) of its capability to treat POP waste.

2. **Emerging** – Technology in the beginning of commercial operation

   Technologies with modest commercial experience of POP treatment or those recently commercialized belong to this category. These technologies are usually available in medium-to-full scale configurations, but there are usually no sufficient data at the moment to fully document and confirm the effective full scale performance. It is sometimes possible that no full scale units have ever been installed, or there has not been feedback from recently installed facilities, however the trial tests should adequately prove their efficiency for POP treatment. Even if no full scale experience exists, such technologies can be considered to be available immediately or in the short term to address full scale POP treatment projects.

3. **Transition** – Technology that can be commercially applied for POPs destruction

   This category encompasses mature commercial technologies or those at the beginning of commercial operation, which were not originally designed for POP stockpiles destruction, but that are likely to suit this application “by design” (usually, there are little or no practical data but it appears possible in view of theoretical considerations). The definition of “transition” therefore derives from a potential of such technology to adapt to a new application rather than from “transition scale”. Such technologies do not fit emerging nor promising categories, because the emerging technologies are those demonstrated efficient for POP stockpile destruction, and the promising are those operating on the lab or pilot scale only.

4. **Promising** – Only pilot or laboratory tests completed

   These are the technologies for which it is difficult to estimate when the commercial full scale units will appear. These technologies have operated on the bench or pilot
scale, therefore few data on their performance is available. These can also be the technologies which have been recently commercialized (by commercialization it is often meant designing a processes, its patenting, and establishing a legal entity to license the technology), but still do not have other than pilot experience, therefore there is no data available to proceed with evaluation of the most important criteria in this review (e.g. DE, DRE, throughputs, POP strength). Possibly these technologies may have been demonstrated or operated for treatment of other chemicals on the small or pilot scale, but were not tested for POP treatment. It is also possible that certain limitations do not allow that they be directly applied to POP treatment, but it can be thought that, given necessary upgrade, this possibility can be considered feasible. Technologies (methodologies) in the research phase are not considered, except those where significant progress was made towards technological development (pilot pant construction and process patenting, tests with real objects, etc.) For such technologies only tentative or approximate assessment can be made, so the rating of certain criteria will be indicative or some criteria cannot be included at all, such as costs, application experience, DE/DRE, etc.

To reassume the above considerations the general scheme for technology status definition presented in the table below may appear useful. There are four basic criteria to take into account, namely technology commercial status (e.g. availability as of commercial product), scale (of existing units), applicability proof (to POPs), and detailed data availability and reliability (information on the above-mentioned and other aspects of the technology).

<table>
<thead>
<tr>
<th>Status</th>
<th>Commercial status</th>
<th>Scale</th>
<th>Applicability proof</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Established</td>
<td>established</td>
<td>large</td>
<td>applied</td>
<td>available</td>
</tr>
<tr>
<td>2. Emerging</td>
<td>emerging</td>
<td>large/medium</td>
<td>applied/demonstrated</td>
<td>recent/limited</td>
</tr>
<tr>
<td>3. Transition</td>
<td>established/emerging</td>
<td>large/medium</td>
<td>theoretical/trial</td>
<td>limited</td>
</tr>
<tr>
<td>4. Promising</td>
<td>none/neo-commercialized</td>
<td>lab/pilot</td>
<td>trial</td>
<td>limited/available</td>
</tr>
</tbody>
</table>

The 15 technologies considered in this review are classified as follows:


BCD GPCR PLASCON SR
Ball Milling SCWO SET
CerOx GeoMelt PACT MSO PWC
HydroDec Silver II SPHTD

Justification

The classification of technologies and the above-mentioned definitions of categories are indicative and were elaborated for the current review only. The proposed classification categories do not follow any official standard and were designed in order to reflect the general development of technology, since it usually means availability and reliability of data and therefore indicates the extent to which the evaluation of technology is reliable. Previously made attempts of classification according to technology development were also taken into account, e.g. see a recent review by the Scientific and Technical Advisory Panel (STAP) of the GEF\textsuperscript{66} and a document by the Technical Advisory Group (TAG) for the global UNIDO project.\textsuperscript{67}

\textsuperscript{66} UNEP, 2004a.
\textsuperscript{67} UNIDO, 2001.
Established

The BCD and GPCR processes are both successful examples of an innovative technology for the chemical treatment of POPs. The GPCR process is commercially licensed in Japan, Canada, USA, Australia and was in the full scale commercial operation for 10 years. The BCD technology operated in USA, Australia, Mexico, Spain, and Czech Republic. There is a lot of documentation available on both technologies and a good record of their full scale operation for the treatment POPs, since the early 90’s.

PLASCON is the only one of 3 plasma arc processes considered in this review, which is recognized as commercially established. All three processes (PLASCON, PWC, and PACT) have operated on the full scale for a long time and technically seem to have equal capabilities of destroying POPs, however only the PLASCON process has had enough full scale experience of POP treatment. The PLASCON process has been in commercial operation in Australia since 1992\(^{68}\). The first units were installed at a chemical company to destroy a waste stream containing organochlorines. In the early 1998, a PLASCON unit was installed at BCD Technologies, Brisbane, to destroy concentrated PCB liquids.\(^{69}\) Now, PLASCON is a well established technology proven for treatment of PCB, ODS, and other waste types.

A variety of Sodium Reduction (SR) processes can be considered as a single technology in this review, because of the simplicity and similarity of the process in all its configurations, even though the technology was commercially licensed by different vendors. Most SR processes are specially designed for PCBs and have a long history of commercial operation. Being the most simple, SR is also the oldest solution for PCBs treatment, which has commercially operated for nearly 20 years in a number of countries (Canada, Germany, USA, South Africa, Japan, etc.).

Emerging

The second category comprises 3 technologies: Ball Milling, SCWO, and SET. Ball Milling is represented by two different technologies offered by different companies, namely the MCD process by EDL (New Zealand) and the DMCR process offered by Tribochem (Germany). The Ball Milling falls within this category mainly because of a significant progress by the MCD process in the recent years. A full scale project is underway since 2004 which deals with the remediation of a highly pesticide contaminated site in New Zealand using this technology. DMCR utilizes essentially the same chemical principle as MCD, but operates on the pilot scale. It has been demonstrated in small scale projects and trials to be capable of destruction of various POP wastes.

SCWO technologies (several vendors exist), even if sometimes considered developed (read: “commercialized and with considerable experience” in the STAP review), are given “emerging” as there are only pilot/medium scale units capable of concentrated POP treatment. According to recent information,\(^{70}\) a commercial scale SCWO unit has recently begun operating in Japan and another process has been recently approved for use in the US Chemical Weapon Programme. Bench/pilot scale tests have been performed for PCBs, chlorinated solvents, and pesticides. According to some sources, there is a SCWO plant by SRI International in Japan for PCB treatment that operation since 2002.

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68 CMPS&F Environmental, 1997.
69 Rae, 1999.
70 UNEP, 2004a; UNEP, 2004b.
The SET process developed by Commodore Applied Technologies operates commercially in the USA since 2001\textsuperscript{71,72} and has a long history of pilot/demonstration scale in the USA. In 1996, the SET was given a national permit by US-EPA for the PCB treatment in soil and later on for PCB oils.\textsuperscript{71} The technology is well documented, also regarding POP destruction, including high strength. However, the experience of stockpiled POP treatment is limited (mainly soils have been treated). There is mention of the vendor’s delisting from the American Stock Exchange for a number of reasons.

Transition

The five transition technologies are CerOx, GeoMelt, MSO, PACT, and PWC. These technologies have either operated on the full scale (GeoMelt, PACT, PWC) or are in the phase of scale-up (CerOx, MSO).

The CerOx technology is operating commercially in the USA for 4 years; since then, 2 small-to-medium scale systems for mixed waste treatment have been sold in the USA (University of California Irvine and at Merk in New Jersey). The technology can be considered in principle applicable to high strength POPs. However the efficiency of CerOx technology towards POPs destruction is uncertain, because only laboratory scale validation tests of POP destruction have been documented by now.

The AMEC’s GeoMelt process is operating on the commercial scale in the USA, Australia, and Japan since the early 90’s for the destruction of a range of contaminants in soils. However, the considered in this review ex-situ in-Container Vitrification (ICV) configuration, which was designed for remediation of highly contaminated soils and which is applicable to concentrated POP if mixed with soil, appeared in the end of nineties. The process was proven to destroy POPs, but only limited trial data exist on POPs treatment, which mainly refer to very low levels of PCBs in soil (ppb and ppm) and one test with 33% HCB.\textsuperscript{73}

MSO technology is sometimes considered “least developed” or demo scale (TAG document) or as “near or at the start of commercialization” (STAP review), which is true if to consider POP treatment. In fact, only few bench and pilot scale trials have been performed for HCB, chlordane, and PCBs. However, according to the vendor and DOE documentation\textsuperscript{74} this technology operated on the commercial scale at least since 1997 (mainly for heavy metals), and there are several facilities installed for the US Army, and one in the Republic of Korea. No mention of the full scale POPs treatment has been done.

The PACT process developed by Retech is offered under different names by other licensees in USA and Europe. The experience of full scale operation dates back to 1997. PACT can be considered commercially established technology. The process was demonstrated capable of treatment of HCB at low level which is the only reported data on POPs.

PWC by Startech is another plasma arc technology. It was reported that PWC is commercially available in the USA since 1996, and that the process has been in demonstration in Canada since 1989.\textsuperscript{75} It was also claimed that the PWC systems can be suited for the treatment of POPs, such as PCBs and hexachlorobenzene (HCB). In 2003, the Startech signed a contract with a Japanese company for the destruction of incinerator ashes and PCBs. However, it is not clear whether the destruction tests have been performed, and

\textsuperscript{71} Vijgen, 2002.  
\textsuperscript{72} UNIDO, 2001.  
\textsuperscript{73} For example, see [Vijgen, 2002], [UNEP, 2004a], etc.  
\textsuperscript{74} US DOE, 1997. See also LLNL website: http://www-cms.llnl.gov/s-t/molten.html  
\textsuperscript{75} CMPS&F Environmental, 1997.
no data on DE/DRE could be found. The process can be considered as established and commercial, but reports on the full scale experience of POP treatment are absent.

**Promising**

Three technologies are considered promising, namely HydroDec, Silver II, and SPHTD. These technologies have operated only on the laboratory or pilot scale by now, but which can be included in this review, because a lot of research has been done demonstrating the unquestionable efficiency of the related processes for POP destruction and the first steps have been undertaken towards prospective commercial operation.

SPHTD is a technology in the research/early development phase. Its development is carried out in the University of Cagliari, Italy. The technology was proven with concentrated POPs, but the existing experience is limited to the lab scale, and the available documentation to scientific results. The process cannot be considered commercial.

The HydroDec was formerly known as *Catalytic Hydrogenation*, which was a technology for PCB treatment developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) of Australia with the assistance of industry partners. The former name still appears in some documentation on the process. CSIRO then granted to Virotec the license to commercialize the HydroDec technology, which was announced commercial in 2004. However, no detailed information on technology performance and its technological arrangement has been made available till now.

As a rule, the technologies that have been or being developed with the focus on POP destruction are considered “promising”, exception being Silver II, offered by AEA Technology group. Silver II is a technology for general organic waste treatment, similar by principle to the CerOx process. It is sometimes called a commercial technology, but should be rather considered promising in the POP context as there are no data on its application to POPs and very scarce data on technology operation in general (missing cost details and documented full scale projects).

**Experience of operation in developing countries**

All 15 technologies have been originally developed applied in developed countries. The criterion of successful technology operation history in the developing world can be complementary to the classification by technology development status. This criterion should help to identify the ease or capability of a technology to be transferred to a developing country. Such experience, present only for few considered technologies, should also appear a useful criterion to validate the proof of a technology to operate in remote areas, or in areas with poor infrastructure. It is therefore another criterion to assess the maturity of technologies. The technologies are divided in two groups, namely those that have operated in developing countries or countries with economies in transition (see table below) and those that have not operated in these countries.

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76 Usually, the infrastructure is represented by a number of external supply facilities which are not included in the configuration but which are required for technology operation, such as electricity, water, natural gas, etc. Technologies that depend on infrastructure are usually installed on industrial sites and cannot operate in remote areas.
According to technology documentation and various reports, BCD currently operates in Mexico and Czech Republic. A SR technology by Fluidex Engineering Ltd. operates in South Africa. A PWC by Startech was sold in Taiwan in 1999 to process chemical industry hazardous waste, as reported by the vendor.

### Process typology

Other possible classification types of the considered technologies and processes involved are proposed below. Classifications by type of chemical reaction of waste destruction, its heat, catalytic nature or type of external mediation, and localization are given. These classifications reflect the chemical nature of the processes and are usually of little practical interest to the user; however it is always useful to keep in mind the general principles of chemistry involved in order to better understand differences and similarities in performance of these technologies.

#### 1. Chemistry
- **Reduction**: Ball Milling, BCD, GPCR, HydroDec, SET, SPHTD, SR
- **Pyrolysis**: PACT, PWC
- **Oxidation**: GeoMelt, MSO, PLASCON, SCWO
- **Electrochemical oxidation**: CerOx, Silver II

#### 2. Heat
- **Thermal**: BCD, GeoMelt, GPCR, MSO, PACT, PLASCON, PWC, SCWO, SPHTD
- **Non-thermal**: Ball Milling, CerOx, HydroDec, SET, Silver II, SR

#### 3. Catalysis
- **Catalytic**: BCD, CerOx\(^{77}\), HydroDec, Silver II\(^1\)
- **Non-catalytic**: Ball Milling, GeoMelt, GPCR, MSO, PACT, PLASCON, PWC, SCWO, SET, SPHTD, SR

#### 4. Mediation/activation
- **Electricity**: CerOx, Silver II
- **Plasma**: PACT, PLASCON, PWC
- **Chemical energy\(^{78}\)**: SET, SR, SPHTD
- **Mechanical**: Ball Milling
- **Catalysis**: BCD, HydroDec
- **Heat**: GeoMelt, MSO, SCWO GPCR

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77 The mediated electrochemical processes (CerOx and Silver II) can be defined as pseudo catalytic since the reagent (metal cation) in is recovered and enters in the reaction turn after turn, constituting thereby a closed cycle similar to that of a catalytic process. The difference is that this cycle is realized artificially by connecting two reversed reactions which occur independently, while the true catalytic cycle should occur in the same reaction medium and in the self-sustainable manner.

78 The reaction between reagents is spontaneous (e.g. sodium processes) and exothermic. Even if the reaction is not spontaneous under normal conditions but highly exothermic, once the reaction is initiated (e.g. the self-propagating reaction is initiated externally) the produced heat is more than enough to sustain it.
Technology options

The technology options is a group of criteria that show if the technology is able to address one or another (or several) mode of application. These options can be, for example, categories of waste that the technology can treat (solid or liquid, organic or inorganic, etc.), or mobility/scalability configurations (portable, fixed, modular). Each waste category or technology configuration constitutes a criterion against which the technology is scored on the binary scale (1 or 0).

Waste categories

Only the technologies that can be soundly applied to the destruction of POP stockpiles are considered, i.e. those able to treat pure POP or concentrated organics containing POPs. In the latter case the POP waste can be mixed with other organic or inorganic matter, like soil or debris, organic solutions (PCB liquids or POP extracts).

General and direct applicability issues

The “general applicability” refers to the original state of the POP stockpile to be treated. The following limitations apply to the choice of technology for this review vs. its general applicability to POP. This review does not address technologies which are only applicable to POP contaminated matrices, e.g. soils with low POP content (less than 1%), gaseous emissions, or contaminated water. However, there are many technologies which are applicable to both concentrated POP and other matrices with low POP content. In such cases, the additional applicability can be a bonus that also needs to be evaluated since soil remediation should often accompany the treatment of the concentrated POP stockpiles. On the other hand, this review includes several technologies that treat only low POP content waste (lower than 1%), in the case if such waste is represented by the bulk organics like PCB liquids, because even diluted PCBs are normally referred to as a stockpiled POP waste.

Thus, the technologies selected for this review in their current development state/configuration or within a reasonable period of further development should be capable to treat one or more of the following types of POP waste (considering the limitations above):

1. Solid POPs – pure chemicals or in mixtures with other organics
2. Liquid POPs – PCB oils and liquids, organic solutions or liquid organic waste containing POPs
3. POPs mixed with inorganic matter

On the other hand, for some technologies it can be required that certain POP stockpiles are pretreated before destruction. For example, it can be dissolved or diluted or mixed with a reagent or other material. Such pre-treatment can be integrated in the plant or can require significant waste handling. In the latter case, it cannot be considered a part of the process. As long as the necessity of such treatment can be critical due to additional cost, risk, and/or other factors, it can be useful to consider the “direct applicability” as another criterion for evaluation. The direct applicability refers to the state in which the POP waste can be loaded in the process, without further handling.

Considering the definition of “direct applicability”, the following 7 categories were adopted in this review to evaluate the applicability options of technologies:
1. Solid organic matter
2. Oils and organic liquids
3. Inorganic solid bound (1 or 2 containing inorganics in any proportion)
4. Slurries (1 or 3 in a form of a pumpable slurry)
5. Humid (any of 1-4 containing small amount of water)
6. Aqueous (aqueous liquid containing 1 or 2)
7. Gaseous

Please note that the categories above can complement each other, so that the user can define more precisely a type of waste of interest by selecting more than one categories. For example, the pure PCB oil is assigned category 2 (all technologies applicable, except SPHTD), but the same oil containing water would conform to categories 2 and 5. In this latter case, Ball milling, MSO, SET, and SR technologies could not be applied to such oil and should be excluded form consideration. If the same oil is mixed with soil, categories 2, 3, and 5 apply. In this case, HydroDec, PLASCON, and Silver II are excluded and the remaining technologies are only SCWO, PACT, PWC, GPCR, BCD and CerOx.

Bearing in mind that many technologies can be applied to the treatment of more than one type of waste and that complex treatment is required for the majority of waste treatment projects (e.g. destruction of stockpiles together with remediation of surrounding territories) this criterion foresees a possibility to choose more then one option for a single technology. Moreover, even though soil remediation and water or gas treatment are not within the scope of this review, these options are also included. However, it should be noted that the evaluation data on technology performance discussed below in this review (e.g. DE, DRE, throughput, etc.) refer to the cases when the technology is applied to the concentrated POPs, and not to the treatment of gases and watery waste streams.

The detailed descriptions of particular categories are given below.

**Category 1: Solid organic matter**

Solid organic POP waste is usually represented by pesticides, which can be stored in containers, landfills, piles, etc. Such solid organic POP waste can contain only small content of inorganics, but can have other organic impurities which normally do not interfere in the treatment process and do not decrease its efficiency. Organic liquids or water can be present in small quantities; given that the state of the matter remains solid and not slurry or liquid. Slurries are considered in a dedicated waste category.

Seven out of fifteen technologies are applicable to bulk solids, namely: Ball Milling79, GPCR, MSO, PACT, PWC, SET, and SPHTD. The other eight technologies (SR, HydroDec, GeoMelt, PLASCON, CerOx, SCWO, BCD, and Silver II) cannot treat directly solid organic matter, which either has to be dissolved in organic liquid (SR, HydroDec) or be a pumpable slurry in water or organic liquid (PLASCON, CerOx, SCWO, BCD, and Silver II). In the case of GeoMelt, neither solid nor liquid waste can be treated directly, as it should be mixed with soil.

79 Ball Milling technology is classified as applicable to bulk solids or liquids only with reference to the DMCR process by Tribochem, while the MCD process by EDL is designed to treat soils with low POP content (max 2% POP reported).
Some technologies that are considered not directly applicable to solids can be in principle applied to solids, but after proper pre-treatment. For example, SR and HydroDec processes, which are designed for treatment of PCB liquids and oils, can be in principle applied to solid organic POPs if these are dissolved in organic solvents. SCWO and MEO technologies (CerOx and Silver II), which only treat fine aqueous slurries or emulsions of organics in water, can process solid organics in the case these are finely suspended in water, e.g. using a sonicator in the case of CerOx process. BCD and PLASCON can also treat pumpable slurries, if the solid organics is suspended in organic solvent.

**Category 2: Organic liquids**

This category refers to any organics in the liquid state, such as PCBs (oils and liquids) and other liquids contaminated with POPs, like solvent extracts of contaminated soil, liquid waste streams from organochlorine industry, etc.

Almost all technologies considered in this review are capable to treat liquid organic waste. Usually, there are no limitations for liquids treatment if the technology is able to process solids; moreover, liquids are usually more easily fed into the reactor. Only two technologies out of fifteen appear not to be applicable to liquids, namely GeoMelt and SPHTD. The reason for GeoMelt is the same as for the organic solids, as this technology can only treat organics mixed with a material that forms a high temperature melt, e.g. soil or sand. SPHTD is a self-propagating process based on the reaction between two solids. In principle, liquids can be processed if adsorbed on a solid material.

**Category 3: Inorganic solid bound**

Any solid or liquid POP waste mixed with or containing suspended inorganics, which are inert to chemical treatment, belong to this category. Such waste can be sludges, sediments, contaminated soils, sand, or stockpiled bulk organic waste containing debris or soil. In the latter case, the inorganic impurities present in relatively big quantities in the bulk organic matter (e.g. 1% and higher) can compromise the functionality of some technologies which are designed only for bulk organic treatment. Technologies, which tolerate the presence of inorganics in the reaction unit, and those, which are provided with the necessary pre-treatment units to separate organics and inorganics, belong to this category.

For many technologies this option is possible using dedicated additional modules, different plant configurations, etc. As far as the demand for soil remediation is usually much higher than for destruction of bulk organics, many technologies considered in this review have been originally developed for soil treatment or such option is foreseen among principal applications.

Nine technologies are able to process contaminated soils, but only six can treat soil without pre-treatment, namely: Ball Milling, GeoMelt, PACT, PWC, SCWO, and SET. BCD and GPCR are equipped with thermal desorption modules. In the case of CerOx, the soil should be finely homogenized in water using the provided sonicator.

**Category 4: Slurries**

Slurries of any solid matter (organics or inorganics or their mixtures) in water, organic solvent or oil are considered within this category.
Usually, the technologies can treat slurries if they can treat liquids, either organic or aqueous, so this category would be superfluous if there were not HydroDec and SR technologies, which seem not to be directly applicable to slurries. However, the obstacle in the case of these two technologies appears not critical if the solid content can be removed by filtering. In addition to these two, the technologies not applicable to slurries are GeoMelt and SPHTD, as they are not applicable to the waste in the liquid state. The rest of technologies are applicable to slurries.

Some limitations can apply. In particular, MEO processes and SCWO can only process fine pumpable slurries of solids in water, PLASCON and BCD can only process slurries of solid organic matter in organic liquids.

**Category 5: Humid or water containing waste**

Any type of waste (solid or liquid), which is humid or containing a small amount of water, sometimes just trace quantities. The threshold water content is dependent on the technology. Some technologies claim that they dispose of special dewatering plants, however, it is not always clear whether and how these units affect cost, throughput, or if are limited to certain types of waste (e.g. only solids). Therefore, this category considers only technologies that are intrinsically applicable to humid waste (by their chemical nature).

Six processes out of fifteen cannot process humid waste, namely: MSO, Ball Milling, SPHTD, SET, and SR. In the case of MSO, the water can react explosively with molten salts. In the processes based on the solid state reactions, i.e. Ball Milling and SPHTD, the presence of water would impede the reaction, because water absorbs the heat and vigorously reacts with the reagents (CaO or Mg are used in Ball Milling and Ca or CaH$_2$ in SPHTD). The same is true for SR and SET, where water would violently react with sodium.

The limit of tolerable water content depends on technology. For processes running in non-aqueous phase the lower water content normally leads to a better performance, however, in some technologies, for example the SET process, the water content should be balanced, since the reaction can involve water.

**Category 6: Aqueous streams**

Aqueous waste streams containing POPs, diluted in water or suspended/emulsified, coming from production processes, waste waters from settling systems, or agricultural wastewaters containing water soluble pesticides, e.g. coming after remediation activities, irrigation run-off waters, or pesticide solutions.

Six processes can treat aqueous solutions, namely: BCD, GPCR, PLASCON, CerOx, Silver II, and SCWO. The last three operate in the aqueous medium. BCD is tolerant to water (e.g. the alkali is fed in the BCD reactor as an aqueous solution). GPCR is usually referred to as applicable to aqueous waste, but such waste should be pre-heated before treatment. PLASCON process also can treat watery waste which is injected in the plasma arc and evaporates.

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80 The SET process includes a dewatering system for the waste with water content over 40%.
The other nine technologies are not compatible with watery waste, and for six of them this issue was addressed in the description of the humid or water containing waste category (see above). Other three are HydroDec, PACT, and PWC. According to the available information, HydroDec process is designed for treatment of organic solutions, but there is no mention on possibility to treat aqueous waste. Unlike PLASCON, other PAT processes (PACT and PWC) are not compatible with aqueous waste, because the dense water conducts electric current and renders the plasma arc treatment ineffective.

**Category 7: Gaseous streams**

This category addresses any gaseous stream, where the chemicals to be treated are present in the gaseous state, as aerosols or vapours. These can be effluent gases containing hazardous chlorinated substances in the gaseous state, like the ones coming from some organochlorine industrial processes, incinerators, etc. In particular, gaseous emissions can contain unintentionally produced POPs, such as dioxins, furans, PCB and HCB.

Few technologies considered in this review have been originally designed to treat POP containing effluents. Such an option, even if present for some technologies, does not appear economically justified comparing to afterburners and other post-treatment technologies specially designed to treat microamounts of POPs. Even though the gaseous streams containing high POP content are not common, this option can be useful for destruction of other halogenated hazards, such as ODS, TCE, light chlorinated solvents, or be coupled with other processes, such as thermal desorption of contaminants from soils.

The three processes that can treat gaseous streams are those operating in the gaseous phase, namely GPCR, PWC, and PLASCON. Among PAT technologies, only PACT cannot process gases, which is a vitrification process. The PLASCON process is designed for gaseous waste treatment, such as halon and CFC wastes. PWC can also process gases. GPCR is based on the gas-phase reaction and is provided with a gas fed module.

The other processes in this review are based on the dense medium reactions and therefore are not likely to be applied to gases. In the CerOx process there is a gaseous reactor which destroys gaseous emissions coming from the primary liquid phase reactor, but it is not designed for the direct feed of gaseous streams.

The following table summarizes the direct applicability options of technologies:

<table>
<thead>
<tr>
<th>Technology</th>
<th>1 solid</th>
<th>2 liquid</th>
<th>3 inert solid</th>
<th>4 slurries</th>
<th>5 humid</th>
<th>6 aqueous</th>
<th>7 gaseous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BCD</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>CerOx</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GPCR</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>HydroDec</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MSO</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PACT</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PLASCON</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PWC</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>SCWO</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SET</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silver II</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SPHTD</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SR</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
As discussed earlier, the general applicability indicates at a general possibility to process a certain type of waste by the technology. In this case, a pre-treatment of the original waste may be required before the waste is treated. The general applicability of technologies to most common types of stockpiled POP waste is presented in the table below:

<table>
<thead>
<tr>
<th>Technology</th>
<th>Solid POP</th>
<th>Liquid POP</th>
<th>POP with inorganics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>BCD</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>CerOx</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>GPCR</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>HydroDec</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MSO</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>PACT</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>PLASCON</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>PWC</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>SCWO</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>SET</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silver II</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SPHTD</td>
<td>X</td>
<td>-</td>
<td>X</td>
</tr>
<tr>
<td>SR</td>
<td>-</td>
<td>X</td>
<td>-</td>
</tr>
</tbody>
</table>

### Technology configurations

The configuration options described here refer only to the technologies mode of operation applicable to POP stockpiled waste treatment. There can be surplus configurations provided for the same technology for waste types other than stockpiled POPs (e.g. inert solids, aqueous waste, or gaseous streams, see the chapter above) that are not taken into evaluation, unless such units can be considered as theoretically applicable to POP stockpiles, e.g. when a technology has not had any POPs treatment experience till now.

**Fixed configuration: stationary units**

If commercial, such units are usually large scale and are installed in the areas with well established infrastructure, e.g. on industrial sites. The fixed units can also be modular in nature (see below). Installing the fixed unit means that the plant is constructed by assembling parts or modules, building/connecting infrastructure and performing other activities that contribute to the costs other than transportation and may take considerable periods of time, which is not applicable in the case of transportable units. Therefore, the fixed plant is a non-portable plant by definition, though in some cases it can be shipped on site in its basic configuration or can be moved within the same site (skid based units). In the event such unit should be relocated to a different site, a new installation process will be required.

Fixed configuration option and other configuration options described below apply only if such units have been built and operated, or if the vendor offers such units, or if such units have been designed and are currently in construction. In the case a technology is still operating on the bench scale, the existing pilot units are assimilated to the fixed unit configuration.

All considered technologies have fixed facilities and are therefore positively scored against this criterion.
**Modular configuration:** units that can be assembled (and disassembled) or built up

This option refers to the technologies which can be assembled in a simplified way from blocks or modules that have been constructed beforehand and which represent consistent parts of the whole process. For example, the modules can represent units for different stages of the process, or pre- or post-treatment units. In other cases, the modules are designed to be joined to increase process capacity. The modular design is aimed to minimize fixed plant installation or to upgrade process activities and therefore to reduce costs.

This category can also comprise the so-called “modular transportable” or similarly named configurations, and it means that single technology modules can be more easily transported. In such cases the whole technology should not be confused with portable technologies (see below), unless it is indeed designed for mobile applications.

Ten technologies are available in modular configuration, namely: Ball Milling, BCD, GeoMelt, CerOx, GPCR, MSO, SET, PLASCON, Silver II, and SR. According to different sources,\(^{81}\) modular BCD and GPCR units have been built. For example, for BCD the modules can be joined to increase throughput. For GeoMelt, the components include electrical, primary treatment, and off-gas treatment modules; these modules can be also designed for various throughputs. In the GPCR process, different modules are provided to treat different waste types on feed. The CerOx and Silver II processes are modular in nature as they are based on a number of small capacity electrolytic cells which are put together in blocks. Such blocks constitute the modules of the process. The modular scalable facilities have been designed also for the MSO process.\(^{82}\) The SOLV process was developed as a modular transportable system, based around the central SET treatment module. Its other units 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. Ball Milling technology can also be called modular since the commercial MCD plant is delivered in the configuration of 5 to 8 modules that fit standard shipping containers. Also for the PLASCON process modules are designed for different process steps and allow a simplified plant assembly. Some SR processes are available as modules, e.g. in the BDS process the modules correspond to different process functions and it is possible to enhance the throughput by replacing single modules.

**Portable configuration:** units can be transported on site in their original form

Portable units, by definition, are non-fixed (mobile) units, which are complete and do not require assembling or installation. Minimal activities can be foreseen for mounting the technology on site. Sometimes such plants are already mounted on ships, trucks and do not require additional set-up. Since portable units are designed to be brought on site to remote areas they are often self-consistent and do not need infrastructure (electricity, water supply, etc.). Normally, portable units operate on smaller scale than fixed ones.

This option applies if availability on the market is documented, but not if such units are planned or designed. Please note that the concept of portability refers to the mobility of the entire unit and not to its transportability in general. Some fixed plants can be transported as modules or entirely but are not considered mobile. Only those units are recognized portable/mobile which are defined so by the technology vendor or it is stated so in other reliable and competent sources, whilst those units defined as “transportable” or “relocatable” are assigned only configuration in this evaluation.

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81 e.g. see [UNEP, 2004a].
For six technologies the existence of mobile (portable) facilities is confirmed, namely: BCD, GeoMelt, GPCR, PWC, SET, and SR. Normally, the mobile concept is present for the more developed and commercialized technologies, which have already been validated on the large scale and extend their market to remote and multiple small scale projects.

A semi-mobile GPCR unit is available as one truck-trailer unit plus another additional trailer unit for each TRBP. A portable scale (single container) plant is also available. The vendor states that the semi-mobile GPCR unit can be transported between countries, to storage locations for on-site treatment. It provides a throughput of 70 t/month for bulk solids and liquids and has lower capital and operating costs than the full scale plant.

A mobile BCD plant designed to treat liquids exists and has been used for treatment of pesticides, PCBs, etc. However, there is mention that this concept has not fitted well with permitting and economic aspects. Today’s BCD units are either fixed or designed as skid mounted re-locatable units.

For the SET process, experience of mobile operation is also confirmed. A SL-2 mobile unit was used for the treatment of PCB contaminated soil in Hawaii, as reported by vendor.

It was also mentioned that the PWC mobile systems have been developed. Installation of the first such system in Ireland was agreed in 2001. By now, data on its operation and/or on other systems are absent.

GeoMelt process is a true portable system. The mobile systems consist of an electrical power transformer, off-gas collection hood, off-gas treatment system, and process control system. All equipment is mobile (trailer mounted) except for the off-gas hood which is transported to the site and then assembled. However, the hood is only required for the in-situ GeoMelt soil remediation configuration, which is not considered in this review, and not for the ICV system.

There is a variety of SR processes, many of which are mobile or can be easily made such. The SR technology per se is an undemanding process, which can be easily operated on the mobile scheme without special arrangements or modifications. For example, the Powertech has a mobile plant that treats 15,000 L/day of PCB oil.

Among the nine technologies which are not available in portable configuration, five can be defined as transportable or relocatable, namely: CerOx, Silver II, PACT, PLASCON, and MCD. For example, the existing small scale CerOx units are self-contained, fully automated, skid designed, and transportable in the ISO standard shipment containers, but designed for permanent installation. The same is true for the Silver II process as the vendor claims that completely mobile and autonomous truck or skid mounted plants can be provided which are capable of being moved to deal with wastes at the point at which they arise. However, both CerOx and Silver II require considerable amount of electricity and therefore cannot operate independently in remote areas and cannot be considered truly portable. Such processes suit the category of transportable modular units which discussed above. PLASCON and

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83 UNEP, 2004a.
84 Vijgen, 2002.
85 Startech press releases, e.g. 27/02/2001, 17/01/2002, 06/06/2001, etc. see vendor website.
87 AEA Technology Products and Systems Overview, see http://www.aeat.com/prodsys/divisions/OCD.html
PACT processes also cannot be considered mobile. The smaller transportable PACT-5 units can fit into standard ISO shipping containers, but there is no mention of mobile operation. Transportable PLASCON units are defined as “relocatable centralized facility.” The modular configuration of MCD (Ball Milling) can be installed in the remote areas and operate in the autonomous regime, but is designed for permanent setup.

For the remaining four technologies (SPHTD, HydroDec, MSO, SCWO) no concept of mobile plants has been developed, mainly because the majority of these technologies are less developed. For SCWO and MSO it was mentioned that transportable units are currently under development.

**Scalable configuration:** units are scalable or different scale units are available

This option indicates the availability of a technology as of different scale plants, whether from the same or from different vendors, or as modular plants with a possibility of building up capacity by adding more modules. A technology is considered scalable also if at least two different scale plants have existed or if fixed and portable/transportable units of different capacity are available.

The technology is considered non-scalable if only one scale units have been built till now. Lab scale plants, plants which are planned but which have not been built yet, as well as the plants which exist but are not applicable for stockpiled POPs are not considered as an additional scale. The scalability as defined by this criterion does not refer to the possibility of the same plant to satisfy different loads of waste.

Most of technologies considered scalable, which are mainly commercially established or emerging technologies, i.e. which have operated on at least one pilot and one larger commercial scale. In some cases the scalability option is assigned because of the existence of more than one vendor offering different scale technologies (e.g. for SR and Ball Milling which represent technology classes and not single technologies). The same is true for the technologies for which an additional portable configuration is available (BCD, GPCR, PWC, SET) or which can be provided as modular units that can be joined together (CerOx, Silver II, etc.). For the GeoMelt technology, different capacity in-container systems are documented. PLASCON, PACT, MSO, and SCWO are all commercial technologies which have operated on different scales, including pilot units and one or more of larger scale commercial units.

Only two technologies are not considered scalable, namely: SPHTD and HydroDec. The former is still in the development phase and the latter is a neo-commercialized process for which the existence of commercial units was not sufficiently documented.

The above discussed available configurations of technologies are summarized in the table below:

88 CMPS&F Environmental, 1997.
89 UNEP, 2004a.
90 DOE, 1997.
91 This assumption, as well as that of considering pilot units as an additional process scale, is temporary and will be updated as more detailed information from vendors is collected. It is understood that only the commercial scale units that are currently available should be taken in consideration. However, for many technologies the available data do not clarify if the plants formerly documented are still in operation and if such plants are still manufactured.
Technology technical criteria

Performance criteria

DE

Destruction Efficiency (DE) is defined as the total mass of treated substance (POP in our case) $m_{\text{input}}$, fed into the process, minus the mass of the substance in all products, by-products and environmental releases $m_{\text{output}}$, divided by the total input mass (to give a percentage).\(^{92}\)

DE is different from the Destruction and Removal Efficiency (DRE), since the latter only takes into account the products in stack emissions (see next chapter). In other words, DE is the true conversion degree of the treated substance, i.e. a part of the initial amount of the original substance that was chemically converted into other substances, whether these substances are present in the gaseous, liquid or solid state.

$$DE = \frac{m_{\text{input}} - m_{\text{output}}}{m_{\text{input}}} \cdot 100\%$$

Both DE and DRE are usually expressed as the “number of nines”, e.g. 99,99% or 99,9997% that would be called “four nines” or “five nines”, respectively. DE is one of the main characteristics to consider in order to evaluate the technology efficiency. For classification of technologies according to this parameter the following scoring scheme is proposed:

<table>
<thead>
<tr>
<th>Score</th>
<th>DE, No. of nines</th>
<th>No. of technologies(^{93})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&lt; 2</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>5 ≤</td>
<td>5</td>
</tr>
</tbody>
</table>

Obviously, the DE value would depend on the type of waste treated, as well as on some other factors, such as configuration, scale, conditions, nature of feed, etc. Therefore, the technology does not perform uniformly for different waste types or under different conditions, and there are different data for different application projects or trial studies. Due to the lack of data it is usually impossible to produce scores for different technologies that would be normalized to a uniform waste type. In this connection, rough scoring scales

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\(^{92}\) UNEP, 2004a.

\(^{93}\) The number of technologies in the current review assigned the given score (see description below)
have been adopted for DE and other technical criteria reported below in this evaluation. In the case of DE, the five-level scale is adopted, namely only scores of 2, 4, 6, 8, and 10 apply (see the table above). Whenever more than one DE value are reported in the same or different sources, the minimum reported DE is considered for this evaluation, and preferably that one which has been obtained for a more concentrated POP waste, or for the chlorinated chemicals that can be assimilated to POPs. Preference is given to the data that have been obtained in the existing large scale units rather than in the pilot or laboratory studies.

Several particular principles and recommendations for selection of valid DE data are given below:

If the DE data on concentrated waste treatment is missing or is not applicable (for the maximum allowable concentration of POP in the feed see the “strength” criterion), the DE for non-concentrated bulk organic wastes (e.g. diluted PCB oils) are considered, but not the data obtained for contaminated soils or other inorganic matrices. The contaminated soils are often pre-treated in a separate unit to separate the contaminant, so the measured DE would correspond to the process of POP removal from soil and not to the main step where POP destruction occurs. Moreover, the POP substance can strongly adsorb on soil, therefore it would not be exposed to treatment to the same extent as the POP in bulk organics or in water emulsions.

If the same “threshold” remaining POP levels are reported for treatment of waste types with different POP concentration (e.g. 2 ppm remaining level is usually considered as sufficient by most legislations for PCB treatment), the waste of higher strength should be considered in the first place for calculating DE. The lowest DE for the highest performance would be obtained thereby, which is of interest for this review.

Please note, that DE is to be regarded as an indicative criterion which is valid only for evaluation of the efficiency of original waste destruction, but which does not take into account the risk of new POPs formation and other potential dangers related to the secondary waste coming from the process. In certain cases, such waste can represent more danger than the waste which is treated. Neither DE nor DRE reflect the degree of the mineralization of chlorine, which is an important factor determining the potential products toxicity and risk of new POP formation.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>DE (nines)</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>6</td>
<td>3</td>
<td>Data from vendor (EDL).</td>
</tr>
<tr>
<td>BCD</td>
<td>8</td>
<td>4</td>
<td>See for example [UNEP, 2004b] and vendor website.</td>
</tr>
<tr>
<td>CerOx</td>
<td>8</td>
<td>4</td>
<td>DEs are not less than 4 nines for chlorinated organic pesticides and other organic wastes [UNEP, 2004a].</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>2</td>
<td>1</td>
<td>DEs of the melt ranged from 90 to 99.99% [Vijgen, 2002].</td>
</tr>
<tr>
<td>GPCR</td>
<td>10</td>
<td>5</td>
<td>DEs of not less than 99.999% are reported.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>10</td>
<td>5</td>
<td>See [Costner, 1998].</td>
</tr>
<tr>
<td>MSO</td>
<td>10</td>
<td>6</td>
<td>Over 6 nines for PCB, HCB, etc. [UNEP, 2004a]</td>
</tr>
<tr>
<td>PACT</td>
<td>-</td>
<td>n/a</td>
<td>Vitrification process.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
</tbody>
</table>

94 See [UNEP, 2004a], BCD presentation at the South American regional workshop on the environmentally sound destruction of POPs and the decontamination of POP containing waste in the framework of Basel and Stockholm conventions, Brazil 2004, and other sources.

95 The DEs for vitrification processes are often not reported as it is difficult to quantify the undestroyed contaminant within the vitrified mass. Theoretically, the high temperature treatment of organic matter should transform any undestroyed organic content and the products of full or partial decomposition in the gaseous phase, where they are destroyed or precipitated in the post-treatment systems. However, in practice there is often a non-uniform or insufficient heating which results in residual POPs. It is also often assumed that any undestroyed waste present in the vitrified slug is immobilized and is innocuous, but this assumption can be argued.

96 DEs are unknown for PLASCON, as well as for the other PAT. In some cases (for PLASCON, as well as for some other technologies), the documented DEs seem to be confused with DRE, because both have the same magnitude. As a rule, DEs are far lower than DREs.
DRE

The Destruction and Removal Efficiency (DRE) is a relatively indirect measure of estimating process efficiency as it considers only the undestroyed original chemical present in gaseous emissions, and does not take into account other process streams (solid and liquid residues).98 However, the DRE can be useful for assessment efficiency of the so-called open systems, i.e. where the gas emissions are substantial and cannot be contained. For example, if the plant is installed in the vicinity to the habitation centres, the DRE can be a critical criterion in determining the public opinion. Moreover, as it was previously discussed the DE data for certain technologies are not reported, so DRE appears to be the only criterion to estimate process efficiency.

DRE is calculated in a similar manner as DE and is expressed by the following equation:

\[
\text{DRE} = \left( \frac{m_{\text{input}} - m_{\text{output gases}}}{m_{\text{input}}} \right) \cdot 100%,
\]

where \( m_{\text{output gases}} \) is the mass of the treated chemical (POP waste) in the gaseous emissions.

The reference table according to the number of nines is reported below:

<table>
<thead>
<tr>
<th>Score</th>
<th>DE, No. of nines</th>
<th>No. of technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4, 5</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>6 ≤ , or no emission</td>
<td>10</td>
</tr>
</tbody>
</table>

97 Other facts refer to the chlorinated solvents and PCBs, where the latter have been used at the highest of 500,000 ppm but the result is considered outcast (20 ppm remaining) because of insufficient sodium feed, as reported by the vendor.

98 For example, the Technical Advisory Group of the UNIDO global project for adoption and implementation of non-combustion technologies for destroying POPs express the following opinion on DRE: Total destruction efficiency (DE) is almost never reported or calculated for incinerators, cement kilns and other combustion technologies because these devices typically fail to achieve high total destruction efficiencies. Rather, most regulatory agencies only require a measure of the so-called “destruction and removal efficiency” (DRE). This measure only takes into account contaminants that are present in the stack gases (air emissions), but ignores toxic contaminants of concern released as solid and liquid residues (as waste ash and waste water). Modern incinerators achieve high reported DREs by using filters, scrubbers and other stack gas cleaning devices to capture pollutants of concern, remove them from the device’s gaseous emissions, and transfer them to solid waste and/or liquid waste residues. As a result, when only a device’s DRE is considered, and when a measure of its total DE is avoided, this encourages the selection and deployment of technologies that transfer contaminants from stack gases into other media (water and ground). The use of DE as a measure, on the other hand, encourages the selection and deployment of technologies that efficiently destroy and eliminate POPs and other organic pollutants.” [UNIDO, 2001]
It can be noted that the scoring system for DRE is more demanding to the number of nines than that for DE. This is connected to lower remaining levels of pollutants in gaseous emissions than in solid or liquid residues. At the same time, the scoring system for DRE is rougher than that for DE. A two-level scoring scheme is adopted using the common 10-grade scale, since the DRE of most technologies do not differ substantially. There are no technologies performing below four-nines DRE which could be defined as “insufficient”; four- and five-nines DRE can be recognized as “approaching to standards” and there are only three of such; the rest show six or more nines and are recognized as “sufficient”.

As far as the regulatory limits for DRE of hazardous waste destruction facilities in developed countries are usually 6 nines (e.g. in the US), almost all technologies are “adjusted” to this value. The at least “six-nines” DRE is often considered indisputable for the “closed” technologies (not producing emissions). However, even closed or very clean technologies can perform differently with different types of waste or on different scales. Many technologies declare the possibility to treat concentrated POPs, however the related DRE/DE are not reported or such experiments if any refer to the trial scale. For some technologies DREs are simply unknown.

There are five technologies for which the reported tests confirm the minimum 6-nines DRE (BCD, GPCR, MSO, PLASCON, SCWO). Please note that most “open” technologies, for which over six-nine DREs are reported, are equipped with scrubbers and other post-treatment devices that assure these high DREs, but the technologies usually do not conform to these levels in the off-gases before post-treatment. This implies a certain risk of POP emission when there is malfunctioning of the post-treatment system. This issue is partially considered in the containment criterion given below.

There are five closed technologies (CerOx, SET, Silver II, SPHTD, SR) which have been also evaluated as “over six-nines”. These technologies produce small amounts of emissions and therefore cannot reach high DRE. Even if the percent of the original POP chemical in the emissions can be high (this is to be considered in risk criteria), the content of the chemical in the emissions with respect to its original load is very low. It should be borne in mind that for some of closed technologies the six-nine DRE is assumed a-priori, because the real data are unavailable, for example, for the processes which have not been tested with the concentrated POPs (Silver II, CerOx) or for those still in the development phase (SPHTD). Therefore, it is difficult to estimate the extent to which the DRE of closed technologies differ from one another. For some closed technologies the situation can differ depending on configuration or provider. For example, the only available data on Ball Milling technology comes from EDL, whose MCD plant is configured for soil treatment. In this process only “four-nines” DRE was demonstrated, since the emissions probably arise from the stage of soil preheating, i.e. before chemical treatment. On the other hand, the Ball Milling process from Tribochem (DMCR) when applied to solid POPs or PCB liquids should not produce significant emissions. However, the latter process is still in development and no relevant data on DRE are available, so only the data on MCD are taken into account.

The two technologies that according to available data perform below “six-nines” DRE are GeoMelt and PACT. It was not possible to evaluate whether progress has been made recently to improve the post-treatment systems in order to reach the “six-nines” DRE. For example, it was mentioned that the DRE performance of the recent PACT plants was improved, but no well documented data could be found. The GeoMelt process is designed for soil treatment and is not capable of processing concentrated POPs. The reported DRE for this process vary from four to six nines, but the real DRE would probably depend on the concentration of the POP chemical in the feed.
The DRE scoring data and references are summarized in the table below:

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>DRE (nines)</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>5</td>
<td>4</td>
<td>Data on MCD performance with EPA hazardous waste (RecraWasteCharacterization) as reported by vendor (EDL).</td>
</tr>
<tr>
<td>BCD</td>
<td>10</td>
<td>6</td>
<td>DRE exceed the US Federal, State, and Territory requirements for solid treatment of PCB contaminated materials (&gt;99.99999%) as reported by vendor.</td>
</tr>
<tr>
<td>CerOx</td>
<td>10</td>
<td>n/a</td>
<td>No data reported. Closed non-thermal process.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>5</td>
<td>4</td>
<td>DRE, after the gas post-treatment are in the range of 99.9999999% [Vijgen, 2002].</td>
</tr>
<tr>
<td>GPCR</td>
<td>10</td>
<td>6</td>
<td>See for example [UNEP, 2004a].</td>
</tr>
<tr>
<td>HydroDec</td>
<td>*</td>
<td>n/a</td>
<td>No data reported. Cannot be considered “closed” or “zero-emission” as it is stated that gaseous emissions exist, but they are recycled and post-treated. It was only reported that PCBs levels in the post-treated stock gases after the PCB treatment are below 15 ng/m³ [Costner, 1998].</td>
</tr>
<tr>
<td>MSO</td>
<td>10</td>
<td>7</td>
<td>DRE for chlordane after baghouse is 99.999999% [Costner, 1998; UNEP, 2004a].</td>
</tr>
<tr>
<td>PACT</td>
<td>5</td>
<td>4</td>
<td>The at least “four-nines” DREs are guaranteed for POHC (Principal Organic Hazardous Substance) [ESTCP, 2003]. Destruction tests with HCB confirm the minimum of six-nines DRE [Womack, 1999].</td>
</tr>
<tr>
<td>PLASCON</td>
<td>10</td>
<td>6</td>
<td>See for example [Costner, 1998].</td>
</tr>
<tr>
<td>PWG</td>
<td>*</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>SCWO</td>
<td>10</td>
<td>6</td>
<td>Recent data for pesticides and PCBs from [UNEP, 2004b]. Earlier data report only “five-nines” DRE for pesticides, PCBs, and chlorinated solvents [Costner, 1998; Vijgen, 2002; CMPS&amp;F Environmental, 1997].</td>
</tr>
<tr>
<td>SET</td>
<td>10</td>
<td>n/a</td>
<td>No data reported. Closed non-thermal process.</td>
</tr>
<tr>
<td>Silver II</td>
<td>10</td>
<td>n/a</td>
<td>No data reported. Closed non-thermal process.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>10</td>
<td>n/a</td>
<td>No data reported. Closed non-thermal process.</td>
</tr>
<tr>
<td>SR</td>
<td>10</td>
<td>n/a</td>
<td>No data reported. Closed non-thermal process.</td>
</tr>
</tbody>
</table>

**Maximum POP throughput**

This parameter can also be also defined in other documents as process capacity or production rate. The latter term is sometimes used but may not be very exact since the technologies considered in this review refer to destruction and not to production. The maximum POP throughput parameter aims to evaluate and compare the performance of technologies according to the total quantity of one or more POP chemicals that the technology can process in the waste stream. The net POP content is considered, which can be present in the concentrated (bulk pesticides) or diluted form (PCB in oils pesticides in soil, etc.). Thus, the pure POP throughput is calculated from the gross plant throughput and the percent of POP chemical present in the waste that can be treated in this plant per time unit (for reference see also the Maximum treatable POP strength criterion). If different throughput plants exist and different strength POP wastes can be treated, the combination of two is considered which produces the bigger pure POP throughput value. However, when considering full scale commercial plants, which have both soil treatment and bulk organics treatment options, preference is given to option that treat bulk organics when calculating the pure POP throughput.

Maximum scale single plants are considered for calculation, but not bigger scale configurations obtained by multiplication of single modules. Data on the existing plants are considered only, but not on projected or designed plants which have not been built and operated yet.

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99 The score is not available for technologies which cannot be considered “closed” and for which no DRE data exist.
Taking into account the distribution of the current pure POP throughput data, the following scoring system is proposed:

<table>
<thead>
<tr>
<th>Score</th>
<th>Maximum POP throughput, tons/month</th>
<th>No. of technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&lt; 100</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>100 ≤ ≤ 350</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>350 ≤</td>
<td>1</td>
</tr>
</tbody>
</table>

If the technology has never operated on the commercial scale and/or its throughput was not reported, it is scored 2. Most technologies are scored 2, which leaves space for further corrections and updates, because many technologies are still in the development phase and the bigger scale units are expected to appear soon.

In the table below, the evaluation and related scoring of technologies against the Maximum POP throughput criterion is presented with reference to the information from original sources.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Throughput, tons/month</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>2</td>
<td>29</td>
<td>The vendor (EDL) reports the throughput of 2-12 t/hr (soil). Presuming that the most contaminated soil is fed at 2 t/hr and has 2% POP contamination, the throughput is 40 kg/hr of pure POP or 29 t/month. Even though the other vendor (Tribochem) claims that its DMCR process can process pure POPs, this technology operates on the pilot scale, and there is no well documented throughput data on Tribochem plants.</td>
</tr>
<tr>
<td>BCD</td>
<td>6</td>
<td>100</td>
<td>According to the vendor (BCD), the PCB waste of over 1% can be processed in batch solid processors that can handle from 1 to 5 tons of material per batch; pure HCB can be loaded 1 t per batch and would be reacted in 2 hrs. Thus, it can be expected that no more than 3 batches of concentrated POPs can be processed per day. Two batches of 3 tons pure POPs per day make nearly 100 t/month of POP. For more info see the BCD website, [UNEP, 2004a], and other sources.</td>
</tr>
<tr>
<td>CerOx</td>
<td>2</td>
<td>12</td>
<td>The CerOx process is highly scalable. Different single modules, each consisting of several cells, are capable to process from 25 to 220 gallons/day. Joining together single units the treatment packages are obtained. The vendor claims that a basic treatment package can process 4,000 gallons/day (50% organic content). Joining these packages, the throughput can be further multiplied up to 10 times as much. However, to the best of our knowledge, none of these bigger has been constructed yet. Assuming that System 16 which can process 220 gallons/day (50% POP organics), its monthly throughput reaches up to 12 t/month of pure POP.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>6</td>
<td>120</td>
<td>According to the vendor, throughput of the ICV system can treat 4 t/day of concentrated POPs which is 120 t/month.</td>
</tr>
<tr>
<td>GPCR</td>
<td>2</td>
<td>75</td>
<td>The maximum throughput of 75 t/month is reported by the vendor, which corresponds to the maximum capacity of the TRBP pre-treatment unit which processes pure organic solids, liquids, or liquids with suspended solids.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>2</td>
<td>1</td>
<td>The new commercialized HydroDec demonstration unit processes 3,000L oil per day. PCBs over 50 ppm can be treated at only 2% capacity which means that even assuming that 100% PCB can be processed the throughput would hardly exceed 1 ton pure POP per month.</td>
</tr>
<tr>
<td>MSO</td>
<td>2</td>
<td>5</td>
<td>Throughput data from different sources differ. Whereas 100 kg/hr is reported by [Costner, 1998] (without waste type specification), only 7 kg/hr throughput for chlorinated solvents is reported by vendor (LLNL) [Adamson, no date]. The latter is also in accordance with the data from DOE [US DOE, 1997] which quote two MSO designs of 5 and 60 kg/hr each. Thus, 7 kg/hr (5 t/month) is accepted as the more confirmed data.</td>
</tr>
<tr>
<td>PACT</td>
<td>6</td>
<td>104</td>
<td>The throughput is 104 t/month [ESTCP, 2003], but it is not clear if pure POPs can be handled at this throughput. As there are no data on POP treatment by this technology this was accepted as the only available data.</td>
</tr>
</tbody>
</table>
It is reported that a 150 kW unit can process up to 70 kg/hr of pure POP waste at operating 24 hours per day and 6.5 days per week, which equals 43 t/month [information from vendor].

The reported throughput data from different sources differ substantially. According to the vendor, their units satisfy the industrial sizes of 5, 10, 20, 50, and 100 t/day, and that larger scale facilities are under proposal (multiple 100 tons/day vessels with centralized gas scrubbing).

The pilot SCWO plants can process up to 360 t/month, according to different sources, e.g. [UNEP, 2004b]. Maximum 20% organics can be present in the load, which means 58 to 72 t/month of pure POPs can be processed.

The current commercial systems can treat up to 10 t/day or 300 t/month [UNEP, 2004a]. Considering the maximum POP content of 25% the POP throughput is 75 t/month.

The 12 kW systems can process 30 kg/day of organic waste, i.e. less than 1 t/month. Bigger plants designed for the ACWA programme, such as 60kW, 400 kW, and up to 1 MW, can process up to 60 t/month, which would be probably less for pure POPs.

Different throughput data are reported by different vendors. For example, Powertech reports 15,000 L/day of PCB, which is approximately 450 t/month. Other vendors report higher throughputs, which count up to several thousands tons per month, e.g. 3,300 t/month (Safety Kleen), 4,100 t/month (Bilger), etc. However, all these numbers refer to very low strength PCB, usually less than 1% (e.g. 0.15-1.2% PCB for Safety Kleen), therefore the high strength throughputs barely reach several tons. The highest throughput is demonstrated by Ontario Power who claims to process pure PCBs at 22 tons per month.

Please, note that the above considerations are based on the estimation of the maximum possible throughput, which is guaranteed by vendors or considered possible according to other sources but which has not necessarily been proven with pure POPs. Moreover, these data are not always accompanied with respective DE or DRE. In some cases DE/DRE are calculated for tests with lower throughput or with lower POP concentrations. Thus, the data above require continuous update.

Maximum POP strength

The criterion of Maximum treatable POP strength (concentration of POP in the waste) refers to the content of the chlorinated organic matter in the waste flow that is fed directly into the reaction module. It does not mean that more concentrated POPs could not be treated. For example, the concentrated waste can be diluted/emulsified/dispersed in organic solvents/oils or mixed with soil or other pre-treatment can be applied.

On one hand, this criterion is designed to estimate the robustness of the chemical process involved, i.e. its ability to destroy more concentrated POP; this is useful for the cases when dilution or other pre-treatment operations connected with handling of concentrated waste are undesirable. On the other hand, in some cases the waste is already diluted and some less robust technologies may appear satisfactory. The POP maximum strength data are sometimes required for calculation of the POP throughput data, as explained above, because the gross throughput values reported for different technologies can refer to waste types with different content of the POP substance. Note that technologies assigned 100% POP throughput are not necessarily those classified as applicable to bulk solid or liquid organics in the Direct applicability criterion described previously in Waste categories (Technology Options chapter). Whereas, the latter criterion addresses the possibility to feed

100 Recent data [UNEP, 2004a] report that PWC was demonstrated to treat 50-100 kg/hr (2.4 t/day) and that commercial units are designed for 10 t/day. Earlier data [CMPS&F Environmental, 1997] report throughput of up to 2,000 t/day.
100% organics (which can be either concentrated or diluted POP) directly in the process, the present criterion addresses the maximum treatable concentration of POP in the feed.

For comparison, the applicability of technologies to 100% organic waste is compared with their applicability to 100% POP in the table below:

<table>
<thead>
<tr>
<th>Technology</th>
<th>100% organic solid/liquid</th>
<th>100% POP strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>BCD</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>CerOx</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>GPCR</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>HydroDec</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>MSO</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>PACT</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>PLASCON</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>PWC</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>SCWO</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>SET</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>Silver II</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>SPHTD</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>SR</td>
<td>X</td>
<td>-</td>
</tr>
</tbody>
</table>

The following table describes the scoring system for **Maximum POP strength** criterion:

<table>
<thead>
<tr>
<th>Score</th>
<th>Maximum treatable POP strength, %</th>
<th>No. of technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&lt; 20</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>20 ≤ &lt; 80</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>80 ≤</td>
<td>8</td>
</tr>
</tbody>
</table>

In the following table the related available data are discussed to justify the scoring of technologies:

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Max POP strength, %</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>10</td>
<td>100</td>
<td>The MCD full scale plant treats low strength POP contaminated soils with less than 2% POP. For the DMCR plants high strength POP applicability is claimed by vendor.</td>
</tr>
<tr>
<td>BCD</td>
<td>10</td>
<td>100</td>
<td>Sometimes it is stated that BCD reactors can process 100% POP; however, it should be borne in mind that solids can be fed in the reactor only as slurries in the carrier oil. Organic liquids, e.g. PCB up to 100% can be fed directly. There does not seem to be any special pre-treatment for concentrated waste (e.g. sonication, dissolving), so the applicability to pure POP is assumed. However, according to some sources, BCD reactors are limited to the treatment of 30-55% strength POPs.</td>
</tr>
<tr>
<td>CerOx</td>
<td>6</td>
<td>50</td>
<td>It is claimed that organic solids can be processed only as 50% slurry in water, which requires pre-treatment by crushing and sonication. Applicability to 50% POP is assumed, but there is no information on whether concentrated POPs can be treated as other organics.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>6</td>
<td>33</td>
<td>According to the information from vendor, soil contaminated with 33% HCB was treated in trials.</td>
</tr>
<tr>
<td>GPCR</td>
<td>10</td>
<td>100</td>
<td>Bulk solids POPs, such as concentrated pesticides can be processed using the TRBP unit, which is integrated in the process. Similarly, high strength liquid PCBs can be processed in the LWPC unit.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>2</td>
<td>&lt; 20</td>
<td>Data for the recent plant configuration are missing. However, POP concentration must not be very high from the trial tests results using Catalytic Hydrogenation technology, where maximum 4% PCB and DDT solutions were reported (UNEP, 2004a). Low strength POPs applicability (below 20%) is assigned.</td>
</tr>
</tbody>
</table>

---

101 The waste is considered “concentrated” if it contains 80% or more of pure POP matter.
102 According to [Rahuman, 2000] the formation of salt can impede the BCD process with higher concentrations of chlorinated organic content.
TECHNOLOGY EVALUATION

<table>
<thead>
<tr>
<th>Process</th>
<th>Cost (USD/MG)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSO</td>
<td>10</td>
<td>Pure solids can be loaded directly in the melt, according to the process description. However, there are no documented data confirming pure POP treatment. It is expected, that destruction rate, DE, and risk of new POP formation would depend on the POP concentration in the feed.</td>
</tr>
<tr>
<td>PACT</td>
<td>10</td>
<td>The vendor claims that any kind of waste, including liquid and solid organics, can be processed. The waste is introduced directly in the reactor. It is supposed that pure POPs can be processed; however, information on such applications is missing.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>10</td>
<td>It was reported that tests have been performed with a mixture of Arochlor 1260 and TCB (65:35) with DRE in the range of 6 to 9 nines (UNEP, 2004a), which means that the process is applicable to concentrated POP liquids (solids cannot be processed).</td>
</tr>
<tr>
<td>PWC</td>
<td>10</td>
<td>The same as PACT, this process is indifferent to the POP content. Concentrated POPs can be directly treated without any pre-treatment (CMPS&amp;E Environmental, 1997).</td>
</tr>
<tr>
<td>SCWO</td>
<td>6</td>
<td>The process can treat waste streams containing up to 20-25% organics (or pure POPs), according to different sources (CMPS&amp;E Environmental, 1997; Rahuman, 2000).</td>
</tr>
<tr>
<td>SET</td>
<td>6</td>
<td>POP strengths of up to 250,000 ppm (PCBs) have been tested, as reported by vendor. It is claimed that the process is also applicable to the full strength solid wastes, such as bulk pesticides, but there are no documented data. 500,000 ppm PCBs have been also treated, however the result was not satisfactory (20 ppm remaining) because of insufficient sodium feed, so the maximum strength of 25% is assumed.</td>
</tr>
<tr>
<td>Silver II</td>
<td>2</td>
<td>There are no data on POPs destruction by this process. However, it can be supposed that the performance with POPs would be similar to other organics. According to [Board on Army Science and Technology, 2002], the solid organic waste is transformed in slurry and then mixed with water to reduce the organic content to 20%.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>10</td>
<td>Full-strength POPs can be processed according to the technology developer.</td>
</tr>
<tr>
<td>SR</td>
<td>2</td>
<td>Applicability to PCBs of up to 15,000 ppm (strength 1.5%) is reported (e.g. FASSCO process). There are also indications that nearly pure PCBs can be treated (Ontario Powers process). However, it is suspected that the PCBs are diluted before treatment, since there are numerous comments in different sources including other evaluation reports that the SR technologies are in principle not applicable to the high strength POPs, unless these are diluted before treatment.</td>
</tr>
</tbody>
</table>

Cost criteria

The technology cost details are probably the less precise and less available data, because of a number of factors. Some technology vendors do not provide any cost information, or this information can only be considered indicative, e.g. for technologies in development or near the start of commercialization. Even for commercial technologies the cost of the process is a very complex function depending on the plant configuration (different process configurations usually exist), on the place of operation (country regulations, site specifics, infrastructure, need of transportation), and on the type of waste treated (type of chemical, concentration, matrix, type of storage, etc.). In this connection, only two basic cost categories have been considered in this review, namely the setup costs and the operation costs.

Minimum set up cost

This criterion is designed to consider the minimum reported or projected cost of the technology set up, as reported by the vendor. In the idealized case, the Minimum set up cost criterion should consider pure capital cost of the smallest scale commercial scale unit and has to be independent from country/site factors and to consider only the cost of the unit. The real set up costs increase with additional options and operations required in particular cases. Such costs often depend on process configuration, distance from vendor, site characteristics, available infrastructure, and other factors. Therefore, the following cost categories should be usually added to the idealized setup costs: 1) royalties, taxes and other permitting costs, 2) lease, 3) site and building modifications, 4) energy and telecom
installation, 5) commissioning and decommissioning, 6) transportation, 7) labour, 8) reporting, and so on.

To score technologies against the Minimum set up cost criterion the following scoring system is proposed:

<table>
<thead>
<tr>
<th>Score</th>
<th>Set up cost, USD</th>
<th>No. of technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1,300,000 ≤</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>300,000 ≤ &lt; 1,300,000</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>&lt; 300,000</td>
<td>1</td>
</tr>
</tbody>
</table>

The following table summarizes the scoring results of the Minimum set up cost criterion providing relevant comments and references for each technology:

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Min set up cost, USD</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>BCD</td>
<td>6</td>
<td>800,000</td>
<td>The cost of a 2,500 gallon BCD system ranges from 800,000 USD to 1,400,000 USD, depending on the design and configuration of the system for either mobile or stationary use, as reported by the vendor.</td>
</tr>
<tr>
<td>CerOx</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>GPCR</td>
<td>2</td>
<td>&gt; 5,000,000</td>
<td>It is reported that installation and commissioning of a semi mobile plant costs 5,000,000 USD + site preparation, while the full scale plant costs 10,500,000 USD.103</td>
</tr>
<tr>
<td>HydroDec</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>MSO</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>PACT</td>
<td>2</td>
<td>9,000,000</td>
<td>Initial costs are estimated over 9 millions [ESTCP, 2003].</td>
</tr>
<tr>
<td>PLASCON</td>
<td>6</td>
<td>1,000,000</td>
<td>The capital cost of a 150 kW unit is approximately 1,000,000 USD, depending on configuration [UNEP, 2004a].</td>
</tr>
<tr>
<td>PWC</td>
<td>2</td>
<td>1,600,000</td>
<td>The 400 lb/hr (180 kg/hr) unit costs approximately 1,600,000 AUSD (1,300,000 USD) [CMPS&amp;F Environmental, 1997].</td>
</tr>
<tr>
<td>SCWO</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>SET</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>Silver II</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>SR</td>
<td>10</td>
<td>&lt; 300,000</td>
<td>The SR plant costs are usually in the range of several hundred thousand USD and can be less than 300,000 USD (information on BDS technology)</td>
</tr>
</tbody>
</table>

Minimum operation cost

This criterion considers the cost per ton of POP waste, which is usually represented by the sum of energy and consumables costs. Estimation of technology operation costs appears not less complex task than for setup costs. It is obvious that also in this case the estimation cannot be perfect since no common denominator can be found. Infrastructure and consumables costs are usually the determining factor in operation costs, but the cost of consumables and infrastructure can depend on the type of waste treated. The operation costs also depend on the plant configuration and should also include costs connected with waste transportation, labour, disposal, amortizing, and so on.

In the idealized case, the minimum cost values should be considered for technology comparison (e.g. those for the smaller units), but it is not always clear from the available documentation whether the reported values refer to the most economic configuration. At the same time, the evaluation foresees that the technology is applied to pure or more concentrated POP waste, but for some technologies such tests have not been performed or the reported costs refer to the diluted POP waste. In the latter case it cannot be always stated that the operation costs are proportional to POPs concentration, e.g. whether the

103 GPCR presentation at the South American regional workshop on the environmentally sound destruction of POPs and the decontamination of POP containing waste in the framework of Basel and Stockholm conventions, 2004 Brazil.
costs can be extrapolated for pure POP matter. Moreover, the reported operation costs can sometimes not consider pre-treatment costs, which can be indispensable for concentrated POP waste treatment. In addition, the reported operation costs are usually expressed in price per ton, however the price per time component is not considered.

Taking into account the considerations above, the Minimum operation cost criterion cannot provide realistic evaluation for the cost per ton of pure POP. Selecting data for evaluation, the preference is given to the minimum cost data reported for medium-to-high strength POPs, but if no such data are available, any cost data, e.g. for low strength POPs or for other organic waste can be considered, given that the relevant plant configuration can be in principle applicable to process POP wastes above 1%. Where possible, the cost data related to the treatment of bulk organics, and not soils are taken in consideration.

To score the technologies according to the Minimum operation cost criterion the following system was adopted:

<table>
<thead>
<tr>
<th>Score</th>
<th>Operation cost, USD per ton</th>
<th>No. of technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6,000 ≤</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>4,000 ≤, &lt; 6,000</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>2,000 ≤, &lt; 4,000</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>1,000 ≤, &lt; 2,000</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>&lt; 1,000</td>
<td>5</td>
</tr>
</tbody>
</table>

The above is a preliminary scale which leaves space for higher diapason of operation costs, as it is planned to update the cost data after obtaining information related specifically to the concentrated POP treatment, which would include also additional cost categories related to technology operation, and which is expected to increase substantially. The current scoring of some technologies (see table below) is already based on their operation costs with concentrated POP (e.g. GPCR, PLASCON). The scores for other technologies are probably overestimated, but these can drop as the information on the cost of concentrated POP treatment becomes available.

In the following table, the evaluation data of technologies according to the Minimum operation cost criterion is presented, accompanied with relevant comments and references:

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Operation cost per ton, USD</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>BCD</td>
<td>8</td>
<td>1.053</td>
<td>According to the vendor the operation costs are 728 plus 325 USD per ton for 10% POP waste stream.</td>
</tr>
<tr>
<td>CerOx</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>8</td>
<td>1,000</td>
<td>The operation costs in ICV range from 1,000 to 2,000 USD per ton (information from vendor).</td>
</tr>
<tr>
<td>GPCR</td>
<td>8</td>
<td>1,000</td>
<td>The costs reported in [Vijgen, 2002] are in the range of 2,500-3,000 USD per ton of bulk solid or liquid waste. Other sources report 1,000 USD per ton of pure POP with 50% chlorine content [Danish EPA, 2004].</td>
</tr>
<tr>
<td>HydroDec</td>
<td>-</td>
<td>n/a</td>
<td>No data reported.</td>
</tr>
<tr>
<td>MSO</td>
<td>10</td>
<td>875</td>
<td>Minimum treatment cost is 1,200 AUSD (857 USD) per ton [Costner, 1998].</td>
</tr>
<tr>
<td>PACT</td>
<td>8</td>
<td>1,300</td>
<td>Different operation costs are reported. For example, for Australian unit the cost estimate was 4,000-8,000 AUSD per ton [CMPS&amp;E Environmental, 1997]. In the recent report by ESTCP [ESTCP, 2003] the operation cost for PACT-8 unit was reported to be 2,100 USD per ton. In the evaluation from [Joint service pollution prevention (P2) opportunity handbook, NFESC] the costs around 1,300 USD per ton of organics (PACT 8) are reported.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>8</td>
<td>1,000</td>
<td>The operation cost is 1,000-1,5000 USD per ton (information from vendor).</td>
</tr>
<tr>
<td>PWC</td>
<td>10</td>
<td>268</td>
<td>The operating cost is 375 AUSD (268 USD) per ton [CMPS&amp;E Environmental, 1997], but it should depend on the waste stream.</td>
</tr>
</tbody>
</table>
Experience criteria

Two criteria related to technology experience are proposed, namely full-scale operation experience and commercial experience. The former refers to the time the plants have been operating on the medium-to-large scale; the latter refers to the time the technology has been offered on the market as a proprietary product. These two criteria enable to differentiate between the technologies with practical experience and those commercial technologies that have not had practical experience, but which are in fact ready to meet full scale applications. The evaluation of technologies experience does not take into consideration the type of waste treated (whether POPs or not).

Full-scale operation experience

The full-scale operation experience criterion estimates how long the technology has been operating on the full scale (medium-to-large capacities which are suitable for commercial projects). This criterion also considers the experience of technology operation.

<table>
<thead>
<tr>
<th>Capacity:</th>
<th>Commercial status:</th>
<th>Application scope:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large scale</td>
<td>Commercial scale</td>
<td>Full scale</td>
</tr>
<tr>
<td>Medium scale</td>
<td>Non-commercial scale</td>
<td>Demonstration scale</td>
</tr>
<tr>
<td>Small, laboratory, bench scale</td>
<td>Pilot scale</td>
<td></td>
</tr>
</tbody>
</table>

If referred to process capacity (e.g. throughput or power of the plant) there are basically three scale categories:

1) Large scale (usually tens-to-hundreds tons per month)

2) Medium scale (several times less than the projected full scale, e.g. several to tens of tons per month)

3) Small scale (can be also called laboratory or trial scale, usually less than one ton per month)

If referred to commercial status, there are basically two scale categories:

1) Commercial scale, which means any large scale plants and those medium scale plants which are suitable for commercial operation

2) Non-commercial scale, which means any scale which does not satisfy commercial operation. These are normally all small scale which are non-commercial, but sometimes also medium scale plants (e.g. pilot scale, see below)

According to the project nature, there can be three other definitions, namely:

1) Full scale, i.e. medium-to-large scale plants that are involved in routine practical operation on commercial basis

2) Demonstration scale also refers to the medium-to-large scale plants, which are suitable for commercial use (in the commercial scale category), but which are currently employed in demonstration projects, e.g. to validate process efficiency or to compare different technologies, etc.

3) Pilot scale definition usually corresponds to any plant that is utilized in the process of technology development. Pilot scale plants are therefore not ones that can be utilized in commercial projects and can be used for research and optimization of process operating conditions. The capacity of pilot (scale) units can be small-to-medium scale.
in non-commercial projects (demonstration), but where medium-to-large capacity plants were involved.

To determine the experience of technologies according to the **full-scale operation** criterion, the following scheme was used to score technologies:

<table>
<thead>
<tr>
<th>Score</th>
<th>Experience, years</th>
<th>No. of technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&lt; 3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>3 ≤ , &lt; 6</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>6 ≤ , &lt; 9</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>9 ≤ , &lt; 12</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>12 ≤</td>
<td>5</td>
</tr>
</tbody>
</table>

The table below reports the scores of technologies against this criterion and the related comments and references:

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Experience, years</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>2</td>
<td>2</td>
<td>The first full scale field MCD project for treatment of Mapua site was started in 2004 as reported by vendor.</td>
</tr>
<tr>
<td>BCD</td>
<td>10</td>
<td>14</td>
<td>Even though the BCD technology was commercialized in 1993 the first records on BCD practical applications (within various demonstration projects) date back to 1991 [Vijgen, 2002].</td>
</tr>
<tr>
<td>CerOx</td>
<td>6</td>
<td>8</td>
<td>The first demonstrative project using the early commercial System 4 at the University of Nevada, Reno started in 1998. Currently, there are other projects with newer commercial plants, as reported by vendor.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>6</td>
<td>7</td>
<td>The full scale ICV systems appeared in 1999-2000, but the ex-situ systems have operated since the early nineties, according to vendor and other sources [Vijgen, 2002].</td>
</tr>
<tr>
<td>GPCR</td>
<td>8</td>
<td>11</td>
<td>This process has been used for managing POP waste since 1995 [UNEP, 2004a].</td>
</tr>
<tr>
<td>HydroDec</td>
<td>2</td>
<td>n/a</td>
<td>The process has been commercialized very recently. No demonstration or other commercial scale activities have been performed yet.</td>
</tr>
<tr>
<td>MSO</td>
<td>10</td>
<td>12</td>
<td>The development of MSO was started by Rocketdyne Division of Rockwell, International in the early 1970s, however MSO operated only on the small development scales before the nineties. The LLNL built the first large scale demonstration facility in 1997 which operated till 1999 (see [UNEP, 2004a] and information from vendor). According to [DOE, 1997] the technology operated on the large scale already in 1994.</td>
</tr>
<tr>
<td>PACT</td>
<td>10</td>
<td>15</td>
<td>The technology was operated on the large scale at least in 1992, when the US-EPA report [US-EPA, 1992] on the demonstration Retech’s PCF process (Plasma Centrifugal Furnace, old name) appeared which included demonstration results, cost analysis, etc. According to Retech, the PACT-6 System (formerly PCF-6) was demonstrated under the SITE Program in July 1991, when about 4,000 pounds of waste was processed.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>10</td>
<td>14</td>
<td>The technology has been in commercial operation on the large scale (150 kW) at Nufarm, Australia since 1992 [CMPS&amp;F Environmental, 1997].</td>
</tr>
<tr>
<td>PWC</td>
<td>8</td>
<td>10</td>
<td>A commercial scale unit was commissioned in the USA in 1996 [CMPS&amp;F Environmental, 1997].</td>
</tr>
<tr>
<td>SCWO</td>
<td>10</td>
<td>12</td>
<td>Shinko Pantec’s commissioned an Aqua Citrox® SCWO facility for sludge treatment in July 2000 in Kobe, Japan.105 According to other sources,106, 107 EWT built the first commercial SCWO plant in 1994.</td>
</tr>
<tr>
<td>SET</td>
<td>8</td>
<td>10</td>
<td>The first medium scale demonstration study was conducted in 1996 using an S-4 (55-gallon drum) pilot SET unit (see [FRTR, 2001] and [NFESC, no date]).</td>
</tr>
<tr>
<td>Silver II</td>
<td>4</td>
<td>5</td>
<td>Demonstration of 55 gallon semi-full scale unit within the AGWA program finished in 2001.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>2</td>
<td>n/a</td>
<td>Only laboratory scale experience.</td>
</tr>
</tbody>
</table>

---

105 Patterson, 2001.
107 SCWO in Database on Japanese Advanced Environmental Equipment, GEC.
Many sodium reduction processes are on the market for more than 12 years, e.g. the ABB’s technology operated commercially for more than 15 years on over 30,000 transformers.\textsuperscript{108}

**Commercial experience**

The *commercial experience* refers only to technology commercial status or availability on the market. The commercial experience can be generally defined as the period of technology being offered as a proprietary commercial product, i.e. since the concept of the commercial scale plant has been developed and the IP protected by patents. At this point, the technology owner starts to license the technology. However, it is understood that a commercial technology is an available product, proven, and ready to be installed. Thus, patented and operating technologies can be considered commercial only if the available plants are claimed to be suitable for commercial applications and not only for feasibility studies.

It is difficult to give a precise definition of the commercial experience as it is difficult to define the end of the process which brings an investment-grade technology out of an enterprise or a private or public laboratory for the first-run application in the marketplace. The technology commercialization follows the initial research activities that prove the concept of invention, starts from business planning and securing IP rights (patents) and goes to manufacturing, marketing and distribution, through product developing and scaling up. The end of this process is less defined than its beginning, i.e. date of patenting and its pathway can follow different scenarios. It also makes little sense considering the time passed since the first publication or patent, because this would not estimate the current commercial availability of technology.

This scheme was used to score the technologies against the *Commercial experience* criterion:

<table>
<thead>
<tr>
<th>Score</th>
<th>Experience, years</th>
<th>No. of technologies</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&lt; 3</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>3 ≤, &lt; 6</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>6 ≤, &lt; 9</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>9 ≤, &lt; 12</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>12 ≤</td>
<td>2</td>
</tr>
</tbody>
</table>

This table summarizes the technologies scores and related comments and references for this criterion:

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Experience, years</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>4</td>
<td>5</td>
<td>The process can be considered commercial since the agreement on the treatment Mapua (NZ) site has been made in 2001.</td>
</tr>
<tr>
<td>BCD</td>
<td>10</td>
<td>13</td>
<td>The BCD technology was commercialized in 1993 and since then BCD Group, Inc. has been licensing its processes to private environmental companies.</td>
</tr>
<tr>
<td>CerOx</td>
<td>4</td>
<td>4</td>
<td>The technology can be considered commercial at least starting from 2002, when information on selling its commercial units appeared (Vijgen, 2002). In 2003, the company sold two mixed waste systems which were expected to be operating by 2004.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>6</td>
<td>7</td>
<td>This technology has been operating commercially on the full scale since the eighties in the in-situ configuration (Vijgen, 2002). The first ex-situ ICV systems appeared in the late nineties (1998-1999).</td>
</tr>
<tr>
<td>GPCR</td>
<td>8</td>
<td>11</td>
<td>It is known that Eco Logic used its process for managing POP waste on the full scale in 1995. It is supposed that it was a patented commercial technology then (UNEP, 2004a; Vijgen, 2002).</td>
</tr>
</tbody>
</table>

\textsuperscript{108} Csizer, 2003.
Technology comparative criteria

The evaluation and rating of the so-called comparative criteria reflects the performance factors which are not or cannot be adequately documented. Some of criteria, e.g. those related to “risk”, represent a purely qualitative comparison of technologies based only on general and individual considerations. Others, such as “input” and “output” criteria more refer to technical characteristics of technologies. However, the current comparison of technologies under these criteria is performed in a very rough manner, because the data on technology parameters related to these criteria are missing for many technologies, and also because some of these criteria refer to the assessment of a combination of many different parameters.

General

Ease of operation

In principle, this criterion inversely reflects the technological complexity of process organization and operation. As a result, for a more complex process more highly qualified personnel will be usually required. The increased complexity also means increased risk of malfunctioning, more frequent revisions and more thorough control and higher maintenance costs. Therefore this criterion implies a complex evaluation of a number of factors that are quite difficult to quantify and to bring to a common denominator.

Roughly speaking, the ease/complexity of operation would depend on the process chemistry and its technological arrangement. For example, processes involving more treatment steps or phases of pre- and post-treatment are normally more complex to control. As a rule, harsher reaction conditions also render process operation more complex. Increasing the number of phases and components of the reaction mixture (reagents,
catalysts, and solvents) also presumes a higher complexity. Gaseous phase processes would require a more complex arrangement. Continuous processes are also usually more complex technically, but require less supervision.

As well as for the other criteria discussed consecutively in this chapter, the ease of operation criterion rating was based on individual theoretical considerations. Some justifications for these considerations are given in the table below. Thus, only a rough scale evaluation was performed, where each technology is scored 2, 6 or 10, i.e. complex, medium, or easy.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>10</td>
<td>The process is simple in operation. The organics and the reducing agent are simply loaded in the closed ball mill. The vessel is mechanically shaken and the residuals are discharged.</td>
</tr>
<tr>
<td>BCD</td>
<td>2</td>
<td>High complexity. The process includes pre-treatment for certain waste streams. Oil recycle and off-gas treatment systems for different process streams are present. Since elevated temperatures and flammable materials are involved the process also includes safety devices.</td>
</tr>
<tr>
<td>CerOx</td>
<td>2</td>
<td>Two steps are involved. The reaction in the liquid phase and an electrolytic cell. A complex arrangement is required that foresees liquid circulation in the system with the need of on-line monitoring of the destruction degree. A sonicator and a filter are included to process the feed and to separate solid particles. The post-treatment involves chlorine scrubber, pH adjuster, etc. Electrolytic cell alone is a complex component, which needs to be replaced periodically.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>10</td>
<td>The only step of the process is the loading the solid POP together with soil in the container where the electrical current is conducted. After certain time periods the melt is cooled and vitrified mass is discharged. No other essential technological operations take place.</td>
</tr>
<tr>
<td>GPCR</td>
<td>2</td>
<td>Increased complexity due to a gaseous phase reaction in the main reaction module. The process also requires pre-treatment modules to transform waste into gas. Due to a lot of off-gas generated there is a post-treatment system with a possibility of gas circulation in the process. The process is continuous and requires on-line gas monitoring. The additional gas treatment is foreseen to transform methane into hydrogen gas that enters into reaction.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>6</td>
<td>There is little technical information on the process arrangement. However it can be assumed that the ease of operating this process is similar to BCD, due to a similar chemistry. In any case that waste would require dilution and there is probably additional complexity in the design due to the hydrogen gas feed.</td>
</tr>
<tr>
<td>MSO</td>
<td>6</td>
<td>A one-step treatment process, similar to Ball Milling and GeoMelt, simple by design as most thermal treatment technologies. However, the waste is fed on continuous base. The process was considered more complex, because it foresees salt recovery.</td>
</tr>
<tr>
<td>PACT</td>
<td>2</td>
<td>This and other two plasma processes (PLASCON and PWC) are generally complex due to very high temperatures involved (electrical torch is integrated in the process including relevant control equipment). Such processes usually operate on continuous basis, therefore more steps should be linked which are responsible for waste feed, post-treatment, off-gas scrubbing, a system for discharge of the solid vitrified product. Post-treatment sometimes consists of several steps. As well as other continuous processes that involve gaseous reaction at elevated temperatures (or reaction/products in the gaseous state) like GPCR, the PAT require a number of auxiliary units, such as pre-heaters, heat exchangers, coolers, gas circulation engines, etc.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>2</td>
<td>Process is not simple due to the same reasons as all PACT. The construction of the plasma torch and the connected on-fly reaction tube is more sophisticated than in other PAT. For example, precise temperature and flow control in the reaction module is required.</td>
</tr>
<tr>
<td>PWC</td>
<td>2</td>
<td>Detailed technical description of the process organization is missing. It can be suggested that the process organization is intrinsically similar to that of other PACT, however it is not reported whether it operates continuously.</td>
</tr>
<tr>
<td>SCWO</td>
<td>2</td>
<td>Generating supercritical water requires high temperatures and very high pressures. Special steel and other durable materials are required to resist these process conditions (water becomes super acidic in the supercritical state). Running this process in the continuous regime represents another difficult technological task. A complex and thorough organization is required to provide process safety.</td>
</tr>
</tbody>
</table>
**TECHNOLOGY EVALUATION**

<table>
<thead>
<tr>
<th>SET</th>
<th>2</th>
<th>This technology is somewhat similar to SCWO due to an unconventional solvent system (liquid ammonia). The reaction conditions are not that harsh as in the case of SCWO, however, elevated pressures are required. Moreover, the process involves basically two steps: i) preparation of sodium-ammonia solution, ii) treatment of waste slurry. Pre-treatment of waste and post-treatment (neutralization of ammonia) steps are also required. Complexity owes to gas circulation, since the system should be strictly contained to avoid releases of the toxic gas.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver II</td>
<td>2</td>
<td>Not much technical data are available on this technology, however the available information suggests that the process is essentially the same as CerOx by its technological arrangement. Increased complexity is assumed.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>10</td>
<td>The process by design resembles one-step batch thermal processes, such as Ball Milling or GeoMelt. Moreover, the process operates on the laboratory scale only and therefore has a very simple design.</td>
</tr>
<tr>
<td>SR</td>
<td>10</td>
<td>These technologies usually involve quite a simple process organization, if not considering eventual pre-treatment modules. The liquid waste is treated by mixing it with sodium suspension in oil. The reaction is self sustainable and the products does not require complex post-treatment.</td>
</tr>
</tbody>
</table>

**Containment**

By the process containment it is unusually meant whether or to what extent the process is able to contain its streams, i.e. for eventual reprocessing and analysis. The “contained” processes are normally safer and more secure environmentally in principle, whereas the “uncontained” or so-called open processes are more vulnerable as they can generate uncontrolled emissions of toxicants, e.g. in the case of process or post-treatment system malfunctioning.

It is understood that the definition of the process containment can only be approximate and qualitative, because containment represents a complex process characteristic that comprises several factors, namely the nature of discharged streams (e.g. gaseous products, liquid products, scrubber watery waste, etc.), their amounts, quality of post-treatment systems, etc.

The processes that do not contain their streams are usually continuous processes, especially thermal oxidative ones, where the organics is converted into gaseous products. Such technologies need to continuously remove reaction products and secondary streams, which are usually discharged in the environment (either post-treated or not) in the form of off-gases. Low-temperature, reductive, and batch processes are usually better contained.

Theoretically, the processes, where the effluents are duly and thoroughly treated, so that no organic content can escape and is all collected (contained) in a solid, liquid or adsorbed form, should be considered fully contained. The true criterion of containment for such processes can be their DRE which was discussed previously. This is true only partially, because DRE does not consider eventual liquid off-flows; solid discharges do not usually represent problems to contain. The DRE values are usually obtained from control experiments and demonstration tests which are run under idealized conditions and are intended to demonstrate the process ability to meet the required regulations. In practice, not all processes are able to maintain these characteristics in field applications and may become vulnerable at longer utilization times or with different waste types. The operating conditions, quality of process maintaining, and human factor are the factors that can also compromise process performance. The containment criterion, therefore, gives a more basic evaluate of the process cleanliness as it takes into account its intrinsic engineering design regarding the potential to produce uncontrolled emissions.

The technologies are roughly scored 2, 6, or 10 implying poorly, medium, and well contained processes. The evaluation results are summarized in the table below:
<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>10</td>
<td>Low or no gas emissions are expected as the process uses a closed batch reactor where the reductive reaction of the POP molecule occurs. The organic matter remains in the solid state, salts and water are also formed. All products can be collected.</td>
</tr>
<tr>
<td>BCD</td>
<td>10</td>
<td>Good containment can be assumed given that the process reductive (chlorine is converted in salt) is based on the liquid phase reaction of POP at not very high temperatures (organics are converted to gas only partially) and therefore produces little gas emissions, which are going to be effectively cleaned by carbon filters. The oil used in the process is recycled. Used oil and solid residues are collected.</td>
</tr>
<tr>
<td>CerOx</td>
<td>6</td>
<td>Reaction occurs in the liquid phase at moderate temperatures. However, CerOx is an oxidative process and results in the formation of gaseous effluents containing chlorine and VOCs which are potentially toxic. Moreover, the process of cerium regeneration with nitric acid gives rise to the NOx effluents and there are water waste flows arising from the post-treatment steps. Therefore, the process is assigned average containment.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>2</td>
<td>A thermal process where the waste is treated in a container with a melt of soil. It is expected that most organic content is transformed into the gaseous phase where a significant amount of unreacted POP simply evaporates. The off-gases should be very contaminated, unless thoroughly post-treated. No detailed information on post-treatment is available for this process.</td>
</tr>
<tr>
<td>GPCR</td>
<td>6</td>
<td>The GPCR technology is often referred to as a “closed loop” system. It has three outputs: solids, water from the scrubbing system, and stack gas from the fuel. The methane gas produced in the process is captured and reused as a fuel.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>6</td>
<td>There is little information on this process technological arrangement. The chemical nature of the process suggests that that process containment can be scored as average-to-high as the reaction occurs in the liquid phase batch reactor. Only small amount of gas is expected to escape from this system, which is mainly unreacted hydrogen.</td>
</tr>
<tr>
<td>MSO</td>
<td>2</td>
<td>The principle is similar to the GeoMelt process but seems to be more thoroughly designed than GeoMelt to assure a complete destruction of the original chemical. The product stream passes through a tube of molten salt guaranteeing a more complete destruction and effluents are treated in several steps. However, it is still considered as low contained as lots of effluents should be produced, because all the organic content is transformed into gas.</td>
</tr>
<tr>
<td>PACT</td>
<td>2</td>
<td>All plasma arc processes (PACT, PLASCON, and PWC) lead to the full conversion of organics into gaseous products. As the reaction occurs in the oxidative environment chlorine is also volatized which can lead to toxic products. The amount of organics and chlorine discharged by these processes, as gases in the atmosphere or as water from quenching systems, would depend on the quality of post-treatment systems; however the intrinsic containment is low by the nature of the process.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>2</td>
<td>See comments for PACT.</td>
</tr>
<tr>
<td>PWC</td>
<td>2</td>
<td>See comments for PACT.</td>
</tr>
<tr>
<td>SCWO</td>
<td>2</td>
<td>The process products and emissions should be essentially the same as in the MSO process, which involves the same oxidation reaction at high temperatures in the condensed medium. In the case of SCWO, the harsh conditions probably lead to a more complete destruction of contaminants; however, the process produces abundant and continuous aqueous stream on the outlet.</td>
</tr>
<tr>
<td>SET</td>
<td>10</td>
<td>This process is based on the reduction of organics by sodium solution in liquid ammonia at moderate temperatures (similar to SR processes) and is carried out in a closed system under pressure. The process emissions are minimal and mainly consist of ammonia which is easily scrubbed.</td>
</tr>
<tr>
<td>Silver II</td>
<td>6</td>
<td>See comments for the CerOx technology.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>10</td>
<td>Similar to Ball Milling. Notwithstanding very high temperatures involved, this process is well contained by design. The reaction occurs in a closed vessel where no gaseous emissions can escape. The POP matter is reduced into dechlorinated organics which can be collected.</td>
</tr>
<tr>
<td>SR</td>
<td>10</td>
<td>The process is fully contained. The liquid PCB waste is treated at low-to-moderate temperatures by sodium reagent. Organics remain in the liquid phase, giving small amounts of solid polymerisation products and NaCl, which are fully collected. No significant gaseous emissions are produced.</td>
</tr>
</tbody>
</table>

**Input criteria**

This group of criteria refers to the amounts of consumables and power that are required for process operation, which are the process parameters that in principle can be directly linked to numerical data. However, for many processes the data on input streams are absent or not normalized. Ideally the consumption parameters of plants can be compared only given their equal waste throughputs, type of waste treated, type of POP, and the percentage...
of POP in the waste. A very rough and approximate evaluation is performed which is based on the known process chemistry and technological design.

**Electric power requirement**

This criterion serves to estimate the amount of electricity that the process consumes. Normally, the electricity is consumed for heating of the reaction medium, generating plasma, electrochemical reaction, or for motion (engines for compression, circulation, rotation/agitation, etc.). Increased electricity amounts are normally needed in the processes involving high temperatures or plasma or where the electrical power is the driving force of the reaction (e.g. MEO processes). The following table gives an overview of the evaluation:

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score&lt;sup&gt;109&lt;/sup&gt;</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>6</td>
<td>Moderate to average electrical power is required to supply the ball mill motion mechanism.</td>
</tr>
<tr>
<td>BCD</td>
<td>6</td>
<td>The electricity is required in order to heat the reaction module (temperatures over 300°C) and to preheat the oil.</td>
</tr>
<tr>
<td>CerOx</td>
<td>2</td>
<td>Much electricity is required as it represents the driving force of the reaction.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>2</td>
<td>Much electricity is required to melt soil using the electrodes.</td>
</tr>
<tr>
<td>GPCR</td>
<td>10</td>
<td>The process is self-sustainable because the heat, which is required to maintain temperature in the reactor, can be produced by burning the reaction products.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>6</td>
<td>Some amount of electricity is required for heating up the reaction mixture.</td>
</tr>
<tr>
<td>MSO</td>
<td>2</td>
<td>Significant amount of electricity is required for heating, in order to maintain the melt of salt at high temperature.</td>
</tr>
<tr>
<td>PACT</td>
<td>2</td>
<td>Much electricity is required to run the plasma torch.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>2</td>
<td>See PACT.</td>
</tr>
<tr>
<td>PWC</td>
<td>2</td>
<td>See PACT.</td>
</tr>
<tr>
<td>SCPWO</td>
<td>2</td>
<td>Electricity is required for heating and compression, in order to transform water in the supercritical state.</td>
</tr>
<tr>
<td>SET</td>
<td>6</td>
<td>Electricity is required to compress and circulate ammonia in the process. Heating requirements should be insignificant.</td>
</tr>
<tr>
<td>Silver II</td>
<td>2</td>
<td>See CerOx.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>10</td>
<td>No electricity or other source of external energy is required as the process is self-sustainable (self-propagating).</td>
</tr>
<tr>
<td>SR</td>
<td>10</td>
<td>Only minimal electrical power may be required, e.g. for preheating, agitation, etc.</td>
</tr>
</tbody>
</table>

**Gaseous reagent, carrier, and/or fuel requirement**

In the similar manner as for the previous criterion, this criterion gives an estimate of the amount of any gaseous (under normal conditions) substance that the technology consumes or uses for its operation. As before, the evaluation is done in an approximate manner, because it is difficult to see how exactly the consumptions differ for different technologies using the same type of waste, throughput, etc. Possible errors can be due to the lack of relevant technological data. Please note that air is not considered as a gaseous reagent.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>10</td>
<td>No gas is required by technology.</td>
</tr>
<tr>
<td>BCD</td>
<td>6</td>
<td>Moderate amount of nitrogen is required for blanketing, which is not consumed.</td>
</tr>
<tr>
<td>CerOx</td>
<td>10</td>
<td>No gas is required by technology.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>6</td>
<td>Propane is required for thermal oxidation, the final step in the off-gas treatment.</td>
</tr>
<tr>
<td>GPCR</td>
<td>6</td>
<td>Hydrogen gas is required as a reagent. Some natural gas may be required for heating.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>6</td>
<td>See GPCR.</td>
</tr>
<tr>
<td>MSO</td>
<td>10</td>
<td>No gas is required by technology. Only small amount of fuel can be required on start-up.</td>
</tr>
<tr>
<td>PACT</td>
<td>2</td>
<td>Continuous and abundant inflow of plasma gas (He-N₂ and He-O₂) is required for ionization.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>6</td>
<td>Continuous and abundant inflow of plasma gas (argon) and oxygen are required for ionization. The vendor claims that no gas is consumed.</td>
</tr>
</tbody>
</table>

<sup>109</sup> Here and below for the rest of comparative criteria: inversed scoring is used, e.g. higher score means lower consumption.
NON-COMBUSTION TECHNOLOGIES FOR POPS DESTRUCTION

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>10</td>
<td>No water is required by the process except small amount used for scrubbing.</td>
</tr>
<tr>
<td>BCD</td>
<td>10</td>
<td>Small amounts of water are required for scrubbing. In the case of soil treatment steam is used to maintain an inert atmosphere above the hot soil.</td>
</tr>
<tr>
<td>CerOx</td>
<td>2</td>
<td>Water constitutes the reaction medium and is continuously consumed.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>6</td>
<td>No water is required by the process. However, presuming the existence of the off-gas treatment system, the latter would require some water for scrubbing of gaseous effluents produced by this process. As a rule, thermal oxidation processes produce big quantities of gaseous effluents.</td>
</tr>
<tr>
<td>GPCR</td>
<td>6</td>
<td>Some water is needed for scrubbing and some water is added in the process to increase its reducing power. Water can also be used for the steam reforming and water-gas shift reactions of methane formed in the process.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>10</td>
<td>No or just minimal amounts of water can be required for this process.</td>
</tr>
<tr>
<td>MSO</td>
<td>6</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>PACT</td>
<td>6</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>6</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>PWC</td>
<td>6</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>SCWO</td>
<td>2</td>
<td>See CerOx.</td>
</tr>
<tr>
<td>SET</td>
<td>10</td>
<td>No or only insignificant amounts of water can be required.</td>
</tr>
<tr>
<td>Silver II</td>
<td>2</td>
<td>See CerOx.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>10</td>
<td>No or very small amount of water is required by the process.</td>
</tr>
<tr>
<td>SR</td>
<td>10</td>
<td>No or very small amount of water is required by the process.</td>
</tr>
</tbody>
</table>

Reagent and/or solvent requirement

This criterion is designed to evaluate the gross amount of materials other than gas and water (normally reagents, organic and inorganic, solid or liquid, solvents, catalysts, and so on, with the exception of soil) that are required for process operation. The same as in the previously considered criteria in this group, the evaluation is based on a general comparison of technologies, as it is very difficult to quantify the process consumables due to the lack of data.

It should be noted that this criterion aims also to assess the convenience of process inventory. Therefore, in addition to the evaluation of the weight of consumables, it also accounts for their availability. For example, difference is made between valuable reagents and easily available ones, like alkali/salts. The following scoring strategy is assumed: the processes that require stoichiometric amount or excess of one or more reagents are scored 2; those that only require inorganic base to quench hydrochloric acid and CO₂ and eventually need carbon for filtering are scored 6; the processes which are either catalytic or reductive and which do not produce much emissions and, therefore, do not require lots of alkali for scrubbing are scored 10.
TECHNOLOGY EVALUATION

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>2</td>
<td>The process requires excess of inorganic reagent (Mg, CaO, Na, etc.). A hydrogen donor (e.g., an alcohol) can also be added.</td>
</tr>
<tr>
<td>BCD</td>
<td>6</td>
<td>The process requires oil, caustic soda, catalyst, and eventually sodium bicarbonate. The oil is reused.</td>
</tr>
<tr>
<td>CerOx</td>
<td>10</td>
<td>Both cerium salt and nitric acid are recycled, but small amounts can be required to compensate their loss. Base is required for scrubbing.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>10</td>
<td>No reagent is required, except sodium carbonate, which is sometimes used to enhance the process, and alkali for scrubbing.</td>
</tr>
<tr>
<td>GPCR</td>
<td>10</td>
<td>Alkali is required for scrubbing.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>6</td>
<td>A catalyst, alkali, and possibly a solvent are required.</td>
</tr>
<tr>
<td>MSO</td>
<td>6</td>
<td>Carbonate salt is required which reacts with the hydrochloric acid formed. Its consumption is not higher than that of alkali in the scrubber systems of other processes.</td>
</tr>
<tr>
<td>PACT</td>
<td>6</td>
<td>See GPCR.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>6</td>
<td>See GPCR.</td>
</tr>
<tr>
<td>PWG</td>
<td>6</td>
<td>See GPCR.</td>
</tr>
<tr>
<td>SCWO</td>
<td>6</td>
<td>Process requires potash or alkali as a neutralization agent.</td>
</tr>
<tr>
<td>SET</td>
<td>2</td>
<td>Metallic sodium is consumed as a reagent.</td>
</tr>
<tr>
<td>Silver II</td>
<td>10</td>
<td>See CerOx. In this case Ag salt is required instead of Ce in CerOx.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>2</td>
<td>Excess of solid reagent (calcium hydride) is required.</td>
</tr>
<tr>
<td>SR</td>
<td>2</td>
<td>Excess of solid reagent (sodium) is required.</td>
</tr>
</tbody>
</table>

Output criteria

The issues related to the output stream qualitative and quantitative parameters, such as quality (disposability or value) and amounts of waste and emissions on the outlet are evaluated by the output group of criteria respectively. See below descriptions for particular criteria.

Secondary waste disposability

The way of disposal of solid liquid residuals can be different in different cases. Particularly speaking about the POP destruction technologies it is implicit that even the waste from a process, which demonstrates good DRE, is not innocuous and has to be disposed as a hazardous waste. Whereas the amounts of such waste are estimated by the following two criteria, the current criterion aims to give rather a qualitative assessment of the problems and difficulties connected with waste disposal, taking into account risks connected to handling, transport, and toxicity/hazard aspects.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>6</td>
<td>Non-toxic solid residuals are produced (reduced organics and metal salts). Liquid waste amount are assumed zero or minimal. Information is missing on the way of disposal of concentrated organics.</td>
</tr>
<tr>
<td>BCD</td>
<td>6</td>
<td>Limited amounts of solid and liquid effluents having low toxicity, as for most reductive processes (chlorine content is mineralized, and the organic content transforms into saturated hydrocarbons). Most oil is recovered and reused in the process. Worked oil and solid waste are sent to incinerator.</td>
</tr>
<tr>
<td>CerOx</td>
<td>2</td>
<td>Liquid waste streams seem to be considerable and difficult to treat. It was mentioned that watery waste is sent to POTW for disposal. However in the event of POP treatment it is not clear if any additional treatment is required.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>2</td>
<td>The process is expected to generate big amounts of solid vitrified slug with a high degree of contamination. Special disposal would be required.</td>
</tr>
<tr>
<td>GPCR</td>
<td>10</td>
<td>The process produces small amounts of solid waste that is suitable for landfill and of caustic water from the scrubbing system. The organic products are gaseous.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>6</td>
<td>Organics are reduced to original hydrocarbons and metal salts. Limited information on this process.</td>
</tr>
</tbody>
</table>
It is questionable if the residual salt can be reused in the process as it would react with hydrochloric acid coming from POP oxidation. Big quantities of chloride salt would be formed and would require special disposal due to possible presence of incomplete combustion products.

In the plasma processes all the organics are transformed into gas and the inorganics is transformed in the vitrified mass. In addition, liquid and solid wastes include scrubbing water and particulates captured from the gaseous emissions, which can be toxic. Such waste should be disposed as hazardous.

Similar to PACT, regarding the waste from the post-treatment system. However, no vitrified slug is produced.

Big amounts of watery waste would require special treatment. Little information available on how the process residuals are disposed.

POPs are reduced to original hydrocarbons, which are relatively innocuous and eventually can be burnt or reused. Inorganic salts (ammonium and sodium salts) from the scrubbing system also appear to be safe to landfill.

See CerOx.

Only solids are formed (the same as for Ball Milling).

Solid residues
Combined amount of all solid residuals coming from the process is estimated. This refers to solid inorganic salts, vitrified products, carbon filters and deposits, solid organic residuals, etc. Rough estimates are given, based mainly on the theoretical considerations, as the exact data are missing for most technologies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>2</td>
<td>Process products are mainly solid.</td>
</tr>
<tr>
<td>BCD</td>
<td>6</td>
<td>A part of process products are solid (e.g. sodium salts, carbonaceous and organic residuals, carbon filters). Another part of original hydrocarbons stays dissolved in the oil.</td>
</tr>
<tr>
<td>CerOx</td>
<td>10</td>
<td>No or little solid residuals are produced. The original solid organics is oxidized to gases and water soluble salts.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>2</td>
<td>Vitrified slug is formed in big quantities.</td>
</tr>
<tr>
<td>GPCR</td>
<td>10</td>
<td>The process residual streams are mainly gaseous and liquid. Small amounts of solid include particulates from filtering system and carbonaceous residuals.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>10</td>
<td>No-solid making or involving process. The reaction intrinsically occurs in the liquid phase. Only used catalysts may need disposal (very small amounts).</td>
</tr>
<tr>
<td>MSO</td>
<td>2</td>
<td>A lot of solid slug is produced.</td>
</tr>
<tr>
<td>PACT</td>
<td>6</td>
<td>The amount of solid waste can be different depending on the input waste type. In the case if concentrated organic waste is treated the only solids are filters and eventual heavy organic residuals. In the case of inorganic matrices, the vitrified solid product would be formed.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>10</td>
<td>No solid product is expected to be formed as the process operates in the gaseous phase.</td>
</tr>
<tr>
<td>PWC</td>
<td>6</td>
<td>See PACT.</td>
</tr>
<tr>
<td>SCWO</td>
<td>10</td>
<td>No or little solid is supposed to be formed. The residual organics and salts should be dissolved or suspended in water.</td>
</tr>
<tr>
<td>SET</td>
<td>6</td>
<td>Solid products are mainly sodium salts and eventual solid organic residuals in small quantities.</td>
</tr>
<tr>
<td>Silver II</td>
<td>10</td>
<td>See CerOx.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>2</td>
<td>Only solids are formed (the same as for Ball Milling).</td>
</tr>
<tr>
<td>SR</td>
<td>6</td>
<td>Similar to SET. Only sodium salts and, eventually, polymerized organics are solid process residuals. The original reduced hydrocarbons (PCB) are either liquid or stay dissolved in oil.</td>
</tr>
</tbody>
</table>

Liquid residues
Amounts of liquid process output streams are assessed which can be watery and/or organic. Rough estimates are given, based mainly on the theoretical considerations, as the exact data are missing for most technologies.
TECHNOLOGY EVALUATION

Technology Score Comments and references

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>10</td>
<td>The process is essentially solid phase, no liquid is formed.</td>
</tr>
<tr>
<td>BCD</td>
<td>6</td>
<td>The liquid process streams mainly include worked oil which cannot be longer recycled and limited amounts of water from scrubbing systems.</td>
</tr>
<tr>
<td>CerOx</td>
<td>2</td>
<td>The process generates big amounts of watery waste, including used reaction medium and scrubbing waters from gaseous product treatment system and acid reclaim system.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>10</td>
<td>The only liquid process streams are scrubber waters, including water formed from oxidation of organics.</td>
</tr>
<tr>
<td>GPCR</td>
<td>10</td>
<td>Gas phase reaction. Little liquid waste is produced which is mainly used scrubber liquor.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>2</td>
<td>The process operates in the liquid phase and the output process stream is mainly liquid.</td>
</tr>
<tr>
<td>MSO</td>
<td>6</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>PACT</td>
<td>6</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>6</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>PWC</td>
<td>6</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>SCWO</td>
<td>2</td>
<td>Liquid phase process that occurs in a continuous flow of water. The considerable amount of watery waste is produced.</td>
</tr>
<tr>
<td>SET</td>
<td>6</td>
<td>The liquid process waste is formed only if the original POP is liquid, e.g. PCB oils.</td>
</tr>
<tr>
<td>Silver II</td>
<td>2</td>
<td>See CerOx.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>10</td>
<td>See Ball Milling.</td>
</tr>
<tr>
<td>SR</td>
<td>2</td>
<td>Similar to SET in the case of PCB treatment. The difference is that the SR processes are mainly limited to the treatment of liquid POP waste (PCBs).</td>
</tr>
</tbody>
</table>

Gaseous emissions

This criterion performs a rough evaluation, similar to the above, of the general amount of gaseous effluents produced in the process. As the related quantitative data are missing and it is difficult to estimate the amount of gas, which is produced and not captured in the post-treatment systems, the following assumptions were made: 1) the amounts of gas are equal for all oxidative processes, as far as all organic content and chlorine are converted into gas (these technologies are scored 2), except PWC where the pyrolysis gas is collected; 2) reduction processes are scored 10, except those operating at high temperature, i.e. where the gaseous products are formed due to cracking processes (e.g. GPCR, SPHTD) or where the gaseous effluents are one of reagents or the reaction media (HydroDec, SET); 3) the above-mentioned exceptions are scored 6.

Can the products be used?

The last criterion from this group gives an estimate of the usefulness of reaction products. The possibility to use one or more reaction products can be one of the advantages of the process. However, in practice this possibility is different in different cases.

The scoring is different from the previous criteria. The technologies that do not produce a useful product are scored 0; those whose products are of little use are scored 2 or 6; those where the use of products is practically confirmed are scored 10.
NON-COMBUSTION TECHNOLOGIES FOR POPS DESTRUCTION

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>2</td>
<td>In theory, the organic products can be burnt in incinerators to recover heat. However, there is little commercial use for it and such a possibility is not declared by the vendor. Moreover, chloride salts, if not separated, can result in new POP formation during incineration.</td>
</tr>
<tr>
<td>BCD</td>
<td>2</td>
<td>In principle, the reaction products are reduced hydrocarbons. In practice, light organics is captured by carbon filters and the heavy oil together with carbonaceous residuals is not considered useful and is disposed in incinerator.</td>
</tr>
<tr>
<td>CerOx</td>
<td>0</td>
<td>No use of reaction products can be made.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>0</td>
<td>No use of reaction products can be made.</td>
</tr>
<tr>
<td>GPCR</td>
<td>6</td>
<td>Hydrogen and methane are formed, which are partially consumed for the same process (both as reagent and as fuel).</td>
</tr>
<tr>
<td>HydroDec</td>
<td>10</td>
<td>Refurbished PCBs can be reused in electrical equipment.</td>
</tr>
<tr>
<td>MSO</td>
<td>0</td>
<td>No use of reaction products can be made.</td>
</tr>
<tr>
<td>PACT</td>
<td>0</td>
<td>No use of reaction products can be made.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>0</td>
<td>No use of reaction products can be made.</td>
</tr>
<tr>
<td>PWC</td>
<td>6</td>
<td>The organic matter is converted into plasma converted gas which can be used as a fuel or as a feedstock for chemical synthesis. However, the presence of toxic secondary combustion products can be a serious issue.</td>
</tr>
<tr>
<td>SCWO</td>
<td>0</td>
<td>No use of reaction products can be made.</td>
</tr>
<tr>
<td>SET</td>
<td>6</td>
<td>Reaction products, which are the dechlorinated hydrocarbons, in principle, can be useful, e.g. as in the case HydroDec for PCB treatment. However there is no mention on this possibility from the vendor.</td>
</tr>
<tr>
<td>Silver II</td>
<td>0</td>
<td>No use of reaction products can be made.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>2</td>
<td>Hydrogen and hydrocarbons that are formed in the process can be theoretically useful. However, practical value of the process products cannot be determined as the technology is still in development.</td>
</tr>
<tr>
<td>SR</td>
<td>10</td>
<td>Refurbished PCBs can be reused in electrical equipment.</td>
</tr>
</tbody>
</table>

Risk criteria

**New POP formation**

Parties shall “Promote the development and, where it deems appropriate, require the use of substitute or modifies materials, products and processes to prevent the formation and release of the chemicals listed in Annex C [dioxins/furans and other by product POPs]”

Stockholm Convention on POPs, Article 5 (c)

New POP formation possibility is evaluated on the basis of chemistry of involved processes and their technological arrangement. For example, the oxidation processes are normally scored 2, but a higher score can be given to several safer technologies, e.g. the MEO technologies (scored 8), where the oxidation occurs at low temperatures, or some PAT technologies, for example PLASCON (scored 6), where very high temperatures assure a more complete decomposition of dioxin precursors and a very rapid cooling of the product gases suppresses the de novo PCDD/F synthesis.\(^{110}\) Reductive processes are normally scored 10, except those that operate at elevated temperatures, and where new POP (PCDD/F) or other toxicants (PAH) can be formed from precursors (PCB, chlorophenols, etc.) and residual oxygen (such processes are scored 8). New POP formation can also occur in the auxiliary units, e.g. pre-treatment, afterburners or quenching or scrubbing systems, etc. The formation of dioxins in some of the considered processes was evaluated in a recent study by Weber.\(^{111}\)

\(^{110}\) “PCDD/F can be formed during degradation of unburned carbon species (including PAHs, soot etc.) in the presence of a chlorine source (chlorine, metal chlorides). De novo synthesis starts at temperatures of around 250°C with a maximum rate between 300 to 400°C. Therefore this pathway is relevant for all POPs destruction technologies operating at temperatures of more than 200°C but in particular in the cooling zones of high temperature technologies.” [Weber, 2004]

**Technology Evaluation**

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>10</td>
<td>Closed reductive non-thermal process. No risk.</td>
</tr>
<tr>
<td>BCD</td>
<td>8</td>
<td>Reductive process with little risk of POP formation, e.g. due to the condensation at high temperature or eventual presence of oxygen during treatment.</td>
</tr>
<tr>
<td>CerOx</td>
<td>8</td>
<td>An oxidative process that operates at low temperature, very low risk.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>2</td>
<td>High risk of new POP formation as the destruction occurs at high temperatures in the presence of oxygen.</td>
</tr>
<tr>
<td>GPCR</td>
<td>8</td>
<td>Even though the process is reductive, excessive levels of dioxins were found in the emissions of the old Kwinana plant, due to improper process maintenance.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>10</td>
<td>A reductive non-thermal process. No risk.</td>
</tr>
<tr>
<td>MSO</td>
<td>2</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>PACT</td>
<td>2</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>6</td>
<td>A more efficient destruction of dioxin precursors and prevention of de novo synthesis by rapid cooling of the plasma gas. It is believed that the risk is lower than in the other PAT processes.</td>
</tr>
<tr>
<td>PWC</td>
<td>2</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>SCWO</td>
<td>2</td>
<td>See GeoMelt.</td>
</tr>
<tr>
<td>SET</td>
<td>10</td>
<td>A reductive non-thermal process. No risk.</td>
</tr>
<tr>
<td>Silver II</td>
<td>8</td>
<td>An oxidative process that operates at low temperature, very low risk.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>10</td>
<td>A reductive thermal process where the decomposition of contaminants and binding of chlorine in the inorganic salt is very efficient, so the possibility of de novo synthesis should be very low.</td>
</tr>
<tr>
<td>SR</td>
<td>10</td>
<td>A reductive non-thermal process. No risk.</td>
</tr>
</tbody>
</table>

**Reagents hazard**

Danger resulted from the nature of reagents, solvents, and other chemical substances that are introduced in the process. In particular, flammability, toxicity, corrosiveness, and other properties recognized hazardous to humans and the environment are considered. The evaluation is based on the comparative danger and amounts of these chemicals.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>6</td>
<td>The alkaline earth metals and their oxides (e.g. Mg, CaO, etc.), which are used as reagents, are corrosive and can react vigorously with air and water thereby representing a risk of fire. CaO is also a severe irritant.</td>
</tr>
<tr>
<td>BCD</td>
<td>10</td>
<td>No toxic, flammable, or other hazardous reagents are involved.</td>
</tr>
<tr>
<td>CerOx</td>
<td>6</td>
<td>Cerium nitrate (III) at moderate concentration has moderate toxicity and low ignition danger, but is a severe irritant. Nitric acid, which is used in the cerium regeneration system, is also a severe corrosive agent and irritant.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>10</td>
<td>No toxic, flammable, or other dangerous reagents are involved.</td>
</tr>
<tr>
<td>GPCR</td>
<td>2</td>
<td>Hydrogen at high temperatures is used (fire and explosion hazard).</td>
</tr>
<tr>
<td>HydroDec</td>
<td>2</td>
<td>Hydrogen is used as reagent (fire and explosion hazard).</td>
</tr>
<tr>
<td>MSO</td>
<td>10</td>
<td>No toxic, flammable, or other dangerous reagents are involved.</td>
</tr>
<tr>
<td>PACT</td>
<td>10</td>
<td>No toxic, flammable, or other dangerous reagents are involved.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>10</td>
<td>No toxic, flammable, or other dangerous reagents are involved.</td>
</tr>
<tr>
<td>PWC</td>
<td>10</td>
<td>No toxic, flammable, or other dangerous reagents are involved.</td>
</tr>
<tr>
<td>SCWO</td>
<td>10</td>
<td>No toxic, flammable, or other dangerous reagents are involved.</td>
</tr>
<tr>
<td>SET</td>
<td>2</td>
<td>Sodium is a recognized chemical hazard, which is highly reactive with oxygen and water (flame hazard) and provokes burns on contact. In addition, ammonia is also severely poisonous and corrosive.</td>
</tr>
<tr>
<td>Silver II</td>
<td>6</td>
<td>See CerOx.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>2</td>
<td>The process involves excess of highly reactive calcium hydride, which is a flammable solid, reacts with water and is corrosive. Therefore it may provoke fire if improperly stored or treated. Contact may cause burns.</td>
</tr>
<tr>
<td>SR</td>
<td>2</td>
<td>Sodium hazard (see SET).</td>
</tr>
</tbody>
</table>

**Process vulnerability**

This criterion aims to evaluate the risk of incidents in the process, such as vulnerability to ignition/explosion, uncontrolled emissions, and other malfunctioning. Some factors that influence the risk connected to process operation include process containment, contact with oxygen, chemicals involved, temperature, pressure, etc.). This criterion can depend
on the previously described reagent danger whenever the risk of incidents is originally caused by the presence of hazardous substances (e.g. flammable or explosive reagents or solvents).

<table>
<thead>
<tr>
<th>Technology</th>
<th>Score</th>
<th>Comments and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ball Milling</td>
<td>10</td>
<td>The process is closed and safe (low temperature and pressure, moderate chemical hazards).</td>
</tr>
<tr>
<td>BCD</td>
<td>6</td>
<td>Medium safety due to elevated temperatures. The oil which is used as reagent can be flammable under these conditions in the case of process malfunctioning.</td>
</tr>
<tr>
<td>CerOx</td>
<td>8</td>
<td>The process is relatively safe as it operates at low temperatures and pressures. The only danger can be attributed to possible NOx emissions.</td>
</tr>
<tr>
<td>GeoMelt</td>
<td>10</td>
<td>The process is safe. It uses a very simple thermal treatment scheme where there are no reagents, no pressure, and no other vulnerability that may lead to fire or uncontrolled emissions.</td>
</tr>
<tr>
<td>GPCR</td>
<td>2</td>
<td>Gaseous hydrogen is highly explosive. Treatment of organic matter with hydrogen at high temperatures in the gaseous phase represents an increased danger.</td>
</tr>
<tr>
<td>HydroDec</td>
<td>6</td>
<td>Hydrogen is involved as reagent. However, hydrogen is continuously fed and consecutively consumed in the liquid reaction phase at relatively low temperatures and pressures.</td>
</tr>
<tr>
<td>MSO</td>
<td>6</td>
<td>Moderate vulnerability, because of the risk of fire at contact of the melt with the organic matter at high temperatures in the presence of oxygen.</td>
</tr>
<tr>
<td>PACT</td>
<td>10</td>
<td>The process is relatively safe. Treatment represents an oxidation process designed in a way similar to incinerator which does not allow fire to escape. Little danger of explosion/fire since the full oxidation of the organic matter takes place immediately in the reaction zone. The process is electrically maintained and can be shut down quickly.</td>
</tr>
<tr>
<td>PLASCON</td>
<td>10</td>
<td>Similar to PACT.</td>
</tr>
<tr>
<td>PWC</td>
<td>6</td>
<td>Similar to PACT and PLASCON. The only weak point is that the oxidation is not exhaustive (pyrolysis), so the pyrolysis gas formed can be considered flammable.</td>
</tr>
<tr>
<td>SCWO</td>
<td>2</td>
<td>Increased vulnerability because of very high pressures involved.</td>
</tr>
<tr>
<td>SET</td>
<td>2</td>
<td>The process involves elevated pressures and the use of hazardous and flammable reagents.</td>
</tr>
<tr>
<td>Silver II</td>
<td>8</td>
<td>Similar to CerOx.</td>
</tr>
<tr>
<td>SPHTD</td>
<td>2</td>
<td>The process is based on the closed explosion-like treatment of solid waste with highly reactive calcium hydride, which involves very high temperatures and pressures, and formation of hydrogen. The technology represents a risk of explosion/fire in the event of depressurizing.</td>
</tr>
<tr>
<td>SR</td>
<td>6</td>
<td>The process is quite simple in operation as no high pressures/temperatures are involved. However the use of sodium compromises the process safety.</td>
</tr>
</tbody>
</table>
4. Applications

In the previous chapter a preliminary in-house assessment of basic parameters of the technologies was performed on the basis of the information available from existing published materials, such as technology reviews by independent experts and environmental organizations. It is expected that the existing data be updated and validated and that a more profound system of criteria be adopted for the DST, the latter being the goal of this work. It is proposed that this DST be issued in the form of software, available to the partners and beneficiaries of UNIDO projects.

In this chapter we describe the basic principles of functionality of the proposed DST, provided also examples of operating the first existing prototype. Several recommendations follow, in particular the complete set of criteria and the technology selection algorithm to be introduced at a later step.

Structure and functionality of the decision-support tool

The evaluation algorithm basically aims at the comparison of technologies in the database; using the existing results of technologies evaluation (scores) against the set of criteria proposed in this review. The algorithm is based on the two realms of technology evaluation, namely selection and prioritization (comparison), which refer to two consecutive phases of the evaluation process.

For example, in the selection phase the user selects only those technologies that satisfy a desired score according to criteria of preference. Usually, these criteria presume binary scoring of technologies (one or zero) and refer to the technology status, applicability, and configuration. The technologies which do not satisfy the desired scores are excluded from further consideration.

After the selection phase, if the reduced list includes more than one technology, the user can perform a more profound evaluation, considering also other aspects, which are addressed by the criteria of cost, performance, experience, input and output, risk, and others, which provide scoring on the 10-grade scale. After defining the criteria of preference, the user obtains a prioritized list of technologies according to the sum score of all selected criteria in this phase.

Examples

The following two general examples illustrate the basic functionality of the DST algorithm. The assessment data used for this demonstration were taken from the database of the present review. This demonstration, including the comparison of some technologies was

112 The selection phase can be also excluded from the algorithm, as well as there should be a possibility of manual selection of technologies from the main list.
performed for demonstrative purposes only and had the only aim to show the functionality of the selection algorithm.

**Example 1**
Task: Urgent destruction of a big pesticide landfill (partially mixed with soil) with high POP content in an industrial facility with high DRE achievable and low risk of formation of new POPs.

**Selection:**
Step 1: Direct applicability:
- Soil (inorganic)
- Solid organics
  - Reduced list: GPCR, Ball Milling, PWC, SET, PACT
  - Sieve: Content of POP: 100%
  - Reduced list: GPCR, Ball Milling, PWC, PACT

**Prioritization:**

<table>
<thead>
<tr>
<th>Criterion</th>
<th>GPCR</th>
<th>Ball Milling</th>
<th>PACT</th>
<th>PWC</th>
</tr>
</thead>
<tbody>
<tr>
<td>DRE</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Throughput</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>New POP formation</td>
<td>8</td>
<td>10</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Total score</td>
<td>20</td>
<td>17</td>
<td>13</td>
<td>12</td>
</tr>
</tbody>
</table>

Therefore, the GPCR represents the most favourable option, followed by Ball Milling. Plasma arc processes receive similar and relatively low scores, mainly because they show lower DRE and higher risk of new POP formation.

**Example 2**
Task: Economic and complete destruction/detoxification of PCB oils in a remote area by a proven approach

**Selection:**
Step 1: Direct applicability:
- Organic liquids
  - Reduced list: All technologies except SPHTD and GeoMelt

Step 2: Status
- Developed
  - Reduced list: GPCR, BCD, PLASCON, SR

Step 3: Mobility status
- Mobile configuration
  - Reduced list: GPCR, BCD, SR

---

113 Ball Milling would be excluded if the two different processes MCD and DMCR representing this technology were separated (DMCR does not fit large scale applications and MCD is not applicable to concentrated organics).
Prioritization:

<table>
<thead>
<tr>
<th>Criterion</th>
<th>GPCR</th>
<th>BCD</th>
<th>SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE</td>
<td>10</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Cost</td>
<td>8</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Full scale experience</td>
<td>8</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Total score</td>
<td>26</td>
<td>26</td>
<td>26</td>
</tr>
</tbody>
</table>

Thus, GPCR, BCD, and SR receive equal scores and can be considered as equally appropriate for the given task. Nevertheless, if the user changes importance (weight) of criteria, this situation changes. For example, in the event the user gives more importance to the DE criterion, the GPCR technology receives a higher score. If the user gives importance to the cost, then SR becomes the preferred option. Should the more experienced technologies be given more importance, BCD and SR would be prioritized.

Software

The first prototype of DST software has been created recently in ICS-UNIDO which is intended to provide a versatile tool for criteria manipulations, such as described in the examples above. This software follows the line of similar DST packages developed in ICS, like DARTS (Decision Aid for Remediation Technology Selection), DAWTS (Decision Aid for Water Treatment Technology Selection), etc.

The first prototype software tool provides the user with a limited set of basic features:

1) selection of technologies of the choice to be simultaneously evaluated and compared with one another;
2) selection of the preferred criteria to be applied for evaluation;
3) assignment of the weight to each of selected criteria;
4) discrimination of technologies from the database on the basis of selected binary criteria (phase 1);
5) ranking of selected technologies, or those of satisfying phase 1, according to their summary scores against a set of selected decimal criteria.

Two figures below exemplify the interface of calculations applied to example 2 (see the previous chapter), as performed by the DST software tool. The two screenshots below refer to the selection and prioritization phases of the algorithm, accordingly.
The prototype DST software performing selection steps of example 2 (see above)

The prototype DST software performing the prioritization of chosen technologies. Different weightings are chosen for different criteria as suggested in example 2 (see above)
Recommendations

For the final DST a more advanced system of criteria is required. The data for its database will be collected via consultation of technology vendors and developers, e.g. by means of questionnaires, as well as via independent assessment by a board of experts. It is proposed that the assessment of technologies be organized in two separate sections, related to quantitative and qualitative data, respectively. The former part will be more based on the data obtained from technology representatives regarding exact and documented process characteristics. The latter part will more rely on the opinion of independent experts, regarding certain qualities of technologies that cannot be quantified or where synthesis of more process characteristics is required. Such envisaged system of criteria is proposed below.

Proposed detailed criteria system

Quantitative criteria

1. Treatment options:
   a. pure solid organic matter containing POPs;
   b. liquid POPs, e.g. PCBs and/or organic solutions;
   c. POPs (solid or liquid) containing or mixed with inorganic/inert impurities;
   d. POP contaminated soils;
   e. POP contaminated water;
   f. POP contaminated gases;
   g. sludges and slurries of POP or of POP contaminated matrices in water;
   h. humid or water containing waste;
   i. emulsions of organic liquids, containing POPs, in water.
   There can be limitations regarding different properties of waste to be treated, e.g. water content, particle size, viscosity, content of solid matter in liquids, content of organics in the feed, content of inorganics in the feed, etc. Sometimes, a pre-treatment can be required for a waste type exceeding the limitations. Emphasis should be placed on the possibility of treatment of other contaminated objects, such as containers, PCB equipment, debris, etc.

2. Pre-treatment
   If for one or more of the above treatment options cannot be performed directly, different types of pre-treatment can be required, for example:
   a. mixing;
   b. dilution;
   c. filtration;
   d. crushing;
   e. dewatering;
   f. pre-heating;
   g. other.
   It should be specified if the pre-treatment can be provided as a separate module of the same technology or if a separate technology is required.

3. Maximum allowable POP content (%) in the input stream that enters in the reactor (either directly or after proper pre-treatment) for the following waste types:
   a. bulk organic (solid/liquid/mixed);
   b. inorganic (inert matrix bound/mixed);
3. Applications
   c. aqueous (suspension/emulsion/solution);
   d. gaseous (vapours/gases/particulates).
   The same values should be assessed for the streams that enter in the pre-
treatment system.

4. Configuration
   a. Fixed configuration (permanent plant which is not designed to be transported
      after installation).
   b. Modular. The modules can refer to different steps of the process or to facilitate
      plant assembling or be designed to build up the process throughput.
   c. Portable or mobile. The plant can be either “Easy to transport”, i.e. it should
      be assembled on site or be “True portable”, which means that the plant is
      ready for operation, as transported, without or with minor on-site installation
      and with minimum or no need of infrastructure.

5. The process regime
   a. Continuous flow
   b. Batch
   c. Mixed (e.g. continuous pre-treatment + batch main process or vice versa)

6. The scale(s) and scalability
   a. Maximum throughput expressed as pure POP amount that can be routinely
      treated. It may be useful to assess this parameter separately for different
      matrices (treatment options, see above) as it may vary from one matrix to
      another. In case when non-concentrated POP should be treated (e.g. soil) it
      is sometimes more appropriate to assess the maximum gross throughput,
      because it can be independent from the POP content, e.g. be conditioned by
      the pre-treatment system power.
   b. Availability of different throughput plants either for the same or different
      configurations (fixed, mobile, etc.) or for different streams/matrices (bulk
      organics, liquids, soils, etc.).
   c. Throughput multiplication or possibility to increase throughput by adding
      together treatment modules should be assessed.
   d. The throughput can be often widely tuned for the same single plant, so the
      range of possible throughputs can be assessed as a separate parameter
      (scalability) or be considered within criterion “availability of different
      throughput plants” (see above). This option should be assessed only if the
      throughput of the plant remains economically sound.
   e. The minimum, economically rational or advised throughputs can also be
      assessed if necessary.

7. Operation time
   The time per day or days per week that the plant can operate non-stop at the
   maximum or optimal throughput is implied.

8. Destination of application:
   a. on industrial sites (infrastructure required);
   b. in remote areas (less or no infrastructure required);
   c. both options possible.
9. Power and consumables (not recycled) per ton of treated matter (or pure POP). It is useful also to specify whether the power or reagent consumption increases with increase in the POP content in waste or chlorine content or if it depends on the organic content in waste.
   a. Electric power consumption.
   b. Amount of gas consumed as reagent, fuel, or carrier.
   c. Amount of water required.
   d. Amount of organic matter (other than gas – reagent, solvent, etc.).
   e. Amount of inorganic matter (other than water and gas).

10. Chemicals (not quantitative)
   a. List of chemical substances consumed/required by the technology.
   b. List of principal chemical substances released by the technology.

11. Disposal of waste
   a. Solid waste can be discharged to the land.
   b. Solid waste can be deposited to MW landfill.
   c. Solid waste should be deposited to hazardous waste landfill.
   d. Solid waste requires further treatment in order to be deposited to landfill.
   Similar assessment should be made with regard to the aqueous waste disposal, i.e. if it can be dumped directly to the sewage or be deposited in hazardous waste pools or be further treated.

12. The amount of waste produced by the technology per ton of POP processed
   a. Solid organic waste
   b. Solid inorganic waste
   c. Liquid organic waste
   d. Aqueous waste
   e. Gaseous emissions

13. Possibility of reuse of any of process residuals/products

14. Possibility of energy production in the process that can be used externally. Estimate per ton of POP processed.

15. DE and DRE. Preferably, both DE and DRE observed in different plants/applications should be considered, assessing both minimum and maximum values. It is also useful to assess DE and DRE separately for different matrices, such as:
   a. concentrated POPs (over 50% PCBs, stockpiled pesticides);
   b. high-strength POP waste (over 0,5% - organic mixtures/solutions);
   c. low-strength POP waste (below 0,5% - PCB fluids, etc.);
   d. contaminated objects (several % - soil, sludge, etc.);
   e. other (e.g. water, gaseous effluents).
   For gas post-treatment it is useful to assess both DRE before and after gas post-treatment.

16. Maturity (proposed parameters for assessment)
   a. Time the technology has been operating full scale.
   b. Amount of POP destroyed till now.
   c. Since when the technology can be considered commercial.
   d. Time the technology operated on pilot scale and when started operating.
   e. Time the technology was developed and when its scale up started.
f. Number of full scale plants installed worldwide.
g. For technologies not originally designed for POP treatment: when was the
technology applied for POP destruction for the first time.

17. List of countries, where the technology has special licenses/permits for POP
treatment (for qualitative assessment). Experience of operation in developing or
transition economy countries can be assessed separately.

18. Cost of operation expressed as cost per ton of pure POP/ton of mixed waste.
Total sum should be provided and, if possible, breakdown of costs should be
given (electricity, consumables, labour, disposal, monitoring, maintenance, pre-
treatment, etc.). It is also useful to assess separately costs for different matrices,
as these may vary (e.g. concentrated POPs, organic liquids, sludge/soils).

19. Capital cost. Where applicable min and max values should be given for different
plants. Breakdown of costs can be made (equipment, rent, royalties, labor, etc.).

Qualitative criteria (based on relative assessment by independent experts)

20. Ease of operation
   a. Personnel qualification level.
   b. Automation level.
   c. No. personnel required.

21. Envisaged capability to efficiently and irreversibly destroy POP substances
    (considering chemical, physical, and technological factors)

22. Containment (technological design or process nature that allows not to produce
    emissions by containing process streams)

23. New POP formation danger, considering risks connected to both process chemistry
    and technological design

24. General hazards of products/waste, including risk connected with waste
    disposal

25. General hazard of reagents, related to their handling, storage, and transportation

26. General technology operation risks, such as vulnerability to fire and exposure
    to toxicants, or probability of malfunctioning. Complex assessment including
    engineering design, operating conditions, etc.

Proposed algorithm for technology evaluation

A schematic representation of the proposed selection & comparison algorithm of
technology evaluation, to be applied to the assessment data collected in accordance with
the proposed set of criteria given above, is presented below.

Realm I: Selection

Several basic steps of selection are proposed, where one or more steps can be
skipped (disabled) or their sequence can be changed.
First Step: Selection according to object

A) Direct applicability (the user prefers that only those technologies be considered that can be applied to the object as is, without any eventual pre-treatment steps)

B) Indirect applicability (the user wants to consider any technology that is in principle applicable to the object, even if some pre-treatment not foreseen in the basic technology configuration is required)

In both cases the user is then invited to select one or more objects (types of waste) that the technology should be applied to:

- Solid organic matter
- Organic liquid
- Aqueous waste
- Gaseous
- Mixed with inorganics
- Pumpable slurry

Limitations (sieves)\(^\text{114}\)

The user is asked to specify desired limits according to:

- Water content in humid waste
- Size of particles
- Content of organics
- Content of inorganics
- Content of chlorine (or of POP)

Second Step: Selection according to status

B) Simplified approach

C) Detailed approach

If (A), one or more of following is selected:

- Commercial established
- Commercial emerging
- Promising
- Transition

If (B), the following matrix applies:

- Commercial status (4 levels, from none, emerging, neo, commercial)
- Operating scale (3 levels, small, medium, large)
- Applicability to POP proof (4 levels, none/theoretical, trial, demonstrated, applied)

Supplementary possibilities:

- Mark technologies that operate(d) in developing countries
- Rank technologies according to the number of countries where they operated or the number of medium to large scale international projects
- Visualization of countries

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\(^{114}\) These criteria provide additional limitations of technology applicability to one or another waste type. The sieves can have a more complicated scale than two-grade (applicable or not applicable). For example, the applicability of technologies to wastes with different water content, different particle size, different content of organics, can be defined more precisely. Sieves should apply for selection according to direct applicability (A).
Third Step: Selection according to mobility
- Fixed plant (higher installation costs, bigger scale, waste is to be transported to industrial site)
- Portable (on-site application, lower installation costs, smaller scale)
  ➔ Reduced list

Fourth Step: Selection according to modular design
- Modular design allows to increase capacity
- Modular design allows to change configurations
- Modular design allows simplified assembly and transportation
  ➔ Reduced list
- Desired maximum throughput (pure POPs) (3 or more levels)
  ➔ Reduced list

Realm II: Prioritization
In this realm, the user adopts the multicriteria analysis algorithm (see below) in order to perform a concerted comparison of technologies from the list against a set of criteria. The user is given the possibility to choose desired criteria among the following and to assign weights to criteria.

- DE
- DRE
- Throughput full-strength POP
- POP strength
- Set up cost
- Operation cost
- Experience
- Ease of operation
- Containment
- Electric power requirement
- Gaseous reagent, carrier, and/or fuel requirement
- Water requirement
- Reagent and/or solvent requirement
- Secondary waste disposability
- Solid residues
- Liquid residues
- Gaseous emissions
- Products can be useful
- New POP formation danger
- Technology operation danger
- Reagents toxicity danger
- Reagents other danger
  ➔ Prioritized list
5. **Technology vendor reference points**

1. **Ball Milling**
   MCD™ (Mechanochemical Dehalogenation)

   *Environmental Decontamination Ltd (EDL), PO Box 58 609, 139 Cryers Rd, East Tamaki, Auckland, New Zealand*
   Contact person: Mr. Bryan Black
   T +64 9 274 9862; F +64 9 274 7393; Email: bblack@edl.net.nz
   http://edl.net.nz/index.php

   DMCR (Dehalogenation by Mechanochemical Reaction)

   *TRIBOCHEM, Georgstrasse 14, D-31515 Wunstorf, Germany*
   Contact person: Dr. Volker Birke
   T +49 5031 67393; F +49 5031 8807, Email: birke@tribochem.com
   http://www.tribochem.de

2. **BCD (Base Catalyzed Decomposition)**
   *BCD Group, Inc., Cincinnati, OH 45208, USA*
   Contact person: Mr. Thomas Opperman
   T +1 513 899 4869; Fax: +1 513 899 4869;
   Email: Opperman_t@bcdinternational.com
   www.bcdinternational.com - recently acquired by:
   *DoloMatrix International Limited, Level 6, 1 Elizabeth Plaza, North Sydney, NSW 2060, Australia*
   Tel.: +61 2 8920 9755; Fax: +61 2 8920 9766; E-mail: info@dolomatrix.com
   http://www.dolomatrix.com

3. **CerOx™ (Mediated electrochemical oxidation by Ce IV)**
   *CerOx Corporation, 2602 Airpark Drive, Santa Maria, CA 93455, USA*
   Contact person: Mr. Matt van Steenwyk or Mr. Norvell Nelson
   T +1 805 925 8111; F +1 805 925 8218;
   Email: info@cerox.com, mattvs@cerox.com
   njnelson@cerox.com http://www.cerox.com

4. **GeoMelt™**
   *AMEC Earth and Environmental Inc., GeoMelt Division:*

   North/South America:
   *AMEC Earth & Environmental, Inc., 1135 Jadwin Avenue, Richland, WA 99352, USA*
   Contact person: Leo Thompson
   T +1 509 942 1114; F +1 509 942 1122; Email: leo.thompson@amec.com
UK/Europe:
AMEC Earth & Environmental, Inc., 11 The Boulevard Crawley, West Sussex RH10 1UX, UK
Contact person: Don Fraser (AMEC GeoMelt Director)
T +44 1293 584 208; F +44 1293 562 219; Email: don.fraser@amec.com

Asia Pacific Region:
AMEC Environmental Asia Pacific, Level 1, 431-439 King William Street, Adelaide, South Australia 5000
Contact person: David Osborne
T +61 8 8410 3133; F +61 8 8410 3122; Email: david.osborne@amec.com
http://www.geomelt.com

5. GPCR™ (Gas-Phase Chemical Reduction)
Hallett Environmental & Technology Group Inc., 18 Robb Blvd Unit#7, Orangeville, Ontario, Canada L9W 3L2
Contact person: Craig McEwen
T +1 519 747 3952; F +1 519 747 9011; Email: cmcewen@heatgroup.com

Bennett Environmental Inc., 1540 Cornwall Road, Suite 208, Oakville, Ontario, Canada L6J 7W5
T +1 905 339 1540; F +1 905 339 0016; Email: info@bennettenv.com
http://www.bennettenv.com

6. HydroDec™ (Hydrodechlorination)
Hydrodec Group plc, Gainsborough House, 33 Throgmorton Street, London ECN 2BR, UK
T +44 20 7861 8630; F +44 20 7861 9631; Email: enquiries@hydrodec.com
http://www.hydrodec.com

For CHD technology see:
Kansai Electric Power Co and Kanden-Engineering Co.
http://www.kanden-eng.co.jp

7. MSO (Molten Salt Oxidation)
Lawrence Livermore National Laboratory, Chemistry and Materials Science, 7000 East Avenue, Livermore, CA 94550, USA
Contact person: Peter Hsu
T +1 925 422 0317; F +1 925 424 3281; Email: hsu7@llnl.gov
http://www-cms.llnl.gov/s-t/molten.html

8. PACT (Plasma Arc Centrifugal Treatment)
Retech Systems LLC, 100 Henry Station Road, Ukiah, CA 95482, USA
Contact Person: Leroy Leland
T+17074671724;F+17074624103;EMail:leroy.b.leland@retechsystemsslc.com
http://www.retechsystemsslc.com

9. PLASCON™ (Plasma Conversion)
SRL Plasma Pty Ltd., BCD Technologies Pty Ltd., PO Box 119, 2 Krypton Street, Narangba, Queensland 4504, Australia
Contact person: Mr. Dibley
T +61 7 3203 3400; F +61 7 3203 3450; Email: srlplasma@gil.com.au, sales@
10. **PWC™ (Plasma waste converter)**  
*Startech Environmental Corp.*, 15 Old Danbury Road, Wilton, CT 06897-2525, USA  
T +1 203 762 2499; F +1 203 761 0839; Email: starmail@startech.net  
http://www.startech.net

11. **SCWO (Supercritical Water Oxidation)**  
*SRI International*, 333 Ravenswood Avenue, Menlo Park, CA 94025-3493, USA  
Contact person: Indira Jayaweera  
T +1 650 859 4042; Email: indira.jayaweera@sri.com  
http://www.sri.com

*General Atomics*, 3550 General Atomics Court San Diego, CA 92121-1122, USA  
Contact person: Michael Spritzer  
T +1 858 455 2337; F +1 858 455 4111; Email: Michael.spritzer@gat.com  
http://demil.ga.com

*Foster Wheeler Development Corporation*, 12 Peach Tree Hill Road, Livingston, NJ 07039, USA  
Contact person: K.S. (Al) Ahluwalia  
T +1 973 535 2246; F +1 973 535 2242; Email: al.ahluwalia@fwc.com  
www.fwc.com

*Chematur Engineering AB (CEAB)*, Box 430, SE-691 27 Karlskoga, Sweden  
T +46 586 641 00; F +46 586 791 700; Email: info@chematur.se  
http://www.chematur.se

*HydroProcessing, L.L.C.*, 3201 Longhorn Blvd Suite 101, Austin, TX 78758, USA  
T +1 512 339 9981; F +1 512 339 9827; Email: info@hydroprocessing.com  
http://members.fortunecity.com/emulloy/index.htm

12. **SET™ (Solvated Electron Technology)**  
*Commodore Applied Technologies, Inc.*, 150 East 58th Street, New York, NY 10155, USA  
T +1 212 308 5800; F +1 212 753 0731  
http://www.commodore.com

13. **Silver II™ (Mediated electrochemical oxidation by AgII)**  
*Accentus plc (subsidiary of AEA Technology plc)*, 551 Harwell, Oxfordshire, OX 11 0QJ, UK  
T +44 870 190 2921; F +44 870 190 2920; Email: enquiry@accentus.co.uk  
http://www.aeat.com

AEA Technology Engineering Services, Inc., 241 Curry Hollow Road, Pittsburgh, PA 15236, USA  
T +1 412 655 1200; F +1 412 655 2928  
http://www.aeatech.com
14. SPHTD (Self-Propagating High-Temperature Dehalogenation)
Centro Studi sulle Reazioni Autopropaganti, Dipartimento di Ingegneria Chimica e
Materiali, Piazza d'Armi, 09123 Cagliari, Italy
Contact person: Prof. Dr. Ing. Giacomo Cao
T +39 070 675 5058; F +39 070 675 5057; Email: cao@visnu.dicm.unica.it

15. SR (Sodium reduction)
Dr. Bilger Umweltdconsulting GmbH
Bilger Dispersed Sodium (BDS) Technology
Hanau, Germany (www.bilgergmbh.de; www.earthfax.com/Bilger/bds.htm)

Decoman srl,
Milan, Italy (www.decoman.it)

EarthFax Engineering Inc. (BDS Technology)
Midvale, USA (www.earthfax.com)

Envio Germany GmbH & Co. KG
Dortmund, Germany (www.envio-group.com)

Fluidex Engineering Ltd. (GE Energy)
Gauteng, South Africa (www.fluidex.org)

Kinectrics, Inc. (now member of AEA Technology Group)
Ontario, Canada (www.kinectrics.com)

Kobelco Eco-Solutions Co., Ltd.
Kobe, Japan (www.kobelco-eco.co.jp)

Manitoba Hydro
Manitoba, Canada (www.hydro.mb.ca)

Nippon Soda Co. Ltd.
Japan (www.nippon-soda.co.jp)

Orion BV
Drachten, The Netherlands (www.orionun2315.nl)

Powertech Labs, Inc.
Vancouver, Canada (www.powertechlabs.com)

Safety-Kleen
Ohio, USA (www.safety-kleen.com)

Sanexen Environmental Services Inc.
Quebec, Canada (www.sanexen.com)

TASSCO
Ontario, Canada (rusiniaks@ica.net; T +1 905 851 1803; F +1 905 8519210)
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http://www.basel.int

SITE technology profiles, ninth edition  
http://clu-in.org/products/site/demon.htm

Stockholm Convention on persistent organic pollutants  
http://www.pops.int

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http://cpeo.org/index.html

UNIDO POPs activities http://www.unido.org/doc/29685

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NFESC, no date. Solvated Electron Technology. Findings and Recommendations by NFESC Technology Application Team

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UNEP, 2004c. *Technical Guidelines for Environmentally Sound Management (ESM) of Wastes Consisting of, Containing or Contaminated with Polychlorinated biphenyls (PCB), Polychlorinated terphenyls (PCT), and Polybrominated biphenyls (PBB) (Draft)*, available at [www.basel.int](http://www.basel.int)


UNEP, 2004e. *Technical Guidelines for Environmentally Sound Management (ESM) of Wastes consisting of, containing or contaminated with the pesticides Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex or Toxaphene (Draft)*, available at [www.basel.int](http://www.basel.int)


Presentations and conference materials


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<td>National Research Council, 1996.</td>
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<td>Rahuman et al., 2000.</td>
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Information from vendors

The following companies and organizations are acknowledged for having responded to the ICS-UNIDO questionnaire and/or providing other feedback and useful data on their technologies that helped in the preparation of this review.

AMEC Earth and Environmental, Inc. (GeoMelt™)

BCD Group, Inc. (BCD)

Centro Studi sulle Reazioni Autopropaganti, Dipartimento di Ingegneria Chimica e Materiali, Cagliari University (SPHTD)

Dr. Bilger Umweltconsulting GmbH (BDS, SR)

Hallett Environmental & Technology Group Inc. (GPCR™)

SRL Plasma Pty. Ltd. (PLASCON™)
Appendix 1. Technology evaluation results

In this appendix the results of the technologies evaluation performed in Chapter 3 are summarized in for each technology. Descriptions of criteria and parameters are given as footnotes. Please refer to the detailed description of criteria given in Chapter 3.

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### Output (inversed)

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### Risk (inversed)

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### Risk (inversed)

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### Risk (inversed)

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<tr>
<td>Products can be useful</td>
<td>6</td>
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</tbody>
</table>

### Risk (inversed)

<table>
<thead>
<tr>
<th>Category</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>New POP formation</td>
<td>10</td>
</tr>
<tr>
<td>Reagents hazard</td>
<td>2</td>
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<tr>
<td>Process vulnerability</td>
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13. Silver II

<table>
<thead>
<tr>
<th>Maturity</th>
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</thead>
<tbody>
<tr>
<td>Commercial established</td>
<td>0</td>
</tr>
<tr>
<td>Commercial emerging</td>
<td>0</td>
</tr>
<tr>
<td>Transition</td>
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<tr>
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<table>
<thead>
<tr>
<th>Applicability</th>
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<tbody>
<tr>
<td>Solid organic matter</td>
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</tr>
<tr>
<td>Oils and organic solutions</td>
<td>1</td>
</tr>
<tr>
<td>Inorganic solid bound</td>
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<td>Slurries</td>
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<td>Humid or water containing waste</td>
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<td>Aqueous solutions</td>
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<table>
<thead>
<tr>
<th>Performance</th>
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<tbody>
<tr>
<td>DE</td>
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<tr>
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<td>POP throughput</td>
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<table>
<thead>
<tr>
<th>Cost</th>
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<tbody>
<tr>
<td>Set up cost</td>
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<td>Cost operation</td>
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<table>
<thead>
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<tr>
<td>Experience of commercial operation</td>
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<table>
<thead>
<tr>
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<tbody>
<tr>
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<table>
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<tbody>
<tr>
<td>Electric power requirement</td>
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<tr>
<td>Gaseous reagent, carrier, and/or fuel requirement</td>
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</tr>
<tr>
<td>Water requirement</td>
<td>2</td>
</tr>
<tr>
<td>Reagent and/or solvent requirement</td>
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</tr>
<tr>
<td>Output (inversed)</td>
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</tr>
<tr>
<td>---------------------------------------</td>
<td>---</td>
</tr>
<tr>
<td>Secondary waste disposability</td>
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</tr>
<tr>
<td>Solid residues</td>
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# 14. SPHTD

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<table>
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<tr>
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</thead>
<tbody>
<tr>
<td>DE</td>
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</tr>
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<tr>
<td>POP throughput</td>
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<td>POP strength</td>
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<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Set up cost</td>
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</tr>
<tr>
<td>Cost operation</td>
<td>n/a</td>
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</tbody>
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<table>
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<tr>
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<tr>
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<tr>
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<tr>
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<td>Output (inversed)</td>
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</tr>
<tr>
<td>--------------------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Secondary waste disposability</td>
<td>6</td>
</tr>
<tr>
<td>Solid residues</td>
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</tr>
<tr>
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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>New POP formation</td>
<td>10</td>
</tr>
<tr>
<td>Reagents hazard</td>
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<td>Process vulnerability</td>
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## 15. SR

### Maturity

<table>
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<tr>
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<tbody>
<tr>
<td>Commercial established</td>
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### Applicability

<table>
<thead>
<tr>
<th>Property</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Solid organic matter</td>
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<tr>
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### Configuration

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<tbody>
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<tr>
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### Performance

<table>
<thead>
<tr>
<th>Property</th>
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<tr>
<td>DE</td>
<td>6</td>
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<td>DRE</td>
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### Cost

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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<td>10</td>
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</table>

### Experience

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<tbody>
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<td>10</td>
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<tr>
<td>Experience of full scale operation</td>
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</tbody>
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### General

<table>
<thead>
<tr>
<th>Property</th>
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<tbody>
<tr>
<td>Ease of operation</td>
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<tr>
<td>Containment</td>
<td>10</td>
</tr>
</tbody>
</table>

### Input (inversed)

| Property                                                        |   |
|                                                               |---|
| Electric power requirement                                     | 10 |
| Gaseous reagent, carrier, and/or fuel requirement              | 10 |
| Water requirement                                              | 10 |
| Reagent and/or solvent requirement                             | 2 |
### Output (inversed)

<table>
<thead>
<tr>
<th>Category</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary waste disposability</td>
<td>8</td>
</tr>
<tr>
<td>Solid residues</td>
<td>6</td>
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<tr>
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<td>Gaseous emissions</td>
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<td>Products can be useful</td>
<td>10</td>
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### Risk (inversed)

<table>
<thead>
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