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DESTRUCTION TECHNOLOGIES FOR POLYCHLORINATED BIPHENYLS (PCBS)

BY

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ABSTRACT

A critical, necessarily not exhaustive, review of destruction technologies for polychlorinated biphenyls (PCBs) is reported. PCBs are one of the best known of the twelve compound classes defined as Persistent Organic Pollutants (POP).

Although the production of PCBs has been banned all over the world since several years, as PCBs were and in many instances still are used as dielectric fluids (e.g. some trade names: Aroclor in the U.S.A., Sovtol in the ex U. S. S. R. Countries, Clophen in Germany, Kanechlor in Japan, and so on) and for other industrial uses, their presence in anthropogenic products/equipment/appliances and their dispersion in the environment is still relevant and extremely differentiated. The present PCBs destruction technologies analysis take therefore in account the need for criteria in assessing performances of already developed technologies and, when necessary, optimizing or boosting under development innovative processes.

Key Words: PCBs, remediation, waste, treatment

1. INTRODUCTION

There is growing demand in the public opinion (as reflected from governmental and non governmental organizations and from the scientific community efforts) that stocks, stores and environmental reservoirs of obsolete chemicals and POPs-contaminated wastes must be rapidly identified, properly collected and properly destroyed in order to stem their continued migration into the general environment.

Persistent organic pollutants are highly stable organic compounds used as pesticides or in industry or unintentionally produced as the by-products of industrial processes (mainly incineration) and / or other human activity.

The criteria to classify a pollutant as POP are under continuous evolution [1], due to the progress in understanding their environmental fate and the necessity to prevent and remedy their effects on human health and environment: lipophilicity, persistence (resist photolytic, chemical and biological degradation) and toxicity. As POPs are semi-volatile they may be transported around the planet in the atmosphere and as they are fat-soluble by definition (accumulate in the fatty tissues of living organism) a bio-magnification process generally takes place.

Differently from other POPs classes, PCBs are – or were – industrial products, mainly synthetic oils. In common with many of them (PCDD/F and pesticides) is the fact that they contain chlorine.

Combustion technologies that have historically been used to attempt the destruction of POPs stocks and POPs contaminated materials may fail to meet the stringent environmental conditions progressively being set in the last decade. Indeed, combustion technologies themselves are identified as major sources from which POPs and other hazardous substances are released to the environment.

Thus the threat of POPs for the environment and health of population on a planetary scale is so serious that it requires urgent and effective measures. Several actions were therefore established under UN agencies (UNEP, UNIDO, ICS-UNIDO, etc) in 1998-2000 within the UNEP program for negotiation rounds of the Intergovernmental Negotiating Committee were held on elaborating the legal documents on international prohibition of POPs. Various aspects of POPs and PCBs have been covered by UNEP Chemicals on following topics: Inventory of World-wide PCB Destruction Capacity [2], Guidelines for the Identification of PCBs and Materials Containing PCBs [3], Inventory of Information Sources on Chemicals PERSISTANT ORGANIC POLLUTANTS [4], Survey of Currently Available Non-Incineration PCB Destruction Technologies [5]. Prior to the POPs negotiations, UNEP organized a series of regional/subregional awareness raising workshops on POPs and PCBs, which covered developing countries and countries with economies in transition to prepare the governments and other partners for the negotiations and encourage immediate action on POPs at the national and regional level including case studies.

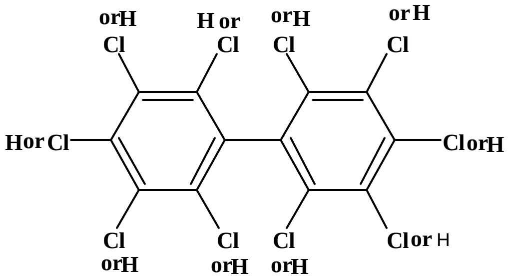
Within the plan of action of UN organizations with support of the International Centre for Science and High Technology (ICS)-UNIDO an Expert Group Meeting (EGM) on *"Clean Technologies for the Reduction and Elimination of POPs"* was held in Trieste, Italy, from 4-5 May 2000. Also ICS-UNIDO in collaboration with the Russian Federation State Duma Committee on Environment, a sub-regional meeting of the international group of experts was held in Sait-Petersburg from 16 to 19 October 2000 on the theme "*POPs reduction-elimination in North-Eastern Europe*". The meeting was organised by the Saint-Petersburg Regional Foundation for Scientific and Technological Development.

The purpose of this paper is to review the existing technologies to treat PCBs, presenting their limitations and some technical, environmental, social and economic criteria to choose the most proper technique.

2. FACTS ABOUT PCBS [6]

Chemical Structure: The chemical structure of the PCBs is the following. The variety of possible positions for the chlorine atoms give rise to 209 structures (containing at least one chlorine atom) called congeners. Congeners with the same number of chlorine atoms, but in different positions are termed isomers.

PCBs are either oily liquids or solids and are colorless to light yellow in color. They have no known smell or taste. There are no known natural sources of PCBs. Some commercial PCB mixtures are known in the United States by their industrial trade names, such as Aroclor and Askarel.



Chemical Structure of PCBs

PCBs don't burn easily and are good electricity insulating material. They have been used widely as coolants and lubricants in transformers, capacitors, and other electrical equipment. Products containing PCBs are old fluorescent lighting fixtures, electrical appliances containing PCB capacitors, old microscope oil, and hydraulic fluids.

PCBs can be released into the environment from hazardous waste sites that contain PCBs, illegal or improper dumping of PCB wastes, and leaks from electrical transformers containing PCBs. PCBs may be carried long distances in the air and they remain in the air for approximately 10 days. In water, a small amount of the PCBs may remain dissolved, but most sticks to organic particles and sediments. PCBs in water build up in fish and marine mammals and can reach levels thousands of times higher than the levels in water.

One might get exposed to PCBs by using old fluorescent lighting fixtures and old appliances such as television sets and refrigerators; from the leak, small amounts of PCBs into the air when they get hot during operation; eating food, including fish, meat and dairy products containing PCBs; breathing air near hazardous waste sites that contain PCBs; drinking PCB-contaminated well water; repairing or maintaining PCB transformers.

Animal experiments have shown that PCB mixtures produce adverse health effects that include liver damage, skin irritations, reproductive and developmental effects, and cancer. People exposed to PCBs in the air for a long time have experienced irritation of the nose and lungs, and skin irritations, such as acne and rashes. It is not known whether PCBs may cause birth defects or reproductive problems in people. Some studies have shown that babies born to women who consumed PCB-contaminated fish had problems with their nervous systems at birth. However, it is not known whether these problems were definitely due to PCBs or other chemicals.

There are tests to find out if PCBs are present in human blood, body fat, and breast milk. Blood tests are probably the easiest, safest, and best method for detecting recent exposures to large amounts of PCBs. However, since all people in the industrial countries have some PCBs in their bodies, these tests can only show if one has been exposed to higher-than-normal levels of PCBs. However, these measurements cannot determine the exact amount or type of PCBs one has been exposed to or how long exposition was. In addition, they cannot predict whether any harmful health effects will be experienced.

In order to better define emission limits for polychlorinated dibenzodioxins /dibenzofurans (PCCD/F), Toxicity Equivalence Factor (TEF) have been defined for each of the compounds in these classes of POPs, and the limit imposed is expressed as toxic equivalent (TEQ), that is the toxic equivalent quantity given by the product between the single compound concentration and its TEF. E. g. European limit for PCDD/F concentration in flue gases from waste incinerators is 0.1 TE ng/Nm^3. TEF have been defined also for PCBs.

The TEF may be assumed as an order of magnitude estimate of the toxicity of a compound, relative to the toxicity of TCDD that is derived using careful scientific judgement after considering all available data [7]. The relative potency of a compound obtained in a single in vivo or in vitro study will be referred to as a relative potency (REP) value. TEFs, in combination with chemical residue data can be used to calculate toxic equivalent (TEQ) concentrations in various media, including animal tissues, soil, sediment and water. TEQ concentrations in samples containing PCDDs, PCDFs and PCBs are calculated using the following equation:

$$\mathbf{TEQ = (\Sigma\,[PCDDi \times TEFi]n) + (\Sigma\,[PCDFi \times TEFi]n) + (\Sigma\,[PCBi \times TEFi]n)}$$

Substantial evidence indicated that the TEF approach is equally valid for human risk assessment as for wildlife, although wildlife risk assessments usually attempt to estimate population-level effects (unlike traditional human risk assessments, which focus on protecting individuals) because effects on populations are of greater ecological relevance than are effects on individuals. The criteria used for including a compound in wildlife TEF scheme are the same as those used for human TEFs. Compounds must:

- show a structural relationship to the PCDDs and PCDFs
- bind to the Ah receptor
- elicit dioxin-specific biochemical and toxic responses
- be persistent and accumulate in the food chain.

Table 1 [7] gives the TEF values of PCBs and PCDD/Fs. Although a comparison between TEF must be regarded as very preliminary and not exhaustive, it is evident that PCBs roughly present 2 to 3 lower order of magnitude toxicity with respect to PCDD/Fs.

In order to reduce the toxicity in the environmental media it is therefore absolutely necessary, when destroying PCBs, to verify that in the products generated by this compound conversion, there is no PCDD/F in concentrations 2 to 3 order of magnitudes lower than the concentrations detected analyzing PCBs.

According to the former considerations oxidative processes, mainly PCBs incineration, must be considered with extreme caution.

Destruction Efficiency (DE): The overall destruction of an hazardous compound is calculated on the basis of total weight of the same into the process, minus the sum of the compound found in all products, by-products, and environmental releases, divided by the compound input. (DE is reported as a percentage).

Destruction and Removal Efficiency (DRE): Destruction and removal efficiency is intended as the efficiency in destruction *and* removal from a main stream, generally the flue gases. It is calculated similarly to DE, but as it is referred only to one stream may be useful to evaluate cleaning equipment, while may be misleading for a whole process evaluation.

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. (e. g. bottom ash and waste water).

3. SOURCES OF PCBS

The origin of the PCBs is exclusively their deliberate manufacture, primarily for the use as dielectric fluids in electrical transformers and capacitors, but also for the use in carbon-less copy papers and inks. Other uses of PCBs include: waxes, heat exchange fluids, cutting oils, flame retardant, insulating paper for electric cables, adhesives, dust-removing agents, hydraulic fluids, special lubricants, paints, vacuum pump oil, waterproofing products and certain plastics. ***Table 2*** shows PCB use in the US between 1929-1975 and ***Table 3*** gives the common trade names of PCBs in different Countries.

4. POPS AND PCBS PRIORITIES IN ENVIRONMENTAL CONCERNS

Eradicating persistent organic pollutants (POPs) from the global environment requires eliminating their sources, whether such sources are specific facilities, processes or materials. It also requires destruction of stockpiled POPs and associated environmental contamination. POPs stockpiles are estimated to include more than one million tons of PCBs distributed globally [6,8] and more than 100,000 tons of obsolete pesticides in countries that are not members of the Organization for Economic Cooperation and Development [9].

The technologies used for destroying stockpiles of persistent organic pollutants (POPs) must meet the following fundamental performance criteria:

- **Destruction efficiencies of effectively almost 100 percent for the chemicals of concern:** The determination of 100 percent destruction efficiency is necessarily based on findings of extremely low concentrations of the chemicals of concern, **approaching zero** in any and all residues, or outflow streams using the most sensitive analytical techniques available worldwide. As the absolute zero may be criticized as utopist, or baffled as technically not feasible, the only possible criterion to set how low the required concentration must be, when considering toxic substances such as POPs, must be certain absence of any present and future harm to human health and environment. Although expensive, complete analyses of the all out flowing streams, residues, possible leaks must be carried out with a frequency sufficient to ensure compliance with this criterion during startups, shutdowns and routine operations.

- In order to better attain the above mentioned goal, priority is recommended for technologies that imply **containment of all residues and out flowing streams** for screening and, if necessary, reprocessing. This is to ensure that no chemicals of concern or other harmful compounds, such as newly formed persistent organic pollutants or other hazardous substances, are released to the environment. Technologies which may require **uncontrolled releases** (e.g.: relief valve from high-pressure vessels) or environmental spreading of POPs, even at hardly detectable levels (e.g.: incineration processes with high gaseous mass flow released to atmosphere), should be carefully scrutinized and possibly avoided.

Determining the extent to which a technology meets these criteria during both preliminary tests and routine operations has many aspects including but not limited to the following:

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

In recent years, several international and national agencies and organizations have evaluated innovative destruction technologies, some of which are now in commercial-scale operation in one or more countries. This effort has been accomplished in the stronger and stronger consciousness of the environmental problems related to industrial development. Doubtless environmental concerns for a sustainable development range from greenhouse gases limitation, through POPs, to PTS (Persistent Toxic Substances). In such a complex situation the necessity to set priorities and define specific criteria is a must.

The hopeful aim of the present paper is to enlighten innovative technologies to be implemented in order to eradicate present and future environmental effect of PCBs.

It has to be considered that, notwithstanding international relevant achievements on the PCBs issue (see e.g. [2] and [4]), the most diffused destruction technologies for PCBs, that is incineration processes, do not completely satisfy the above proposed criteria.

As the *destruction* term has to be intended with respect to present and future *toxicity* or *environmental hazard*, to *specific chemical compounds*, not of course to matter, it seems proper to carefully investigate *chemical processes*, that could offer a much most specific and safer approach to solve the problem.

Like the most advanced "clean" combustion technologies, these newer technologies will have high resource demands; nevertheless, in the framework of the whole environmental remediation perspective, they may result even cheaper and industrially reliable.

5. REDUCTION/DESTRUCTION TECHNOLOGIES FOR PCBS

In 1976, the USA Congress enacted the Toxic Substances Control Act (TSCA), which directed the EPA to control the manufacture, processing, distribution, use, disposal and labeling of PCBs. More than twenty years ago knowledge on POPs and on PCBs health and environmental effects were of course less extensive and detailed than nowadays; available technological solution were limited mainly to landfill disposal and incineration, while innovative chemical treatment technologies were less proven. ***Table 4*** shows a list of disposal methods as they were defined by U.S. EPA some years ago for different types of PCB materials. Each of the approved PCB disposal methods is described below.

As a matter of fact sensible technological progress are reported in the last decade for different *chemical transformation* technologies. Some of them have been also officially checked and approved by governmental organizations, so that in principle, at least in some more advanced Countries, innovative and safe PCBs destruction technologies are at a stake to play a relevant role.

It must be noticed that these technological progresses have been and are possible under very specific circumstances, such as long term resource availability, strong environmental awareness and sound scientific knowledge.

It is well known, (it was even analyzed and theorized – see e.g. M.M. Waldrop: *Complexity – The Emerging Science at the Edge of Order and Chaos*. New York Simon & Schuster, 1992) that successful industrial applications may be conceived, evolved and widespread *against* basic rational premise. The last century *creeping technological development* of internal combustion engines vs. fuel cell may be regarded as emblematic.

In its efforts to promote ***sustainable industrial development*** ICS – UNIDO may not refrain to focus that under development or emerging Countries may not be in a position to consider and properly exploit these innovative environmental technologies.

Furthermore, accordingly to own and major international environmental organizations surveys, the PCBs diffusion in the environment originating from these Countries is compromising the global environment, so that immediate and proper ***industrial*** action is absolutely needed.

Aim of this paper is to contribute in increasing awareness in scientific community and decision makers about this topic.

6. REMEDIATION TECHNOLOGIES

More than 100 national governments agreed to a Global Programme of Action, which aims to phase out POPs and in particular PCBs. It has been estimated that 31% of the total world production of PCBs (370,000 tons) have already been released to the environment. More than 60% remain in use or in storage. Only 4% have been destroyed [8].

As one might expect from these figures, there is a major controversy surrounding the best choice of technology for the destruction of the enormous quantities of PCBs currently in storage. Destruction method includes high temperature incineration and various chemical methods. The best technology for destroying PCBs almost certainly remains yet to be determined and likely there may not be a unique best solution. As a matter of fact in most cases it is the physical form of the waste, rather than the specific compound or constituents that requires remediation, which determines the applicability of a particular treatment technology [10].

In many instances the “separation” steps, before and after the transformation process, may be much more onerous that the specific process itself.

7. EVALUATION OF DESTRUCTION TECHNOLOGIES

Evaluation criteria setting is a useful, necessary, sometime mandatory exercise; nevertheless some criteria may be involuntarily misleading, inapplicable or become obsolete. As an example a valuable analysis included the following [9]:

a). Capability of treating a variety of wastes with varying constituents with minimal pretreatment or characterization;

b). Secondary waste stream volumes that are significantly smaller than the original waste stream volumes and which contain no toxic reaction byproducts;

c). Complete mineralization of organic contaminants;
d). Offgas and secondary waste composition;
e). Cost; and
f). Risk.

As this paper is focused on PCBs destruction technologies, the following comments will be related to the above mentioned evaluation criteria. The versatility in point a) is necessary when "mixed wastes" are treated, as in [9]. A certain variety of contaminants is very likely when considering many remediation activities; vice-versa in case of PCBs stocks destruction or substantially only PCBs contaminated wastes treatment more advanced technologies may be much more effective. Although this distinction appears purely theoretical it reflects the necessity to adequate technological solutions consequently to present scientific knowledge. PCBs are not synthesized in nature, but were conceived and widely produced as **industrial** products. Production and use ban, in spite or their effective properties (stability, conductivity), does not necessarily imply that destruction technologies similar to typical "waste" technologies (such as landfill disposal and incineration) are suited for PCBs; generic waste treatment is out of the scope of this paper, but doubtless PCBs specific properties such as fire resistance, toxicity (intrinsic and potential for partial oxidation), etc. may require extremely high efficiencies, not always available when also variety capability is looked for.

When treating generic wastes the aim is a harmless *volume* reduction, or undesirable *mass* site segregation. In destroying PCBs the need is *transforming chemicals* in order to avoid any present and potential toxic effect.

The criterion b) intrinsically excludes incineration, unless pure oxygen is used instead of air. In the case of PCBs the toxicity increase related to even extremely limited partial oxidation reinforces the pregnancy of the requirements. Furthermore toxic diffusion in the environment is augmented when gaseous streams are released, so that even considering comparable total amounts in liquid or solids streams, the polluting effect may be much more hazardous when dispersed in flue gases.

As long as it concerns PCBs and PCBs – like compounds, halogen conversion and off gas / secondary streams composition *must* be quantitatively specified. These necessities is considered the most relevant in under-development or emerging Countries, where sophisticated analytical resources and equipment may not be available. International cooperation and support is therefore the only possible way to properly address technological choices and implement adequate compliance.

Cost, as well risk, are of course an high priority criterion; costs definition would better be spitted in capital and operating costs, in turn reactive and energy consumption, manpower, management, license fee, etc. Risk evaluation should include load flexibility, transient control, emergency management, dismantling activities.

Finally, aspects such as technological possible and proven scale / throughput capacity should be carefully addressed for innovative technologies.

8. HISTORIC TREATMENT TECHNOLOGIES

In the past, POPs and other materials that are difficult to destroy have commonly been managed by storage, burial in landfills, and/or burning in combustion systems (e.g., dedicated incinerators, industrial boilers or cement kilns). Also a few nations still allow injection in deep wells. Among these practices, only combustion systems accomplish some degree of destruction.

8.1. Landfill Cap System and Deep Well Injection

Landfill capping is one of the most common forms of remediation technologies. It is used to cover buried waste materials to prevent contact with the environment and to effectively manage the human and ecological risks associated with a remediation site. The design of landfill caps is specific and depends on the intended functions of the system. The most critical components of a landfill cap are the barrier layer and the drainage layer. Landfill caps can range from a one-layer system of vegetated soil to a complex multi-layer system of soils and geosynthetics. In general, less complex systems are required in dry climates and more complex systems are needed in wet climate; the system complexity also depends on the type of waste (phase, hazardous or solid waste). The materials used in the construction of landfill caps include low- and high-permeability soils and low-permeability geosynthetic products. The low-permeability material drains water and prevents its passage into the waste. The high permeability materials collect the water that percolates into the cap.

Landfill caps may be temporary or permanent. Temporary caps can be installed before permanent closure to minimize generation of leachate until a better remedy is selected. These caps are usually used to minimize infiltration when the underlying waste mass is undergoing settling. A more stable base will thus be provided for the final cover, reducing the cost of the post-closure maintenance. Landfill caps can also be applied to waste masses too large for other treatments. Disposal in a landfill is not a proper method for liquid pesticides or highly mobile waste. Inorganic pesticides or liquid pesticide waste containing about 5 percent organic material can be solidified or stabilized prior to disposal in a landfill [11].

For persistent substances, burial in landfills is not a destruction technology, it is only a method of containment. Moreover, it is a relatively ineffective method of containment. Constituents in buried wastes can and do escape into the surrounding environment, primarily through leaching into groundwater and volatilizing into the air. PCBs are known to escape from landfills by volatilizing into the surrounding air [12] and are known to evaporate more rapidly with increased moisture in soils, sediments and even with increased relative humidity of air [13].

Injection of hazardous chemicals down deep wells is not a widely used technology. In fact, FAO (1996) designated deep well injection as "unsuitable because of the environmental risk and lack of control" [14]. Little is known about the long-term chemical behavior of chemicals that have been injected down deep wells - potential reactions between hazardous waste and underground rocks, clay, sand, water, brines, oil, gas, etc., or the effects such reactions might have on migration and toxicity. Once hazardous materials leave the well bore and enter the porous layer into which they are injected, it is not possible to track their movement. Their whereabouts become known only when they are found as groundwater contaminants.

8.2. High temperature incineration

This has been one of the most applied remediation technologies for the treatment of a variety of contaminant sources including pesticides, PCBs and explosives. It is a high temperature (870 ^{o}C to 1200 ^{o}C) destructive ex situ treatment of polluted soil; the waste and/or contaminated soil are fed into the incinerator, under controlled conditions, the high temperatures in the presence of oxygen volatilize and combust the contaminants into innocuous substances. Though variety of designs are available most incinerator designs are fitted with rotary kilns, combustion chambers equipped with an afterburner, a quench tower and an air pollution control system. Removal efficiencies of more than 99.99% are feasible. For PCBs and dioxins the high temperature incinerators can achieve destruction and removal efficiencies up to 99.9999% [15].

Modern incinerators are commonly described as destroying pesticides, PCBs and similar chemicals very efficiently. However, recent tests suggest that incinerators achieve destruction efficiencies that are lower than those achieved by certain non-combustion technologies. In addition, some incinerators burning POPs (pesticides and PCBs) and other waste are associated with the spread of undestroyed and newly formed POPs (dioxins and furans) into the surrounding environment, contaminating air, soil, vegetation, wildlife and human populations [16].

The U.S. EPA has approved high efficiency incinerators to destroy PCBs with concentrations above 50 ppm. Incinerators destroying PCB liquids must meet technical requirements like 2-sec residence time at 1200°C and 3% of excess oxygen, alternatively, 1.5-sec residence time at 1600°C and 2% of excess oxygen in the stack gases. The destruction and removal efficiency (DRE) for non-liquid PCBs must be equivalent to 99.9999% (less than 1 ppm).

8.3. Cement kilns

The main processes employed in making cement clinker can be classified as either "wet" or "dry" depending on the method used to prepare the kiln feed. In the wet process the feed material is slurried and fed directly into the kiln. In the dry process the kiln exhaust gases are used to dry raw material while it is being milled.

At the very high temperature of the cement kiln, and with the long residence times available, very high destruction efficiency is possible for hazardous waste. The highly alkaline conditions in a cement kiln are ideal for decomposing chlorinated organic waste. Chlorinated liquids, chlorine and sulphur are neutralized in the form of chlorides and sulphates. The quantities of the inorganic and mineral elements added in treating chlorinated waste are limited (usually is a small fraction of the large feed requirements of a commercial kiln). No liquid or solid residues requiring disposal are generated since all residues are bound within the product.

The most appropriate waste for disposal in cement kilns are those which provide additional energy value as a substitute fuel, or material value as a substitute for portions of the raw material feed (eg calcium, silica, sulphur, alumina or iron). Liquid waste or low ash waste can be relatively easy to burn in cement kilns. The material is fed in dry or in slurry form (especially for the 'wet' process), or as a fuel supplement into the burning zone of the kiln. In this zone, the temperature of 1450°C is able to perform high destruction efficiency as the gas passes though the kiln.

For the typical counter current process configuration, polluted-soils and solid waste cannot be fed into the firing end of the kiln, since they would discharge in the clinker without adequate treatment; besides, they cannot be fed into the cool end of the kiln, as the waste would volatilize and would not be adequately destroyed. There are two suitable options for feeding the waste. The first one consists on feeding solid material at the middle of the kiln through a specially designed hopper; the kiln temperature at feeding point is approximately 1100 ^{o}C and increases as the materials pass further down the kiln. This involves a major modification to the rotary kiln. It is required a monitoring and verification that complete destruction of stable chlorinated compounds such as PCBs does occur with the desired efficiency [17].

The second option includes a pre-treatment of the solid waste (e.g. thermal desorption, as the approach taken with Catalysed Dehalogenation systems). After such treatment the material can be utilised as a raw material substitute, and the condensate can be incorporated in the liquid feed stream.

When operated properly, destruction of chlorinated compounds in cement kilns can be >99.00 % complete with no adverse effect on the quality of the exhaust gas [18]. The contribution of waste materials to the exhaust gases are relatively minor given that the waste are only used as a minor supplement to the main energy or raw material stream.

Many of the older types of cement kilns are not suitable. Only a few of the cement kilns in developing countries meet the technical requirements that, in principle, would make them suitable for incineration of certain groups of pesticides. Expert advice is needed to assess whether kilns can be used and special equipment is required to inject the pesticides into the kiln. Such equipment is expensive and should only be installed and used under expert supervision.

9. EMERGING AND INNOVATIVE TECHNOLOGIES

Evidence of the environmental and public health impacts of incinerators, cement kilns and similar combustion systems has created strong public opposition to incineration. This factor as well as increasing infrastructural needs, particularly those associated with the management of air emissions and other residues, has encouraged the development of other destruction technologies.

Australia holds a leading position in the use of technologies other than combustion for the destruction of intractable wastes, obsolete pesticides and contaminated environmental media. As a result, Environment Australia has evaluated a wide range of these newer technologies.

9.1. Super Critical Oxidation

ProChemTech determined that the process of super critical oxidation appeared to offer the best means of treating organic contaminated wastewater. Supercritical water oxidation (SCWO) is a high temperature and pressure technology that uses the solubility properties of supercritical water in the destruction of organic compounds and toxic wastes. Under supercritical conditions, with the addition of a proper oxidant (which may be either oxygen or hydrogen peroxide or a combination of both, or nitrate or any other oxidant) carbon is converted to carbon dioxide; hydrogen to water; chlorine atoms derived from chlorinated organic compounds to chloride ions; nitro-compounds to nitrates; sulfur to sulfates; and phosphorus to phosphate [10].

The unique properties of super critical water are the key to the operation of this process. Gases including oxygen and organic substances are completely soluble in super critical water, whereas inorganic salts exhibit greatly reduced solubility under process conditions. Organic substances dissolve in the super critical water, and oxygen and the organic substances are brought into intimate single phase contact at temperatures and molecular densities that allow the conventional oxidation reactions to proceed rapidly to completion.

Process residues are contained and consist of water, gas and solids if the waste contains inorganic salts or organics with halogens, sulfur or phosphorous. The effluent gases contain no oxides of nitrogen or acid gases such as hydrogen chloride or sulfur oxide. The process generates no particulates and less than 10 ppm carbon monoxide has been measured [10].

As the equipment did not exist to apply this technology at the flow rate needed, *ProChemTech* proceeded to design and construct a prototype super critical oxidation unit. Design parameters set were operation in the pressure range of 200 to 270 atmospheres at temperatures between 370 and 480 °C, with the capability to process up to 24 kg/h of wastewater containing 15 to 25% mixed organic pollutants.

The prototype unit was installed and brought on-line in July, 1993. Following almost 100 hours of operation, the following results were obtained on the system influent and effluent by the customer's laboratory using GC/MS procedures, results as mg/l. The pollutants present in the untreated wastewater are totally destroyed in the super critical oxidation process, products of the destruction are carbon dioxide, water, and a limited amount of mineral acids based on the halogenated solvent content of the wastewater.

The National Research Council has pointed out that this system must be constructed of materials capable of resisting corrosion caused by halogen ions. They also note that the precipitation of salts may cause plugging problems in the system [19, 20].

DREs of greater than 99% have been reported for the treatment of numerous hazardous organic compounds using SCWO. For example, bench scale tests have shown DREs of 99.999% or higher for chlorinated solvents, PCBs and pesticides, and >99.99994% for dioxin contaminated MEK (Methyl Ethyl Ketone) [20]. No data have yet been found that allow the destruction efficiencies of this technology to be determined. i.e., the concentrations of undestroyed chemicals in process residues have not been reported for process residues other than gaseous emissions. Similarly, no data were presented describing the concentrations in all process residues of dioxins and other POPs potentially generated.

Environment Australia (1997) notes that end products such as ash and brine require disposal. The Agency also finds that the technology is limited to the treatment of waste that is liquid or has a particle size less than 200 µm, and it is most applicable to wastes with an organic content of less than 20% [21]. SCWO has been applied to a broad range of materials, e.g., aqueous waste streams, sludges, contaminated soils, industrial organic chemicals, plastics, synthetics, paints and allied products, industrial organics, agricultural chemicals, explosives, petroleum and coal products, and rubber and plastic products. It is applicable to the treatment of a range of contaminants including acrylonitrile wastewater, cyanide wastewater, pesticide wastewater, PCBs, halogenated aliphatics and aromatics, aromatic hydrocarbons, MEK and organic nitrogen compounds [10].

Due to the high pressures / relatively high temperatures to be reached to obtain the supercritical properties an interesting technological solution has been proposed, that is the deep-well reactor. A demonstration unit, consisting of a 25 cm diameter stainless steel sub-surface tubular reactor reaching a depth of approximately 1600 m was demonstrated in Colorado, showing insignificant corrosion. It is claimed that, as long as relatively high hydrocarbon content is already in the wastewater feed, no energy input is required to heat up the feed to supercritical temperature. It is therefore in some way reliable the claim of very low operating costs, $120 to $140 per dry ton assuming some pretreatment and certain operating conditions [10].

9.2. Electrochemical Oxidation

This technology, the Dounreay Electrochemical Silver (II) Process was initially developed for the high-efficiency conversion of a wide range of radioactive organic wastes into environmentally acceptable waste streams. In tests with chemical warfare agents, this process, sometimes referred to as mediated electrochemical oxidation (MEO), was successful in destroying an organophosphorus nerve agent to non-detectable levels after one hour and an organochlorine agent, mustard, after two hours [10].

An electrochemical cell is used to generate oxidizing species at the anode in an acid solution, typically nitric acid. These oxidizers and the acid then attack any organic compounds, converting most of them to carbon dioxide, water and inorganic ions at low temperature (< 80 °C) and atmospheric pressure. The organic content of the feed, which can be soluble or insoluble organic liquids or solids, can vary between 5 and 100 percent without affecting the process unduly. Likewise, the water content of the waste can vary over a wide range. Compounds that have been destroyed by this process include aliphatic and aromatic hydrocarbons, phenols, organophosphorous and organosulfur compounds, and chlorinated aliphatic and aromatic compounds.

9.3. Solvated Electron Technology

The SoLV™ process neutralizes halogenated compounds (those containing chlorine, fluorine, bromine or iodine) by exposing them to free electrons in a solvated solution. Solvated electrons are the most powerful reducing agent known. Commodore's SoLV™ process represents the first important commercial use of solvated electrons for remediation purposes. In general terms, the SoLV™ process works as follows:

A base metal, usually sodium, but sometimes calcium or lithium is introduced into liquid anhydrous (water-free) ammonia and instantly begins to dissolve. The solution turns to a vivid blue as electrons are freed. Halogenated compounds, which have a powerful affinity for free electrons, are mixed with the solvated solution and are instantaneously neutralized. For PCBs, ions of chlorine combine with ions of sodium, and sodium chloride is formed, leaving no toxic agents whatsoever. Interestingly, treated soil (assuming no other contaminant such as heavy metals) is not only cleaned but also nitrogen-enriched from the ammonia bath.

The application of solvated electron technology to waste treatment has been developed by Commodore Applied Technologies Inc., which has resulted in a proprietary reagent known as Agent 313 [10]. The technology has been demonstrated in the destruction of a wide variety of halogenated organic compounds including PCBs, dioxins, pesticides, chlorofluorocarbons (CFCs) and chemical warfare agents (e.g., GB, HD, VX and Lewisite) [10]. PCBs have been treated by SET, their treatment residues and the fate of those residues are given below in ***Table 5*** [22].

Decontaminated soils are said to be suitable for return to the site, enriched in nitrogen from trace amounts of residual ammonia. Proponents claim destruction efficiencies of 100 percent for organochlorine pesticides such as DDT, Dieldrin, 2,4-D, and 2,4,5-T. With a few pesticides - Carbaryl, Paraquat, PMA, and Zineb – destruction efficiencies as low as 86 percent were achieved [10].

It is important to note that no data were available that identify and chemically characterize all gaseous, liquid and solid residues of this process. i.e., no information was found that describe the concentrations in process residues of dioxins and other POPs that may potentially be formed during this process.

9.4. Chemical Reduction Reaction

The ECO LOGIC Process involves the gas-phase chemical reduction of organic compounds by hydrogen at temperatures of 850 °C or greater. Organic compounds are ultimately reduced to methane, hydrogen chloride, and minor amounts of low molecular weight hydrocarbons (benzene and ethylene). The hydrochloric acid is neutralized by addition of caustic soda during initial cooling of the process gas. The primary chemical reactions that occur in the ECO LOGIC Process are reductive and involve breakdown of the hydrocarbon structure and hydrogenation of the product carbon to form methane. An incidental reaction of water (as steam) with the methane to form carbon monoxide and carbon dioxide also occurs in the Process at lesser efficiency. Steam is used in the Process reactor for heat transfer.

The process is non-discriminatory; that is organic molecules such as PCBs, PAHs, chlorophenols, dioxins, chlorobenzenes, pesticides, herbicides and insecticides are quantitatively converted to methane. Approximately 40% of the methane produced can be subsequently converted to hydrogen via the water shift reaction and the remaining methane converted to hydrogen in the catalytic steam reformer. Thus, the process can operate without an external supply of hydrogen. For highly concentrated wastes (eg pure Askarel) the process produces an excess of methane. Because the reaction takes place in a reducing atmosphere devoid of oxygen, the possibility of dioxin and furan formation is said to be eliminated. Maintaining greater than 50 percent hydrogen (dry basis) can prevent the formation of PAHs [10].

In commercial-scale performance tests in Canada, the gas-phase reduction process achieved destruction efficiencies and DREs with high-strength PCB oils and chlorobenzenes. Dioxins that were present as contaminants in the PCB oil were destroyed with efficiencies ranging from 99.999 to 99.9999 percent [9]. When chemical concentrations in gases and other residues fall below limits of detection, they are reported as "less than" values, not as zero. As a consequence, values calculated for destruction efficiency approach, but never reach zero. In other words, gas-phase chemical reduction can achieve destruction efficiencies of effectively 100 percent.

Residues generated by the process include product gas from the reactor, scrubber water and sludge from product gas treatment, and small quantities of grit from the reactor. Product gas is either catalytically reformed to recover hydrogen or burned as fuel in one or more of the auxiliary systems - the boiler, catalytic reformer and sequencing batch vaporizer [10]. During typical operations, 30 to 50 percent of the product gas is burned as fuel for the boiler or other auxiliary units [23]. If either the product gas or the ambient air used for combustion air for the boiler or similar units contains hydrogen chloride or other chlorinated species, dioxins may be generated during their combustion. In order to meet the fundamental technical criteria for POPs destruction, both the product gas and combustion air must be treated to remove such chlorine donors and so prevent dioxin formation.

9.5. Dehalogenation Processes

Chemical dehalogenation (or dechlorination) is a chemical process used to remove halogens (usually chlorine) from a chemical contaminant by hydrogen or a reducing radical containing hydrogen donor. Examples of direct chemical dehalogenation include the alkaline polyethylene glycolate (APEG) processes and base-catalyzed decomposition (BCD); they do not include desorption or extraction processes followed by chemical treatment of the condensate or extraction medium. Another dechlorination process is the gas-phase reduction (Eco-Logic process), in which the main difference is the chemical used as reducing reagents.

Further development of the BCD process, incorporated an alkaline polyethylene glycol (APEG) reagent (e.g., potassium polyethylene glycol) as the base. The APEG reagent dehalogenates the contaminant to form glycol ether and/or a hydroxylated compound and an alkali metal salt. Destruction efficiencies are described as "not as high" as some other technologies [24].

For example, the APEG-PLUS process uses potassium hydroxide (KOH) as reducing reagent in a mixture of polyethylene glycol (PEG) and dimethylsulfoxide. In the case of based catalyzed dechlorination, the process key is the hydrogen donor with an oxidation potential low enough to produce nucleophilic hydrogen in the presence of base Na^+ at low temperature. On the other hand, for the Eco-Logic process gaseous hydrogen at high temperature is the reducing reagent to destroy chlorinated organic compounds.

Chemical dehalogenation technologies (BCD and APEG) are applicable to halogenated aromatic compounds, including PCBs, PCDDs, PCDFs, chlorobenzenes, chlorinated phenols, organochlorine pesticides, halogenated herbicide, and certain halogenated aliphatics (e.g. ethylene dibromide, carbon tetrachloride, chloroform, and dichloromethane). If other volatile organic, semivolatile organic, or metal contaminants are present, chemical dehalogenation can be used in conjunction with other technologies, such as low-temperature thermal desorption, solvent extraction, or biodegradation.

In the following, BCD and APEG-PLUS technologies will be presented according to the criteria defined for the technology evaluation. In both cases, but especially in BCD process, the absence of an important number of studies cases that provide analytical data, make difficult the definition of the technology performance. Even when a extensive report including cost and performance data about of APEG process application is available, the information is not enough to complete the cost evaluation.

The BCD/APEG process was successfully demonstrated at the Wide Beach Superfund site in 1991, where approximately 42,000 tons of stockpiled soil contaminated with PCBs, mainly Arochlor 1254, at concentrations ranging from 10 to 5,000 mg/kg, were treated. Gaseous emissions, which are very small compared with combustion systems [10], were treated with cyclone, baghouse, acid gas scrubber, and activated carbon adsorption.

9.5.1.Base Catalyzed Decomposition (BCD)

This process was developed by EPA's Risk Reduction Engineering Laboratory, in cooperation with the National Facilities Engineering services Center (NFESC) to remediate liquids, soils, sludge and sediments contaminated with chlorinated organic compounds, especially PCBs, dioxins, and furans.

In the BCD process (***Figure 1***), contaminated soil is excavated and screened to remove debris and large particles, then crushed and mixed with sodium bicarbonate (one part sodium bicarbonate to ten parts soil). This mixture is heated to 200-400 °C in a rotary reactor. The heat separates the halogenated compounds from the soil by evaporation. The volatilized contaminants are captured, condensed and treated separately. The soil left behind is removed from the reactor and can be returned to the site. The contaminated gases, condensed into a liquid form, pass into a liquid-phase reactor [20].

The dehalogenation reaction occurs when several chemicals including sodium hydroxide (a base) are mixed with the condensed contaminants and heated in the reactor. The resulting liquid mixture can be incinerated or treated by other technologies and recycled. The BCD process eliminates the need to remove the reactants from the treated soil as in the glycolate dehalogenation process.

Figure1: The Base-catalyzed decomposition process (ref. 26).

The Base Catalyzed Decomposition process was initially developed for remediating PCB-contaminated soil, but it was demonstrated that it is also applicable to soil contaminated with other chlorinated as well as non-chlorinated organics. The technology have the following important characteristics:

- The additions of sodium bicarbonate to promote lower temperature desorption and partial destruction of chlorinated organics.
- Steam sweep to create an inert atmosphere above the hot soil. The inert gas suppresses the formation of oxidative combustion products like dioxin and eliminates the possibility of combustion occurring in the rotary reactor.
- A novel control system to allow a wet electrostatic precipitor (WESP) in the off-gas treatment system to operate without the danger of a fire or explosion.

NFESC and EPA have been developing the BCD process since 1990. The BCD process has received approval by EPA’s Office of Toxic Substances under the Toxic Substances Control act for PCB treatment. Complete design information is available from NFESC. Pre-deployment testing was completed at Naval Communications Station Stockon in November 1991. The research, development, testing and evaluation stages were developed for Guam.

The BCD process components are easily transported and safely operated. The process employs off-the-shelf equipment and requires less time and space to mobilize, set up, and take down than an incineration procedure, which is an alternative method for destroying organic pollutants. Other advantages of BCD process is that it uses low-costs reagents in small amounts (1 to 5 wt.% of matrix to be treated) that do not have to be recovered and reused.

In Guam site, the system has operated at rates of more than two tons per hour. The BCD will easily achieve total PCB concentration below 2 ppm in the treated soil. The air pollution control system (APCS) rated with high performance, since the PCBs removal was 99.999 percent and levels of the other organics in the stack were very low. Average combined dioxin and furan concentrations were 32 nanograms per cubic meter. A second air control was performed after all the APCS equipment was installed (including WESP). PCBs emissions fell to 99.99999 percent removal and average dioxin and furan concentrations in the stack fell to 3.6 nanograms per cubic meter. Automatic control ensures the low oxygen content (lower than 10 percent) in the WESP.

Data from Kopper's superfund site in North Carolina are inconclusive regarding technology performance because of analytical difficulties. No additional data were published on the application of this technology in other superfund.

Compounds such as PCBs, which may react with oxygen at elevated temperatures to form even more hazardous compounds such as dioxins, are specially suited to the BCD. The inert stream atmosphere in the rotary reactor and throughout the air capture system excludes most of the oxygen. The sodium bicarbonate breaks down, releasing carbon dioxide and water to add additional inert gases to the system.

The performance of the air pollution control system (APCS) depends on the nature of the organic being removed. High boiling point organic, such as PCBs, are removed largely by condensation and captured on either the WESP or the high efficiency mist eliminator. Semi-volatile water-soluble organics are captured in the water through solubilization. The carbon at the end of the air system captures volatile organics non-water soluble and residual PCB vapors.

The total quantity of organics released in the rotary reactor is an important factor in the overall economics of the system. As the bicarbonate causes only partial destruction of PCBs, all the condensable organics released will be contaminated with PCBs. This contaminated residual must be disposed offsite, typically by incineration.

Factors that may limit and interfere with the effectiveness of chemical dehalogenation are high clay or water content, acidity, or high natural organic content of the soil. In practice, the formation of salt within the treated mixture can limit the concentration of halogenated material able to be treated. In addition, in the process the organic contaminants volatilized in the reactor must be collected and treated and the off-gas must be collected.

Data requirements include soil, sediment and sludge characterization. Site soil conditions frequently limit the selection of a treatment process. Different tests should be conducted to identify parameters such as water, alkaline metals, and humus content in the soils; the presence of multiple phases; and total organic halides that could affect processing time and cost; soil particle size distribution; soil homogeneity and isotropy; bulk density; particle density; soil permeability; soil moisture; pH of the waste; etc. Process-limiting characteristics such as pH or moisture content may sometimes be adjusted. In other cases, a treatment technology may be eliminated based upon the soil classification (e.g., particle-size distribution) or other soil characteristics.

The cost for full-scale operation is estimated to be $270 per metric ton and does not include excavation, refilling, residue disposal, or analytical costs. The treatment time is short, energy requirements are moderate and operation and maintenance costs are relatively low.

The primary factors affecting contaminant removals in the rotary reactor are temperature and residence time. As an example, PCB-contaminated soil requires a temperature of 360 °C and a residence time of about one-half an hour. However, these numbers are approximate because the type of soil contaminated by PCBs is also a factor.

BCD can be used to treat contaminated soils, sludges and filter cakes containing hazardous organic compounds, such as dioxins, furans, PCBs, and certain chlorinated pesticides. If chlorinated compounds are treated (as PCBs), the bicarbonate catalyst increases plant efficiency by allowing the soil to be cleaned at low temperature and chemically destroying some PCBs.

The concentrations of PCBs that have been treated are reported to be as high as 45,000 parts per million, and reduced to less than 2 ppm. The technology is mobile, then the hazardous wastes do not need to be transported. Individual site conditions must be considered to determine the effectiveness of the process [25-29].

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 [30]. No data were presented identifying and chemically characterizing all residues from this process. i.e., the concentrations in all residues of undestroyed chemicals and dioxins and other POPs potentially formed during this process were not revealed.

The ADI thermal desorption process produces a variable amount of dust (usually less than 5% of the original soil feed) and condensates, both are containing dioxins. While these are captured and contained within the system, they must be able to be safely decomposed for the total process to be considered effective [30]. In the recent trials in New Zealand, the solid residues were fed back into the system. This resulted in a reduction of the dioxin levels from an initial level of 1280 ppb TEQ to a value below 0.1 ppb TEQ.

Base-catalyzed destruction is a portable process that detoxifies contaminated soil on site at a rate of .9 metric ton (one short ton) per hour. The system accepts a steady intake of excavated soil that is then mixed with a base chemical, sodium bicarbonate, which acts as a catalyst. Next, the soil is fed into a reactor where heat is applied, converting contaminants into non-hazardous compounds. The treated soil is cooled and is suitable for backfill.

The BCD process offers many advantages over existing chemical dechlorination methods, including the potential for significant cost savings. The operating costs of a full-scale BCD system are projected to be less than one-fourth the operating costs of incineration, currently the most common destruction process.

While generally considered to be a relatively low risk technology, a BCD plant in Melbourne, Australia was rendered inoperable following a fire in 1995. The fire damaged the treatment system and building. It is understood that the fire resulted from a combination of factors. The nitrogen blanket was in place over the reactor, however, on discharge of hot oil into a storage vessel without an adequate nitrogen blanket, the fire occurred in the storage vessel. The auto ignition point of the hot oil was lower than expected and was exceeded [31]. The plant has been rebuilt and is operating on a commercial basis, focusing on PCB contaminated oils, transformers and capacitors, following approval by the regional environmental agency.

As the BCD process essentially involves stripping chlorine from the waste compound, the treatment process may result in an increased concentration of lower chlorinated species (e.g., higher congeners are replaced by lower congeners) [10]. This is of potential concern in the treatment of dioxins and furans, where the lower congeners are significantly more toxic than the higher congeners. It is therefore essential that the process be appropriately monitored to ensure that the reaction continues to completion.

For contaminated soils, costs are said to range from $250 to $400 per ton, in Australian dollars. Costs for PCB contaminated oils are around $1000 per tonne [10].

9.5.2. APEG Plus (Glycolate dehalogenation) [32-37]

Glycolate dehalogenation makes use of a chemical reagent called APEG. APEG consists of two parts: an alkali metal hydroxide (the "A" in APEG) and polyethylene glycol (PEG). Sodium hydroxide and potassium hydroxide (KPEG) are two common alkali metal hydroxides. A variation of this reagent is the use of potassium hydroxide or sodium hydroxide/tetraethylene glycol, referred to as ATEG that is more effective on halogenated aliphatic compounds.

The APEG process consists of mixing and heating the contaminated soils with the APEG reagent. During heating, the alkali metal hydroxide reacts with the halogen from the contaminant to form glycol ether and/or a hydroxylated compound and an alkali metal salt, which are water-soluble byproducts. This treatment chemically converts toxic materials to non-toxic materials.

The glycolate dehalogenation process consists of five steps: preparation, reaction, separation, washing, and dewatering (***Figure 2***). During the preparation step, the contaminated waste (soil, for example) is excavated and sifted to remove debris and large objects such as boulders and logs. Next, in the reaction step, the contaminated soils and the APEG reagent are blended in a large container called a reactor, mixed, and heated for four hours. Vapors resulting from the heating process are collected. The vapor is separated into water and the gaseous contaminants by means of a condenser. The water can be used during a later step in the process and the gaseous contaminants are passed through activated carbon filters to capture the contaminant.

The soil-APEG mixture, after treatment in the reactor, goes to the separator, where the APEG reagent is separated from the soil and recycled for future use in the system. The treated soil contains products of the treatment which are less toxic chemicals resulting from the dehalogenation reaction. These new chemical products are a non-toxic salt and a less toxic, partially dehalogenated organic compound. In particular, the APEG reagent dehalogenates the pollutant to form glycol ether and/or a hydroxylated compound and an alkali metal salt, which are water-soluble by products.

The soil passes from the separation step to a washer, where the water collected in the earlier reaction step is added. The last traces of residual APEG reagent are extracted from the soil and recycled. The soil proceeds to a de-watering phase where the water and soil are separated. The water is treated to remove contaminants before discharge to a municipal water treatment system, a receiving stream, or other appropriate discharge areas. The soil is re-tested for contaminant concentrations. If it still contains contaminants above targeted treatment concentrations, it is recycled through the process or put into an environmentally safe landfill; if the soil is clean, it can be returned to its original location on the site.

Figure 2: APEG treatment process (ref. 33).

APEG process has been used successful to treat contaminant concentrations of PCBs from less than 2 ppm to 45,000 ppm. This technology has received approval from EPA's Office of Toxic Substances. There is available information relative to the performance of APEG process for cleanup of PCB-contaminated soils at three superfund sites.

APEG technology uses standard equipment. The reaction vessel must be equipped to mix and heat the soil and reagents. A detailed engineering design for continuous feed, full-scale PCB treatment system was used in Guam. The concentrations of PCBs that have been treated are reported to be as high as 45,000 ppm. Concentrations were reduced to less than 2 ppm per individual PCB congener. PCDDs and PCDFs have been treated to non-detectable levels at part per trillion. The process has successfully destroyed PCDDs and PCDFs contained in contaminated pentachlorophenol oil.

The APEG process has been selected for cleanup of PCB-contaminated soils at three Superfund sites: Wide Beach, New York, Re-Solve, Massachusetts and Sol Lynn, Texas. This technology has received approval from the EPA’s Office of Toxic substance under the Toxic Substances Control Act for PCB treatment. It uses standard equipment. The reaction vessel must be equipped to mix and heat the soil and reagents. It is estimated that a full-scale system can be fabricated and placed in operation in 6 to 12 months.

Significant advances are currently being made to the APEG technology. These advances employ water rather than costly PEG to wet the soil and require shorter reaction times and less energy, enhancing the economics of the process. Additional information is not available at this time for its consideration.

Table 6 summarizes the results of several more important applications of the technology and their results.

The APEG treatment technology can produce a treated waste that meets treatment levels set by best demonstrated available technology (BDAT), but may not reach these treatment levels in all cases. The ability to meet requires treatment levels are dependent upon the specific waste constituents and the waste matrix.

There are three main waste streams generated by this technology: the treated soil, the wash water, and air emissions. The treated soil needs to be analyzed if it meets the regulatory requirements for the site before final disposition can be made. The pH in the soils must be adjusted before disposal. The chemistry of this technology is specific to halogenated organics. Waste wash water contains only trace amounts of contaminants and reagents and would be expected to meet appropriate discharge standards. Volatile air emissions can be released due to the heating and mixing that occur in the process. They are usually captured by condensation and/or on activated carbon. The contaminated carbon is usually incinerated.

The following factors may limit the applicability and effectiveness of the process:
The technology is generally implemented as a batch process and is not cost-effective for large waste volumes

- Media water content above 20% requires excessive reagent volume
- Concentrations of chlorinated organics greater than 5% require large volumes of reagent
- Regeneration and reuse of reagents may be difficult.

APEG will dehalogenate aliphatic compounds if the mixture is reacted longer and at higher temperatures than for aromatic compounds. It is recommended that a related reagent KTEG be considered for these contaminants.

Treatability tests should be conducted prior to the final selection of the APEG technology to identify optimum operating factors such as quantity of reagent, temperature, and treatment time. These tests can be used to identify water contents, alkaline metals, high humus content in the soils, and total organic halides that have the potential to affect processing times and costs.

The treated soil may contain enough residual reagent and treatment byproducts that their removal could be required before final disposal. Specific safety aspects for the operation must be considered. Treatment of certain chlorinated aliphatics in high concentrations with APEG may produce compounds that are potentially explosive and/or cause a fire hazard. Vapors from heating oily soils, which are often the matrix in which PCBs are found, can also create such potential problems as fires and noxious fumes. Taking appropriate corrective actions during elevated temperature processing can often solve these problems.

APEG units are transported by trailers. Therefore, adequate access roads are required to get the unit to the site. Energy requirements involve heating the reactor and removing the water for volatilization. For the reactor three-phase electrical services is required along with a diesel steam-generating plant. A standard municipal water supply, or equivalent, is adequate for this process.

Contaminated soils or other waste materials are hazardous and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures.

Onsite analytical capabilities are highly desirable. Extraction equipment and gas chromatography/mass spectrometer capabilities should be available to measure contaminants of interest and to provide information for process control.

Cost to use APEG treatment is expected to be in a range of $220 to $550 per metric ton. However, significantly advances to improve the process economy are being made to the APEG technology. They consist in employing water rather than costly PEG to wet the soil and require shorter reaction times and less energy.

APEG/KPEG process is generally considered a stand-alone technology adequate especially for small-scale applications, however it can be used in combination with other technologies. It is primarily for treating and destroying halogenated aromatic contaminants and pesticides. APEG dehalogenation is one of the few processes available other than incineration that has been successfully field tested in treating PCBs.

The concentrations of PCB that have been treated are reported to be as high as 45,000 ppm. Concentrations were reduced to less than 2 parts per million per individual PCB congener. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been treated to non-detectable levels at part per trillion. The process has successfully destroyed PCDDs and PCDFs contained in contaminated pentachlorophenol oil.

The effectiveness of APEG on general contaminant groups was demonstrated for:

- PCBs (sediments, oils, soil and sludge).
- Pesticides halogenated (oils and soil).
- Dioxins/Furans (sediments, oils, soil and sludge).

The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites. The demonstrated effectiveness means that at some scale, treatability was tested to show that for a particular contaminant and matrix, the technology was effective.

9.6. Molten Metal Pyrolysis

The Catalytic Extraction Process (CEP) is an innovative and patented technology in which molten metal acts as both solvent and catalyst and is developed by Molten Metal Technology, Inc.. MMT in Walham, Mass., are using molten iron and other metals to convert hazardous wastes into useful materials, also stabilizes and reduces low level radioactive wastes to a fraction of their original volume, easing their disposal.

In CEP, various industrial wastes are piped into a sealed bath of molten metal (typically iron) heated from 2400 F to 3000 F. The catalytic properties of the high temperature metal break down the chemical compounds in the waste to their primary elements. These elements are extracted as gases, ceramics, and alloys by adding select chemicals and materials, such as oxygen and alumina.

Waste and selected co-reactants are introduced into a refractory-lined, metal-filled vessel. According to DOE, the solid, liquid and gas output streams from this reactor vary considerably depending on the operating variables, e.g., oxidizing or reducing atmosphere. Typically, outputs include 1) a metal product that may be recycled; 2) slag that contains oxidized metals; 3) gases consisting of products of volatilization, oxidation and decomposition; and 4) particulates and metals entrained in the offgas. There are liquid wastes only if wet scrubbers are used to control air emissions [9].

MMT describe their process as a recycling technology that allows organic, organometallic, metallic and inorganic feeds to be recycled into useful materials of commercial value. The company has carried out commercial-scale processing of several types of waste including spent metal/electronic components; chlorinated waste streams; and biosolids from wastewater treatment [9].

Specific waste streams processed using CEP include chlorotoluene, polyvinyl chloride (PVC), surplus metal and weapons components, and heavy residuals from ethylene dichloride and vinyl chloride production. DREs greater than 99.9999 percent were achieved with specific chemicals of concern [38]. The primary end products of CEP are described as follows:

1. Gases, primarily comprised of hydrogen, carbon monoxide and up to 1 percent ethylene, with smaller amounts of other light hydrocarbons;
2. Ceramic slag phase consisting of silica, alumina and calcium chloride, which is skimmed off the top of the bath; and
3. Metal by-products.

Dioxins and furans were reported as non-detectable in product gases at the 0.1 ng TEQ/Nm^3 standard [39]. According to MMT, the gases can be used in the synthesis of organic chemicals, such as methanol; the ceramic materials can be used or buried in landfills; and the metal by-products, which remain as a ferroalloy, can be recovered for use. However, the National Research Council has observed as follows [39]:

The metal furnace does not eliminate the need for a combustion process; the product gases would be oxidized in a separate unit. These gases would likely be very dirty, containing soot from the metal pyrolysis and possibly some slag particulate matter. Gas cleanup will be required before the gas is released. In their evaluation of this technology, DOE cautions that, with induction heating of the metal bath, the method apparently used by MMT, the process must be carefully controlled to prevent equipment damage and possible explosion.

Recently, USEPA recognized MMT's process as achieving the Best Demonstrated Available Technology (BDAT) for processing wastes for which incineration was previously the only approved processing method [9].

DOE estimated capital costs for a typical MMT facility to range from $15 to $50 million, in U.S. dollars, depending on the volume and composition of the waste stream. For example, the MMT unit at Clean Harbors, which has a capacity of 30,000 tons of waste per year, is estimated to cost between $25 and $35 million [40].

9.7. Molten Salt Oxidation

The molten salt process has been used on a small scale since 1950 [9]. In the process, a bed of alkaline molten salt, usually sodium carbonate, oxidizes organic materials at a temperature of 900 to 1000°C. Any chlorine, sulfur, phosphorous, or ash products in the feed are converted to inorganic salts and retained in the salt bed. This process cannot treat soils and other materials with a high content of inert material [20].

With bench and pilot scale systems, liquid 1,2,4-trichlorobenzene (58.6 weight percent chlorine) was destroyed in molten sodium carbonate/sodium chloride with efficiencies of 99.9999970 and 99.9999932 percent at bed temperatures of 900°C and 1000°C respectively. With chlordane, the pilot scale system achieved DREs of 99.99983 percent when samples were taken before the baghouse and >99.9999988 percent when sampled after the baghouse [10]. Destruction efficiency with chlordane was apparently not determined. Indeed, the use of both performance measures, "destruction efficiency" and DRE, in describing the performance of this technology suggests that one may have been used inaccurately. i.e., destruction efficiency can be determined only if all process residues are analyzed for the presence of undestroyed chemicals of concern. It is also important to note that no data were presented describing the concentrations in process residues of dioxins or other POPs potentially formed by the process.

One hazard of the process is potential superheated-vapor explosions when liquid wastes are introduced. Gaseous emissions may require filtering due to the entrainment of very fine salt particles, and the total salt requiring disposal may be several times the weight of the wastes destroyed [10].

Depending on chlorine content as well as the capacity of the facility, the cost (in Australian dollars) of treating organochlorine wastes vary from \$1200 to \$2000 per ton. The residuals from the process are not useful, and must be disposed of properly in a secure landfill. For a feed rate of 1000 kg/h, the cost is in the order of \$1150/tonne. The above costs do not include effluent treatment costs, residuals and waste shipping costs handling and transport costs, analytical costs, and site restoration costs [20].

9.8.Plasma Arc

In plasma arc treatment directing an electric current through a low-pressure gas stream creates a thermal plasma field. Plasma arc fields can reach 5000 to 15000°C. The intense high temperature zone can be used to dissociate waste into its atomic elements by injecting the waste into the plasma, or by using the plasma arc as a heat source for combustion or pyrolysis [10].

The National Research Council (1993) described the waste streams from plasma arc destruction of wastes as "essentially the same as those from incineration..." such as combustion by-products and salts [20].

Various plasma reactors have been developed for the thermal destruction of hazardous waste. Environment Australia considered three available plasma systems in its review of appropriate technologies for the destruction of hazardous wastes. These are:

PACT (Plasma Arc Centrifugal Treatment)
PLASCON (In-Flight Plasma Arc System)
STARTECH (Plasma-electric waste converter)

PACT: The Plasma Arc Centrifugal Treatment (PACT) process developed by Retech uses heat generated from a plasma torch to melt and vitrify solid feed material, including contaminated soils. Organic components are vaporized and decomposed by the intense heat of the plasma and are ionized by the air used as the plasma gas, before passing to the off-gas treatment system. Metal-bearing solids are vitrified into a monolithic non-leachable mass. Gases travel through the secondary combustion chamber and then through a series of air pollution control devices [20].

Liquid and solid organic compounds can be treated by this technology and it is appropriate for treatment of hard-to-destroy organic compounds and wastes contaminated with metals. DREs for organic compounds are greater than 99.99%. However, volatile metals and products of incomplete combustion (PIC) can be generated and may need to be removed by an appropriate scrubber [10]. No data were found to describe the concentrations of undestroyed chemicals in process residues other than gaseous emissions. As a consequence, the destruction efficiencies achieved by this technology are as yet unknown. Similarly, no data were found to describe the concentrations in process residues of dioxins and other POPs that may potentially be formed by this process.

The system can be operated under pyrolytic conditions with a reducing atmosphere to avoid or minimize dioxin formation in the primary chamber and the volume of gases produced in the process have been calculated to be as little as 2 percent of the volume of an incinerator of equivalent capacity. However, it is usual to follow primary combustion with secondary combustion where dioxins can be formed. Since total air emission volumes are less than for conventional combustion processes, the potential impact of emissions is expected to be lower. Treated soils and other materials from this process are generally converted into ash and as such can be returned to the site [10].

The PACT system can be expected to have a relatively high capital cost as well as high operating cost ($4000 - $8000 per ton) [10].

PLASCON: In the PLASCON system, a liquid or gaseous waste stream together with argon is injected directly into a plasma arc. Organic chemicals in the waste disassociate into elemental ions and atoms, recombining in the cooler area of the reaction. End products include gases and an aqueous solution of inorganic sodium salts [10].

PLASCON is not currently configured to treat a range of waste types (e.g., contaminated soil, capacitors, etc.). However, in conjunction with appropriate preprocessing (e.g., thermal desorption) its applicability is broadened. Bench scale tests achieved DREs ranging from 99.9999 to 99.999999 percent. Like the other plasma arc process, no data were found describing the concentrations of undestroyed chemicals in process residues other than gaseous emissions so that the destruction efficiency of this technology remains unknown. However, dioxins were found to occur in scrubber water and stack gases in the part per trillion ranges [10].

The PLASCON system has been operating at Nufarm, a herbicide manufacturing works in Laverton, Victoria, Australia, since early 1992. Totally organic wastes containing a variety of organochlorine compounds are being treated on a small throughput basis. Typically, the waste averages 30% w/w of chlorine. A second PLASCON unit has been commissioned to cope with the increased plant throughput (200 kW system). This system is currently being used to destroy stockpiled CFCs and halons [10].

Operating costs including labor vary depending on the work to be treated and the location of the site. These costs, in Australian dollars, are estimated to be under $3000/tonne but typically range from $1500 - $2000/tonne [10].

9.9. Catalytic Hydrogenation

The potential destruction of chlorinated wastes by hydrogenation over noble metal catalysts has been recognised for many years [10]. However, noble metal catalysts are particularly susceptible to poisoning by a range of elements found in real world situations, thus limiting the applicability of the technology.

The CSIRO Division of Coal and Energy Technology has developed a process for the regeneration of PCB contaminated transformer fluids using hydrogenation catalysts based on metal sulphides, which are extremely robust and tolerant of most catalyst poisons [41]. The process is also claimed to destroy a wide range of chlorinated hydrocarbons, yielding hydrogen chloride and light hydrocarbons as by-products.

In recent trials relatively high concentrations of pure POPs compounds were treated in a hydrocarbon solvent and all were destroyed to below the detection limit of analysis, as shown in ***Table 7***. The proponents claim that the variations in destruction efficiencies reflect differences in the limits of detection rather than real differences in the extent of destruction [42].

Most gaseous effluents are recycled through the reactor, although purge gases are discharged through a catalytic combustor. The proponents claim that no dioxins or furans have been detected leaving the catalytic combustor in gaseous emissions and that PCBs were less than 15 ng/m^3. No data have been found describing the concentrations of dioxins and other POPs in other process residues.

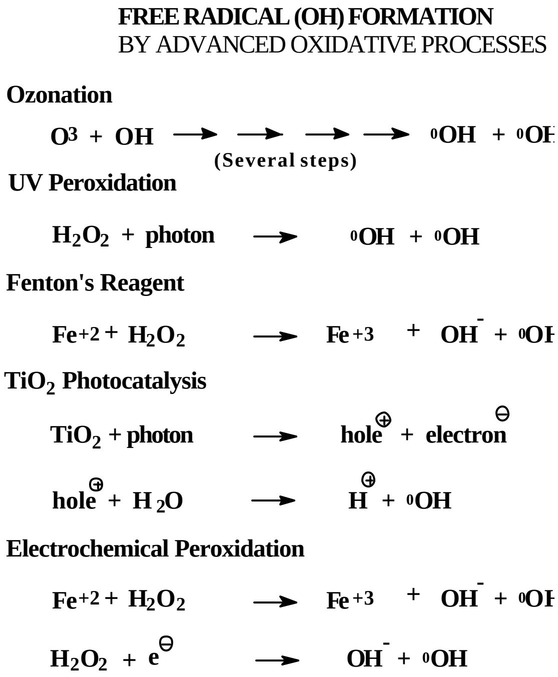
9.10. Ultrasonic Technology

Researchers at ANL are developing an innovative ultrasonic detoxification process that could ultimately be used to detoxify contaminated soil and groundwater at affected sites. ANL is one of the first research organizations to systematically test ultrasonic technology on the detoxification of contaminated soil and groundwater. Bench-scale batch and continuous-flow experimental systems have been set up in the laboratory. The results of initial experiments conducted at Argonne confirmed that the ultrasonic detoxification can be used to reduce the concentrations of CCl_4 in water (to less than 2 ppb) and soil (to less than 1 ppm). A conceptual process design of an ultrasonic soil- detoxification system has been completed.

In addition to the destruction of organic compounds, this process is also potentially able to remove radioactive compounds from the soil matrix, and these metals can be subsequently recovered. Preliminary cost estimates of the technology indicated that it would be less costly than incineration for treating soils and sludges contaminated with PCBs [43].

9.11. Advanced Oxidative Process [44]

Advanced oxidative processes (AOPs) involves the use of O_2, H_2O_2, TiO_2, UV light, electrons, iron or other oxidizing compounds to degrade PCBs and volatile organic compounds (VOCs). AOPs utilize these oxidizing agents to produce free radicals, which indiscriminately destroy organic matter. The following set of reactions (***Scheme 1***) illustrates several reactions that can lead to the generation of free radicals (OH).



FREE RADICAL (OH) FORMATION
BY ADVANCED OXIDATIVE PROCESSES

Ozonation

$$O^3 + OH \xrightarrow{} \xrightarrow{} \xrightarrow{} \xrightarrow{} {}^{0}OH + {}^{0}O$$

(Several steps)

UV Peroxidation

$$H_2O_2 + \text{photon} \longrightarrow {}^{0}OH + {}^{0}OH$$

Fenton's Reagent

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^- + {}^{0}O$$

TiO_2 Photocatalysis

$$TiO_2 + \text{photon} \longrightarrow \text{hole}^{\oplus} + \text{electron}^{\ominus}$$

$$\text{hole}^{\oplus} + H_2O \longrightarrow H^{\oplus} + {}^{0}OH$$

Electrochemical Peroxidation

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^- + {}^{0}O$$

$$H_2O_2 + e^{\ominus} \longrightarrow OH^- + {}^{0}OH$$

Scheme 1: Generation of Free Radicals

Electrochemical peroxidation (ECP) is an advanced oxidative process developed by SUNY at Oswego researchers, which uses electricity, steel electrodes, and peroxide to degrade PCBs and VOCs. The dominant mechanism for this process is Fenton's Reagent enhanced by electricity. Fenton's reagent creates free radicals, which can participate in reactions, which indiscriminately oxidize available organic matter. The following series of reactions illustrates the processes (***Scheme 2***).

ECPs can effectively and economically degrade low PCB concentrations in soil, sediments, and dredged slurries. ECPs have reduced treatment time from hours to minutes to degrade PCBs in sediment and water. Researchers at Oswego have conducted a series of ECP experiments on sediment contaminated with approximately 65 ppm of PCBs from the Superfund site in Massena.

ERC researchers have also conducted bench scale experiments, degrading more than 95% of PCBs in liquids and 68% of PCBs in slurries from a subsurface storage tank (SST) from a state Superfund site. These series of experiments were up-scaled using 200 L of the SST water, and resulted in 85% reduction of PCBs.

Other applications for electrochemical peroxidation includes PCB surface decontamination, dye decoloration, destruction of benzene, toluene and xylene in ground water, simultaneous metal removal and organic destruction, vapor phase treatment and wastewater treatment.

Fenton's Reagent Creates Free Radicals (^{0}OH)

Eq. 1: $Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + OH^{-} + {}^{0}OH$

Free Radicals Produced Can Participate in Reactions Which Indiscriminately Oxidize Available Organic Matter

Eq. 2: $RH + {}^{0}OH \longrightarrow H_2O + R^{o}$

Organic Radicals (R^{o}) Can Also Be Oxidised, Dimerized or Reduced, Resulting in a Variety of Possible Reaction Pathways and Products

Eq. 3: $R^{o} + Fe^{+3} \longrightarrow Fe^{+2} +$ **Oxidized Product**

Eq. 4: $2R^{o} \longrightarrow$ **Dimer Product**

Eq. 5: $R^{o} + Fe^{+2} \longrightarrow Fe^{+3} + RH$

Eq. 3 Allows for the Regeneration of Fe $^{+2}$ from Fe $^{+3}$ which allows for the Propagation of Redox Chain Reactions

RH = Organic Contaminant

Scheme 2: Electrochemical Peroxidation Reaction

9.12. Solvent Extraction – Chemical Dehalogenation – Radiolytic Degradation

This *ex-situ* physiochemical reduces the volume of the pollutant that needs to be destroyed. The technology uses an extracting chemical to dissolve target contaminants from soils in a final solution for treatment with recovery of the solvent used. This process produces relatively clean soil or sediment that can be returned to the original site or disposed on landfill. In some practices, prior to the solvent extraction, a physical separation technique may be used to screen the soils into coarse and fine fractions, which may enhance the kinetics of the extraction process. This pretreatment technology is very useful in mitigating organic waste and heavy metals.

Solvent extraction technology can be applied to soils contaminated with volatile and semi-volatile organic compounds and other higher boiling point complex organics, such as polynuclear aromatic hydrocarbons (PAHs), petroleum hydrocarbons, pesticide/insecticide, polychlorinated biphenyls (PCBs), dioxins, and pentachlorophenol (PCP). Recent US EPA regulatory guidelines allow soil extraction with non-harmful solvents for removal of PCBs. [45].

Solvent Extraction techniques are cost-effective methods to treat PCBs and other chlorinated compounds, but the main limitation is that the contaminants transferred to another phase must be destroyed through a secondary method. Different approaches have been developed to combine solvent extraction with other techniques like chemical dehalogenation with immobilized reagents (CDP) and gamma-ray irradiation. Recent studies shows that the PCB concentration in transformer oil was reduced from 700 ppm to non-detectable levels in less than 5 minutes using chemical dehalogenation. While the results for radiolytic degradation showed that the PCB concentrations decreased with an increased γ-ray dose; nearly 60 mega rads were needed to degrade PCBs from 300ppm down to 1ppm in solvent saturated soil [46].

9.13. Solar Detoxification –Photochemical Degradation

Sunlight energy can be used to degrade organic compounds of synthetic and natural origin. Short wavelengths (295 – 400 nm) of solar spectrum are greatly attenuated by the atmosphere, that radiation is able to generate direct and indirect photolytic processes that can degrade pesticides and PCBs polluting soil and surface waters. Since the mentioned wavelengths are attenuated more strongly than longer visible wavelengths, the rate of photolysis of pesticides is highly dependent on latitude, season and other meteorological conditions; thus, in tropical regions photochemical processes are a key factor to assess pesticides fate and degradation [47].

Solar energy is used to degrade hazardous organic chemicals by direct thermal decomposition or by photochemical reaction. Some advantages include savings in fuel use, improved thermal destruction of contaminants, and a reduction in exhaust gas volumes, including PICs (products of incomplete combustion). These processes can use either thermal energy or a range of photochemical reactions.

In order to use efficiently solar energy is required to concentrate the solar radiation to achieve high temperatures to decompose or destroy the contaminants. Solar radiation is reflected by mirrors (heliostats) and absorbed by a receiver reaching temperatures of up to 2,300^{o}K. No auxiliary fuel is required and it has been demonstrated to show an improvement in the destruction and removal efficiency (DRE) of organics, including pesticides, by a factor of 100 or more against conventional thermal technologies. High destruction efficiencies can be achieved at a temperature of 750 ^{o}C that is lower than the temperature required for thermal incineration.

The main photochemical processes that aid thermal treatment in solar detoxification include photocatalytic oxidation using titanium dioxide (TiO_2) as a catalyst. Ultraviolet radiation is used to promote an oxidation reaction in photocatalytic reactions using a catalyst such as TiO_2 in the presence of oxygen. The reactivity of singlet oxygen, irradiated with visible light in the presence of dissolved oxygen, is used in the dye-sensitizer processes. The reactive species produced can then react with contaminant molecules in the waste.

Oxidative degradation of pesticides, including Lindane in contaminated water has been tested with direct sunlight in a solar furnace. Singlet oxygen was effective against some of the pesticides but reacted slowly or not at all with others. All pesticides were degraded by OH radical generating agents (such as methylene blue). Each system has different capabilities, which needs to be taken into consideration when making comparisons.

9.14. Thermal Desorption Integrated Technologies

In this method the technologies involving thermal desorption as a pretreatment-separation technique integrated with a post treatment-destruction technology are presented.

9.14.1.Thermal Desorption – Catalyzed Dehalogenation

This system is composed by a thermal desorption system linked to the Base Catalyzed Dechlorination (BCD). The system uses an indirectly heated thermal desorber to split organic compounds from contaminated media [48]. The system is designed to achieve feed material temperatures of up to 510^{o}C allowing an effective treatment of soils and sludge polluted with a wide range of low and high boiling point compounds. The system is applicable for hydrocarbons, pesticides, herbicides, PCBs, coal by-products, wood treating compounds, dioxins and furans. The gases produced during the process are treated by a vapour recovery system which includes an oil venturi, an oil scrubber, a water scrubber, a condensing unit and vapour phase carbon adsorption unit.

Contaminants and moisture volatilized from the contaminated material are entrained in the off-gas and are condensed and recovered by the scrubbers/condensers. The condensed mixture is separated and the organic contaminant is collected for recycling via solvent recovery, fuel substitution or treatment using the BCD process. Separated water can be treated by liquid phase carbon adsorption and sand filtration. Most of the treated water can be recycled back to the process for use in the scrubbers and cooling conveyor.

9.14.2. Thermal Desorption – Pyrolysis

The PCS (*Product Control Soméus*) Technology is based on thermal desorption combined with flash pyrolysis technique, and followed by combustion. The main operational units of the system include indirectly heated rotary reactor, indirectly cooled solid material cooler, and multi venturi scrubber, pyrolysis gas combustion chamber, water treatment, auxiliary equipment and automatic operation with continuous monitoring.

The rotary reactor is the main component of the system. Waste is partially vaporized in a reductive environment under low vacuum conditions (0 to 50 Pa). The reactor is cylindrical in shape, arranged horizontally and rotates around its axis. The operating temperature in the reactor ranges from 450 to 800 ^{o}C. The waste may be introduced directly, or after drying in a desorber. If needed, the waste is ground in a mill in order to homogenize to a size less than 5 mm. The waste is decomposed into solid and vapor phases which include heavy metals in water insoluble form, high boiling point organics in the solid phase, and volatile organic compounds, volatile heavy metals and halogens in the vapor phase.

After the pyrolysis, the vapor phase is combusted and rapidly cooled; the gas stream is cleaned in a wet gas scrubber prior to emit. Although dioxin and furan gases are not generally formed in a reductive environment, it is possible that they could be formed following the combustion step. Therefore, after combustion the resulting gases must be treated by scrubbing. The scrubber process water is cleaned, neutralized and water recirculated.

The process applications include the conversion to energy of waste such as solid hazardous waste, PCB contaminated soil, mercury contaminated soil, hospital waste, municipal solid waste, sewage sludge and coal. Besides, the technology can treat a full range of chlorinated hydrocarbons, organochlorine pesticides, all organic and/or inorganic materials with combined contamination of organics, halogens and heavy metals. Although, this technology is not applicable for treatment of liquids (water, flammable liquids and solvents), explosives and/or materials with highly oxidizing nature under heat treatment and materials that cannot be decomposed by thermal treatment at 600 ^{o}C.

9.14.3. Thermal Desorption – Retort System

This technology is adapted to treat contaminated soils containing volatile organic compounds (VOCs) or some semi-VOCs. The process has been configured for the treatment of pesticide contaminated soils, especially for dip sites.

The system involves an indirectly fired retort that is used to remove the volatile materials through an off gas-vent, leaving the treated soil for return to its original site. The retort operates on a continuous basis under negative pressure, and under neutral conditions (i.e. neither oxidizing, nor reducing) resulting in some leakage of air into the system. The treated soil leaves the retort via an overflow washer from where it is transferred to a stockpile.

The retort contents are indirectly heated. A combustion chamber surrounds the retort and the components are initially brought up to operating temperature by heating a batch charge of inert material. When this mass is at opening temperature, feed is started. Bed temperatures are monitored to ensure that conditions are maintained by varying either the feed rate or the firing rate; temperatures are set in the range of 400 – 700 ^{o}C depending on the residence time required, type of contaminant and soil properties. Typically in treating organochloride pesticide contaminated soils the retort operates with a bed temperature of 450 to 500 ^{o}C [49].

Within the retort the pollutants are volatilized and/or decomposed and separate as part of the off-gas. The off-gases are then drawn by a fan through a hot gas filtration system that removes particulate matter, allowing the cleaned gases to go to an afterburner for the residual organics destruction. The afterburner is designed to operate at 1,100 ^{o}C with a two-second-residence time. From the afterburner, the gases are quenched to minimize dioxin and/or furan formation.

Retort process is only able to treat solids and sludge, although liquids (e.g. pesticides formulations) could be treated by first producing a slurry. Treatment of low volatility compounds such as PCBs is not proposed on the current development status.

9.14.4. Vitrification

The soil is treated with high temperature to cause a melt and form a glass when cooled. This technology can either be carried out *in-situ* or *ex-situ*; consists on inserting graphite electrodes into the contaminated encased area and energizing with a high electrical resistance heating (more than 1,700 ^{o}C) to melt soil into a molten block. It is applicable for the treatment of organics (including pesticides and PCBs), inorganics and radionuclides. The organic contaminants will normally be destroyed while the inorganics will be trapped into the vitrified matrix. The Plasma Arc Centrifugal Treatment (PACT) mentioned above is a combination of Plasma Arc and Vitrification techniques [49].

9.15. Biological Technologies

Biological techniques are commonly carried out with indigenous microorganisms since these present superior performance due to the better survival rates compared to strains taken from geographically different locations (non-indigenous inoculants). However, some studies have illustrated that the use of indigenous microorganisms for bioremediation and as hosts for developing genetically engineered organisms does not provide any advantage in dynamic and highly competitive environments. Thus, the survey recommends that the site must be engineered to provide temporal advantages for the non-indigenous microorganisms, or the known inoculants must be able to degrade a specific site better than the native strain [50].

9.15.1. Bioslurry

This is a proper technique for sites that require greater process control, more complete and faster degradation rates. The contaminated soils are mixed with water to form a slurry in order to allow contact between microorganisms and contaminants. Then the slurry is fed into a bioreactor where a controlled amount of air is supplied for mixing and aerating; inoculation may be performed to enhance treatment. If conditions (temperature, nutrient concentration and proper aeration) are optimized, slurry processes are faster than other biological processes. The treated slurry is suitable for direct land application, similar to composted soils [51].

The clean-up time is less than twelve months. Slurry-phase bioreactors are used to remediate soils and sludge contaminated with explosives, petroleum hydrocarbons, petrochemicals, solvents, pesticides and other organic chemicals. Bioslurry is favored over in situ biological techniques for heterogeneous soils, low permeability soils and areas where underlying groundwater is difficult to capture.

9.15.2. Enhanced Bioremediation

Enhanced bioremediation, also called biostimulation or bioaugmentation, is a process to increase the biodegradation rate of contaminated soil by the addition of nutrients and oxygen. The activity of microflora and fauna may be stimulated by circulating water-based solutions through the contaminated soils and/or addition of indigenous/inoculated microorganisms, engineered microbial species or seeding with pollutant degrading bacteria so as to enhance biological degradation of contaminants or immobilization of inorganic contaminants [51]. Although it could be done in anaerobic conditions, it is more advantageous when oxygen is not limiting in order to prevent the formation of persistent by-products such as vinyl chloride resulting from the anaerobic degradation of trichloroethylene.

This technique can be used *in situ* to treat soils contaminated with different pollutants such as petroleum hydrocarbons, solvents, pesticides, wood preservatives and/or nitrotoluenes.

10. RECOMMENDATIONS AND CONCLUSIONS

Due to restrictions on the use of PCBs, occupational exposures will be minimal. The only work place exposures in the future will probably be from replacing or servicing old equipment, transporting PCBs to hazardous waste storage and destruction sites and handling PCBs at these sites. Workers involved in these activities should wear protective clothing and follow decontamination procedures on completion of the work.

The difference between technologies that only separate and/or concentrate a pollutant (e.g. solvent extractions, thermal desorption) and those which destroy the contaminant (e.g. pyrolysis, oxidation, reduction, and biodegradation) must be considered when setting site remediation goals. Those technologies that only immobilize contaminants (e.g. landfill cap systems, stabilization and vitrification) should also be clearly differentiated.

The applicability and availability of the different treatment technologies depends on the location of treatment systems and whether the waste's ability to be transported to the treatment facility. The pesticides or PCBs are transported between countries depending on the availability of treatment systems within the country in which the waste is generated, as well as the quantities involved. While it is desirable to minimize the transport of pesticides and PCBs, the transport and mobilization of these contaminants will continue until enough movable units or *in-situ* treatment systems are performed within the countries that generate the waste.

To select the most proper technology is required to consider several ratable and non-ratable criteria. Among “non-ratable”, or relative criteria, are included public acceptability, risk and environmental impacts, which depend on the specific geographic site location. The ratable criteria may include the applicability of the method (in accordance with its development status), overall cost, minimum achievable concentration, clean-up time required, reliability, maintenance, post treatment cost and ability to use soil after treatment. Social, environmental, technical and economical criteria should be considered during technology selection process, the more criteria involved, and the more suited ones, the better performance obtained. In case of choosing more than one technology to treat a specific waste or soil, should be considered the limitations, impacts and risks appeared due to the combined methods. Environmental Impact and Risk Assessments must be carefully considered in order to avoid or control the emissions of POPs during the remediation process.

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Table 1:Toxic Equivalency Factors (TEFs) for Dioxin-like PCBs

PCB Congener	TEF
3,4,3',4'-TeCB (IUPAC 77)	0.0005
2,3,4,3',4'-PeCB (IUPAC 105)	0.0001
2,3,4,5,4'-PeCB (IUPAC 114)	0.0005
2,4,5,3',4'-PeCB (IUPAC 118)	0.0001
3,4,5,2',4'-PeCB (IUPAC 123)	0.0001
3,4,5,3',4'-PeCB (IUPAC 126)	0.1
2,3,4,5,3'4'-HxCB (IUPAC 156)	0.0005
2,3,4,3',4',5'-HxCB (IUPAC 157) 2,4,5,3',4',5'-HxCB (IUPAC 167)	0.0005 0.00001
3,4,5,3',4',5'-HxCB (IUPAC 169)	0.01
2,3,4,5,2',3',4'-HpCB (IUPAC 170)	0.0001
2,3,4,5,2',4',5'-HpCB (IUPAC 180)	0.00001
Toxic Equivalency Factors (TEFs) for PCDD/F	
Mono-, Di-, Tri - CDD	0
2, 3, 7, 8 - TCDD	1
Other TCDD	0
2, 3, 7, 8 - PeCDD	0.5
Other PeCDD	0
2, 3, 7, 8 - HxCDD	0.1
Other HxCDD	0
2, 3, 7, 8 - HpCDD	0.01
Other HpCDD OCDD	0 0.001
Mono-, Di-, Tri - CDF	0
2, 3, 7, 8 - TCDF	0.1
Other TCDF	0
1, 2, 3, 7, 8 - PeCDF	0.05
2, 3, 4, 7, 8 - PeCDF	0.5
Other PeCDF	0
2, 3, 7, 8 - HxCDF	0.1
Other HxCDF	0
2, 3, 7, 8 - HpCDF	0.01
Other HpCDF	0
OCDF	0.001

Table 2: Industrial use of PCBs (source EPA, 1994)

PCBs use	**Percentage**
Capacitors	50.3
Transformers	26.7
Plasticizer uses	9.2
Hydraulics and lubricants	6.4
Carbon-less copy paper	3.6
Heat transfer fluids	1.6
Petroleum additives	0.1
Miscellaneous industrial uses	2.2

Table 3:PCBs COMMON TRADE NAMES

Aroclor	Chlorinol	Fenclor	Nonflammable Liquid
Arochlor B	Chlorphen	Hyvol	Phenoclor
ALC	Clophen	Inclor	Pydraul
Apirolio	Clorinol	Inerteen	Pyralene
Asbestol	Diaclor	Keneclor	Pyranol
ASK	DK	Kenneclor / Kanechlor	Pyroclor
Askarel*	Dykanol	Magvar	Saf-T-Kuhl
Adkarel	EEC-18	MCS 1489	Santotherm
Capacitor 21	Elemex	No-Flamol	Santovac 1 and 2
Chlorextol	Eucarel	Nepolin	Sovol and Sovtol

*Askarel is also the generic term used for non-flammable insulating liquid in transformers and capacitors. "Askarel" PCBs are chemical mixtures containing many different PCB congeners. They have a heavy, liquid, oil-like consistency, and weigh 1,200 to 1,800 kg/m^3. They are very stable, exhibit low water solubility, low vapour pressure, low flammability, high heat capacity, low electrical conductivity, and have a favourable dielectric constant for use in electrical equipment.

Ref.: 1. U.S. E.P.A. – PCBs Q & A Manual -1994
2. AMAP Report 2000:3 – PCB in the Russian Federation: Inventory and proposals for priority remedial actions. ISBN 82-7971-008-6
3. Interim Draft–PCB Risk assessment review guidance document – January 12,2000 – Versar Inc.

Table 4: Methods approved for PCB disposal

Type of PCB material	**Methods**
Liquid PCBs	
>500 ppm	PCB incinerator
50-500 ppm	PCB incinerator, PCB boiler or PCB landfill
Non-liquid PCBs> 50 ppm	PCB incinerator or PCB landfill
Dredged materials and municipal sewage treatment sludge >50 ppm	PCB incinerator or PCB landfill
PCB transformers	
>500 ppm	PCB incinerator or PCB landfill
50-500 ppm	Drain and dispose as solid waste
Other PCB-contaminated electrical equipment (except capacitors) containing 50-500 ppm	Drain and dispose as solid waste
PCB capacitors	
> 500 ppm	PCB incinerator
50-500 ppm	PCB incinerator or PCB landfill
PCB hydraulics machine containing > 500 ppm	Drain and dispose as solid waste
Other PCB articles	
>500 ppm	PCB incinerator or PCB landfill
50-500 ppm	Drain and dispose as solid waste
All other PCBs >50 ppm	PCB incinerator

Table 5: Solvated Electron Technology:
Materials Treated and the Nature and Fate of Treatment Residues

S.No.	Material Treated	Products	Disposal Options
1.	Concentrated PCBs	Biphenyl, calcium hydroxide, calcium chloride.	Landfill as salts.
2.	PCBs in soils	Biphenyl, calcium hydroxide, calcium chloride, clean soil.	Return soil to ground.
3.	PCBs on surfaces	Biphenyl, calcium hydroxide, calcium chloride.	Collect salts and landfill.
4.	PCB/oil mixtures	Biphenyl, calcium hydroxide, calcium chloride, oil.	Reuse oil. Landfill salts.

Table 6: APEG performance data (ref. 32 and 33).

Site	Contaminant/ Waste form	Concentration before	Concentration after	Volume treated
Signo Trading, NY	Dioxin/liquid	135 ppb	<1 ppb	15 gallons
Montana Pole Butte, MT	Dioxin Furan/oil	147-83,923 ppb	<1 ppb	10,000 gallons
Western Processing Kent, WA	Dioxin/liquid and sludge	120 ppb	<0.3 ppb	7,550 gallons
Wide Beach Erie Country, NY	PCBs (Araclor 1254)/soil	120 ppm	<2 ppm	1 ton
Guam, USA	PCBs/soil	2500 ppm with hot spots as high as 45,860 ppm	<1 ppm	22 tons soil 3,4 tons crushed rock
Bengart & Memel Buffalo, NY	PCBs/soil	51 out of 52 drums, 108 ppm	<27 ppm	52fifty-five gallon drums
Economics Products Omaha, NE	TCDD, 2,4-D, 2, 4, 5-T/liquid	1.3 ppm 17,800 ppm 2,800 ppm	ND 334 ppm 55 ppm	20 gallons
Crown Plating, MO	Organic pesticides/herbicides (Silvex)	Silvex 10,000 ppm Dioxin 24.18	Silvex 32 ppb Dioxin 0.068 ppb	-

Table 7: Catalytic Hydrogenation-Destruction Efficiencies Achieved with Organochlorines [42]

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