Alternatives to incineration for the destruction of organochlorine materials involve the use of non-oxidative conditions and thereby avoid the formation of toxic products such as polychlorodibenzodioxins and furans. These alternatives include the use of plasma arc facilities in which molecules are broken down to atoms and allowed only to recombine to form small molecules, through chemical reductions using gaseous hydrogen or other sources of this element, to nucleophilic substitution reactions which displace chloride ion from the molecules of concern and also bring about other changes. A small group of other thermal technologies includes vitrification of contaminated soil, and combustion of wastes under alkaline conditions in a soda furnace. The chemistry, to the extent that it is known, of each process is discussed, together with description of its advantages and disadvantages and approximate costs of establishment and operation.

Keywords: Plasma, Reduction, Paraffin, Nucleophilic, Vitrification

1 Introduction .................................................. 426
2 Why Not Incineration? ...................................... 427
3 Alternative Technologies .................................... 428
4 Plasma Arc Destruction ..................................... 428
5 Reduction Processes ....................................... 429
  5.1 Base-Catalysed Decomposition ......................... 429
  5.2 EcoLogic Hydrogenation ................................. 431
  5.3 Catalytic Hydrogenation ................................. 432
6 Nucleophilic Substitution .................................. 433
  6.1 Fluidex (PCB Gone) Alkoxide Process ................ 433
  6.2 Ball Milling with Lime .................................. 434
7 Other Processes .............................................. 434
Introduction

Any archeologist will tell you that disposing of unwanted material is a practice as old as humankind. The excavation of thousands of rubbish dumps, some as old as thousands, and in some case tens of thousands of years, gives us information about life in the long distant past [1]. Discarded material is different from the carefully selected and arranged material of a burial site, and in fact often complementary in what we can learn from it. Among the most durable material of the rubbish dump are the stone chips and discarded tools of Neolithic times, followed by ceramics and then food detritus – shells and bones. Putrescible material fares less well over the ages, although vegetable material such as seeds and pollen, and animal matter such as faeces and hair are recognisable even after millennia.

Anything that will decay within a reasonable period of time may be regarded as “disposed of” or even “destroyed”, but the distinction between the two is an important one that we shall apply critically to the wastes of modern society. If we discount slags and ashes from early smelting, then the first industrial wastes becoming available for disposal were those of the nineteenth century chemical industry. Landfilling – to use a modern name for it – was the popular method of disposal, sometimes in natural depressions or old quarry holes and occasionally (at first) in specially dug pits. In other cases waste materials remained above ground, an outstanding example being the calcium sulfide by-product of Le Blanc alkali production, which is stored in large mounds along the south bank of the Tyne, near Newcastle, UK. An interesting case of disposal by entombment of an organic waste was revealed at ICI’s Blackley works, near Manchester, in the 1980s when removal of a road embankment uncovered a red substance which turned out to be an out-of-specification batch of the dye Turkey Red.

Burial of organic wastes must have been quite common, if we are to judge by the contamination uncovered when sites of old works are rehabilitated. It was not until the middle of the twentieth century, however, that the industrial incinerator became a preferred method for the destruction of organics, as environmental laws were passed in many countries to ban the discharging of liquids to rivers and the open burning of waste solids [2]. Burning waste material represented destruction, rather than mere disposal. In the related field of domestic waste disposal, it was specially suitable for reducing the burden placed on landfills, where paper, wood and other combustible materials were frequently set alight but the major impetus for the adoption of incineration of these materials was the prevention of the spread of disease. The eventual predominance of the germ theory...
of disease over the earlier miasma theory came about in the late nineteenth cen-
tury, at about the time that the municipal waste incinerators began to appear in
Britain, to be closely followed by their erection in the United States and contin-
ental Europe. Today, in Europe, landfill space is at a premium and much do-
monic and industrial waste is burned in specially constructed and operated in-
cinerators, while chemical wastes such as PCBs are burned in even more
sophisticated high-temperature incinerators [3].

2
Why Not Incineration?

Incineration of waste materials has a number of advantages, including volume re-
duction (only ash remains to be landfilled) and energy recovery (generation of
steam and/or electricity). Apart from the capital costs of such facilities, then, one
might wonder why there should be opposition to the construction and operation
of high-temperature incinerators. The answer lies in the release to atmosphere of
certain by-products of combustion, notably the highly toxic polychlor dibenzo-
dioxins and -furans by industrial incinerators of the 1980s and early 1990s [4, 5].
These emissions are the subject of an on-going campaign by the non-govern-
mental environmental organisation Greenpeace, which has extended its opposi-
tion to include the use of all chlorinated materials because of the potential pro-
duction of dioxins and furans during incineration of wastes. Polyvinyl chloride,
a plastic material used in packaging and construction, has been a particular
target, but release of dioxins following chlorine-bleaching of paper pulp has also
come in for critical attention.

The regulatory response to concerns about dioxins and furans has been to set
stringent limits for discharges to air. In the United States, for example, 30 ng
Nm$^{-3}$ for post-1990 facilities, and up to 125 ng Nm$^{-3}$ for existing facilities; in Eu-
rope, at first 3 ng Nm$^{-3}$ and later 0.1 ng Nm$^{-3}$ (dioxin/furan quantities are ex-
pressed as Toxic Equivalent – TEQ). Such low emission levels are achieved by care-
ful control of operating conditions and sophisticated treatment of combustion
gases. Before these standards were introduced, however, environmentalists led
by Greenpeace, expressed strong opposition to high temperature incineration
of chlorine-containing materials. Such opposition was a major influence on the
Australian government’s decision to abandon plans to build such a facility in the
early 1990s, and to encourage instead the development of alternative technologies
for destruction of the country’s stockpiles of PCBs and other organochlorines.

Petts [6] offers the following criteria for the adoption of alternative technolo-
gies to incineration:

– the ability to handle large volumes of heterogeneous waste, including munic-
   ipal solid waste,
– versatility in terms of handling both liquid and solid wastes,
– energy consumption requirements and costs,
– the ability to consistently equal, and preferable better, any emissions values
   associated with existing technology, and
– investment requirements and commercial availability.
The extent to which the alternative technologies meet these criteria will be discussed in subsequent sections, but before leaving the Petts list it should be noted that it includes only technical factors and overlooks the citizen distrust of incineration [7] which regulatory authorities and potential technology holders, aware of technical and financial considerations, need to take it into account in their decision making.

3 Alternative Technologies

Destruction of PCBs by non-incineration methods has been practiced in a number of countries but has never posed serious competition to incineration. One reason for this has been simply economic, while another is that most alternative methods are somewhat limited in the kinds of feedstocks they can accept, whereas the incinerators may be used for a broad range of materials of varying chemical nature and physical disposition.

In Australia, where no high-temperature incinerator has been constructed, and government has enforced a ban on exports, the alternative technologies have flourished. Their operation provides the basis for most comment in this essay although the limited experience with alternative technologies in other countries will also be mentioned. We distinguish four classes of destruction technology:

1. Plasma arc destruction,
2. Reductive methods,
3. Nucleophilic substitution,
4. Others.

Dioxins and furans are known to form from other materials under the oxidative conditions which exist in incinerators and in combustion gas streams. The plasma arc method ensures that constituent molecules of the feedstock are broken down with formation of atoms and from the plasma chlorine and carbon atoms may be trapped before there is opportunity for larger molecules to form. The reductive methods are the complete antitheses of incineration, in that chlorine atoms in the molecules of waste materials are replaced by hydrogen, and not only is there no opportunity for formation of dioxins and furans, but any present in the waste are reacted along with other organochlorines. Nucleophilic reactions offer further ways of replacing chlorine and thus obviating dioxin/furan formation. The final category, ‘others’ does not allow of such simple description, but will be discussed in detail in the text that follows.

4 Plasma Arc Destruction

Conceptually the simplest of the alternative technologies is destruction of the chlorinated material in-flight in a plasma where temperatures of several thousand degrees Celsius are reached. This is usually struck in argon gas which, although experiments have been conducted with the cheaper nitrogen, remains the vehicle of choice. The organic molecules are broken down in the plasma to their
constituent atoms (carbon, hydrogen and chlorine, in the case of PCBs and most POPs) and the post-plasma gas stream is quenched with steam or oxygen to prevent recombination of atoms into molecules larger than di- or triatomic. As a result, very high destruction efficiencies (six to eight nines) are achieved and Plascon systems easily comply with emission limits of 0.1 ng Nm\(^{-3}\), including cases where dioxins and furans are known to be present in the feedstocks. Apart from electric power, the only other system requirements are cooling water (a closed loop) and alkali for the rapid quenching of the gas stream. Liquids from the quenching process contain materials such as sodium chloride and bicarbonate which can be disposed of by conventional means. Operating conditions need to be optimised so as to avoid build-up of elemental carbon in the system, with the object being to produce gaseous products which can be released or absorbed.

Plasma arc units for destruction of organic wastes were developed through the joint work of Australia’s government research body, the Commonwealth Scientific and Research Organisation, and the private engineering firm Siddons Ramsset, and are now marketed by the specialist company SRL Plasma Limited. The inventions are protected by a number of patents [8]. The first “Plascon” units were installed at a chemical company which produces 2,4-dichlorophenoxyacetic acid, starting with chlorination of phenol. In 1990 the company was the subject of a Greenpeace “raid” on account of its discharges of dioxin-containing material to sewer. The resulting inquiry recommended cessation of this practice, and the company moved to purification of crude products of chlorination followed by destruction in plasma arc systems of a waste stream containing organochlorines. In early 1998, a Plascon unit was installed at BCD Technologies in Brisbane, where it is used to destroy concentrated PCB liquids.

The plasma arc requires liquid or gaseous feed and is unsuitable for solids, although slurries have been proposed. The presence of fluorinated material in the feedstock leads to production of the highly corrosive hydrogen fluoride which is converted to sodium fluoride in the wash liquor, but extensive use of the Plascon to destroy CFCs and Halons has shown that problems which might thus arise can be overcome by suitable choice of construction materials. POPs derived from agricultural sources occasionally present as mixtures with arsenicals, and it is believed that such mixtures can be processed in the Plascon, with destruction of the organochlorine material and recovery of arsenic by conventional methods from the wash liquor. No commercial venture of this type is known to have taken place, however.

5 Reduction Processes

5.1 Base-Catalysed Decomposition

The Brisbane company, BCD Technologies, has operated for some years the base-catalysed decomposition (BCD) process which was invented some years ago [9] by the US EPA following experiments at their Cincinnati Risk Reduction Research Laboratory into dechlorination including an early process known as KPEG, so
called because it involved potassium hydroxide and polyethylene glycol. Three companies operate the process under licence in Australia: BCD Technologies, ADI (discussed below) and a smaller company in Melbourne, Haz-Waste. The US EPA licenses users in the United States, of which there have been a number although incineration has always been the major destruction route for PCBs, but licensing outside the country is the responsibility of the BCD Group, consisting of three former employees of US EPA. Under their auspices, the process has been licensed in Spain (for destruction of HCH) and in Japan (for PCB contaminated oils), as well as in Australia.

Base-catalysed decomposition is a batch process involving as a hydrogen source hot paraffin (approximately 300 °C) in the presence of an inorganic base (caustic soda or sodium carbonate) and a proprietary catalyst. It destroys POPs under reductive conditions, where no dioxins and furans can form (and existing quantities are destroyed). In one version of the process, the catalyst is carbon derived from in situ decomposition of sucrose. Chemically, the major reactions involved in the process involve hydride transfer from the a hydrogen-rich donor substance (often paraffin, as described below) to the chlorinated molecules, with expulsion of chloride ion which ends up as sodium chloride (salt), disposable by conventional means. Water is also formed and is distilled from the reaction mixture, its volume providing a convenient monitor of the extent of reaction.

The BCD process is most commonly applied to dilute solutions of PCB in paraffin, of the kind which have arisen through draining of PCB-containing equipment in the electricity industry in the 1980s and back-filling with paraffin. Concentrations up to 100,000 mg/kg (10% by weight) are said to be suitable for treatment but in practice the PCB concentrations are generally much lower. Alkali needs to be added in proportion. Representing the organochlorine as Ar–Cl, we can write the following [Eq. (1)] to represent the reactions taking place, although their exact mechanism is unknown:

\[
\text{Ar}–\text{Cl} + \text{NaOH} + \text{–CH}_2–\text{CH}_2–\text{CH}_2– = \text{Ar}–\text{H} + \text{NaCl} + \text{H}_2\text{O} + \text{–CH}_2–\text{CH=CH–CH}_2–
\]

There is some evidence for stepwise removal of chlorines from PCB molecules, and this has raised concerns that part-way through a run there may be produced lightly-chlorinated PCBs which have the highest dioxin-like toxicity. In practice this has not led to releases of such materials. Recovery of biphenyl from reaction mixtures might be expected if the reactions were simply those of hydro-dechlorination, but aromatic substances are also destroyed and carbon is among the reaction products, so the overall suite of reactions taking place is likely to be very complex. The paraffin is degraded, as double bonds are introduced into the molecules bringing about an increase in dielectric constant of the bulk material which makes it unsuitable for further use in the electricity industry. The BCD process typically can reduce PCB levels in paraffin to below 2 mg kg\(^{-1}\), at which level it is acceptable for energy recovery in appropriate furnaces.

Materials presenting for destruction with higher organochlorine concentrations may be diluted with paraffin or blended with lower concentration materials to achieve optimum concentrations for the chemical reaction. A case in point is the neat PCB removed from small capacitors, which is removed by solvent
washing of such equipment. Unfortunately, shredded capacitors cannot be added directly to the BCD process because the alkali used therein would attack the aluminium cases, consuming alkali and producing hydrogen gas, and so removal of PCB from the carcasses is performed in a preliminary step. In some cases the organochlorine has been obtained by indirect thermal treatment of contaminated soil or other material, and is then added to paraffin for hydro-dechlorination.

An improved, faster version of the BCD process has been developed by another Australian company, ADI, in conjunction with a New Zealand Crown Research Institute. The process has been used, in conjunction with thermal desorption, to destroy POPs and rehabilitate soil at the Sydney Olympics site. Designated ADOX, the ADI process uses a proprietary catalyst, said to be among those types listed in the original patents, which makes it much faster than the original BCD process. Batch reactions are complete within two hours, as opposed to eight or more hours for the prototype. There is a hidden advantage in this speed, since failure of the apparatus is less likely to occur when the dechlorination reaction is partly completed and the most toxic, lightly chlorinated, biphenyls are present.

The thermal desorption process developed by ADI results in substantial destruction or organochlorines in an indirectly heated kiln at 250–480 °C. This is achieved by charging the contaminated material together with additional reactants including lime, with the result that only a small proportion of organic material is desorbed. Volatilised material and fines may be recycled into the desorber or taken on for treatment in the ADOX base-catalysed dechlorination unit. The material initially containing up to 100,000 mg kg⁻¹ organochlorines, when discharged from the kiln contains typically less than 0.02 mg kg⁻¹, and less than 1 μg kg⁻¹ dioxins (TEQ). No explanation for the chemistry which might be taking place has been advanced by the proponents, but the process obviously has similarities with some of those described under ‘nucleophilic substitution’ in Sect. 6.

5.2 EcoLogic Hydrogenation

In Kwinana, Western Australia, ELI EcoLogic operated a hydrogenation plant using technology invented in Canada by Eco Logic International Inc. The first commercial plant came on stream in Australia in 1995, and a second one at St Catherines, Ontario, in the following year although this has since ceased operation.

In the process, hydrogen gas at approximately 900 °C brings about non-discriminatory reduction of organic substrates, in which their carbon content appears as (predominantly) the hydrocarbon methane, and other elements are accordingly converted to their hydrides. Thus, PCB and other organochlorines produce hydrochloric acid and methane and, where fluorine is present in the wastes being destroyed it is converted to hydrogen fluoride which may be a corrosion hazard. The EcoLogic process is only superficially similar to hydrogen gas reductions carried out under laboratory conditions – actually selective hydrogenations, although the adjective is seldom used – or in other sections of the chemical industry in that (a) no catalyst is used, the rate at high temperatures being sufficient
ciently high that catalyst is unnecessary, (b) no selectivity is evident, all substances being reduced, and (c) the reducing power of the system is very high, transforming paper into methane and water, for instance. The reductive conditions ensure that no dioxins and furans are produced and that any present in the feedstock are destroyed, the general destruction efficiency for organochlorines reaching eight nines. Arsenic passes through the system probably being converted to arsine in the reactor and back to arsenic trioxide during quenching, which emerges as a contaminant of the wash water.

Initially, the hydrogen for the process was generated by the water gas shift reaction with recycling of the methane so that little extra hydrogen had to be added to the system, and this arrangement proved unsatisfactory and was eventually replaced by commercial hydrogen gas sources. Alternative plans for energy recovery from the methane were abandoned in favour of simple combustion. Similarly, early marketing of the hydrochloric acid produced by the EcoLogic system gave way to neutralisation and disposal of salt by landfilling.

While material may be introduced directly into the reactor, the EcoLogic plant also included a batch vaporiser, an oven or thermal desorber in which containers such as drums or large capacitors may be heated to approximately 400 °C, while hydrogen gas circulates through and flushes volatilised material into the higher-temperature reactor. The combination of vaporiser and reactor has been used to destroy large quantities of PCBs and OCPs, especially DDT, and is especially suitable for equipment such as capacitors. Material after treatment meets stringent requirements for residual PCBs or OCPs, and stack gases contain less than 2 μg Nm⁻³ organochlorines and less than 0.1 ng Nm⁻³ dioxins (TEQ).

In late 1999, trials were conducted with hexachlorobenzene (HCB) waste derived from past operations of an ethylene dichloride plant near Sydney. If this technology is chosen for the destruction of the HCB then a larger scale hydrogenation plant will need to be constructed.

5.3 Catalytic Hydrogenation

A catalytic hydrogenation process, using hydrogen gas and a sulfide catalyst, has been developed by the Coal and Energy Division of Australia’s government research organisation (CSIRO) in conjunction with an electricity distributor, and has recently been applied successfully to destruction of PCBs derived from the electricity industry. Few details are available of costs and scale of operation but it is clearly a useful addition to the suite of technologies available to holders of PCBs and possibly other POPs. The organochlorines are treated in solution at modest temperatures in a closed system.

A major virtue of the process is that, whilst achieving six nines destruction efficiency for PCBs treated in paraffin solutions, the dielectric properties of the paraffin are largely restored and so it may be reused in the electricity industry. The value of such recycled oil, approximately $AUS 1500 ($US 900)/tonne, may be offset against the treatment cost with consequent improvement in the overall economics of the process. The chlorine from the PCB molecules is re-
leased as hydrogen chloride and ultimately removed as sodium chloride, while the aromatic residue may be retained in the oil as biphenyl or hydrogenated biphenyls. The catalytic hydrogenation process would seem to be applicable to other organochlorines as well, although these would need to be dissolved in a solvent such as paraffin which is inert to the hydrogenation conditions and arrangements would need to be made to remove hydrodechlorination products – benzene or cyclohexane, for example, from hexachlorobenzene – from the reaction mixture.

6 Nucleophilic Substitution

6.1 Fluidex (PCB Gone) Alkoxide Process

The process developed by S. D. Myers, and known originally as PCB Gone, is specific for treatment of PCB-contaminated paraffin in electrical equipment and is designed to be operated without removing the equipment from service, resembling in this aspect a kidney dialysis machine. The reagent is a mixture of potassium hydroxide (some descriptions of the process speak of ‘sodium’ and it is possible that metallic sodium is used as the source of the alkali) and a monomethyl ether of a polyethylene glycol having a molecular weight in the vicinity of 350 Dalton. The process bears some similarity to the base-catalysed dechlorination, and one major reaction path would be hydrodechlorination mediated by hydrogen transfer from the polyethylene glycol. As before, the chlorine would appear as chloride ion, in this case part of potassium chloride, but the dehydrogenated polyethylene glycol (being at the aldehyde oxidation level) is likely to resinify under the influence of the strong alkali and be removed in the clean-up step described below. However, it is also likely that chloride ion would be displaced from the PCB molecule by nucleophilic reaction with an alkoxide ion formed in equilibrium from the polymer alcohol, as shown in Eqs. (2) and (3):

\[
\text{CH}_3\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{CH}_2\text{CH}_2\text{OH} + \text{KOH} = \text{CH}_3\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{CH}_2\text{CH}_2\text{O}^+\text{K}^+ + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{CH}_2\text{CH}_2\text{O}^+\text{K}^+ + \text{Cl}^-\text{Ar} = \text{CH}_3\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{CH}_2\text{CH}_2\text{O}^-\text{Ar} + \text{KCl}
\]

For this reason we have classified the technology as one involving predominantly nucleophilic substitution, even though hydrodechlorination must be acknowledged as a co-reaction. In the PCB Gone process the organic by-products of reaction were absorbed by Fullers Earth, and regenerated paraffin was returned to the equipment. The PCB Gone process has been used in the United States, Canada and other countries for some years now, and over 70 million litres of PCB-contaminated oil has been treated to <2 ppm, a level widely adopted as constituting minimal hazard from PCBs, at least to the extent that any such hazard would be outweighed by hazards associated with the oil itself [10, 11].
S. D. Myers’ acquisition of the South African company Fluidex has seen the technology pass into their hands, and be enhanced with superior clean-up procedures involving regeneration of the Fullers Earth beds by proprietary processes. Energy Services International, a company established just north of Brisbane by the electricity distribution company Powerlink, uses a version of this process involving a sodium alkoxide to destroy PCBs which are found dissolved in paraffin oil following earlier efforts to retrofill drained electrical equipment. The facility is relocatable, having been transferred to New Zealand on one occasion but mainly operating in the Brisbane area where it is capable of treating up to 3000 litres of PCB contaminated oil in an eight-hour shift. No information is available about destruction of other than PCB materials and it seems unlikely that it would be used to destroy a broader range of POPs.

6.2
Ball Milling with Lime

Just as the addition of lime to soil contaminated with organochlorines, and treatment in an indirectly heated kiln can destroy a range of organochlorines (presumably through nucleophilic attack – see Sect. 4.1), efforts have been made to bring about reaction of organochlorines with lime, CaO, in ball mills. Research into this possibility was conducted jointly by the University of Western Australia and the Advanced Technology Department of the international minerals company Conzinc Riotinto Australia (CRA). Although the ball mill operated at comparatively low temperature, there was considerable heating at the point of impact of the balls and under these conditions rapid reactions were stimulated. The products of the reaction included graphite, calcium chloride and calcium hydroxide, and were of low toxicity, but simple chemical reactions cannot be written for the process without further information, which is not available. On a laboratory scale, the process was capable of handling a wide range of physical conditions of material, and destruction of PCB and DDT was achieved with high efficiency and no gaseous emissions.

The process has not been commercialised, possibly because of the availability of competing technologies in Australia, but has attracted interest from scientists in Russia.

7
Other Processes

7.1
Soil Vitrification

In situ vitrification technology sometimes known as Geomelt was developed by the Pacific Northwest Laboratories Division of the Battelle Memorial Institute in the 1980s under a contract with the US Department of Energy. Geosafe Corporation was opened in 1989 to commercialise the technology and it has been used since 1993 in the remediation of a number of contaminated sites. The Geomelt
process involves the use of electric currents – relatively low voltage but high amperage – passed between large carbon electrodes to melt the contaminated soil. The obvious application is to inorganic contamination because, after the melting of the target volume is complete the mass is allowed to cool and contaminants remain trapped in the resulting glass. For example, this in situ vitrification has been applied successfully to immobilisation of radioactive wastes remaining after British nuclear tests were conducted in the 1950s in central Australia. Less obvious applications of the technology have involved the treatment of wastes in the United States and Japan containing organochlorines such as PCP, dioxins, PCBs, benzene hexachloride and other chlorinated pesticides. In partnership with Amec Engineering, Geosafe Australia has recently conducted trials in which hexachlorobenzene (HCB) wastes have been successfully destroyed.

In these applications the waste is mixed with soil, sometimes in the presence of alkalis such as sodium carbonate or alumina, and melted at temperatures of 1100–1200 °C in a crucible, while steam is injected around the melt zone. The degradation of organochlorines appears to take place on the surface of soil particles with production of carbon monoxide, hydrogen chloride, and possibly hydrogen. The off-gases pass through a porous refractory, together with additional steam and oxygen, thus converting the carbon monoxide to dioxide and completing the reaction of organic products. Finally, these gases pass to a thermal oxidiser where they experience long residence times at high temperatures, ensuring that destruction efficiencies reach five to six nines, before the emergent gases are quenched and neutralised. Overall, the destruction reaction may be represented by Eq. (4):

\[ C_6Cl_6 + 3H_2O + 4.5O_2 \rightarrow 6CO_2 + 6HCl \]

With the HCB waste, trials were conducted with 16.5 and 33% waste in the mixture, in crucibles holding 300 or 600 kg. If the process is adopted for the approximately 8000 tonne of HCB which is stored near Sydney awaiting treatment, a much larger facility would need to be constructed.

7.2 Soda Furnaces

As well as the highly engineered high temperature incinerators which dominate northern hemisphere waste destruction technology, there have been a number of attempts to use existing furnaces for destruction of PCBs and other POPs. Cement kilns, for example, are widely used for this purpose in the United States, although it is sometimes remarked that, in a reversal of normal priorities, some such kilns produce cement as a by-product of hazardous waste destruction. Cement kilns have the twin advantages of long hold-up times at high temperatures, and a strongly alkaline environment in which organochlorines might be expected to be chemically attacked as well as merely oxidised.

These virtues also attach to the soda furnaces which can form part of the recovery system in pulp mills, where alkaline solutions of degraded lignins are burned and alkali is recovered for use in the wood-pulping process [12]. Temperatures of 1100–1400 °C are reached in the soda furnace and hold-up times as
long as 20 – 30 seconds, and trials at two Russian pulp mills (Archangelsk and Solombola) have demonstrated efficient destruction of PCBs with emission levels of dioxins typically 1 – 5 pg/Nm³, well below conventional emission targets. Other sludges and municipal wastes have also been treated successfully in the soda furnace trials, but no commercial-scale work with PCBs or other POPs has been reported.

The experiments are interesting, however, in that existing furnaces with little modification except perhaps enhanced health and safety conditions for operators, may be used for destruction of hazardous wastes in ways that will be of great interest to developing countries and emerging economies.

8 Concluding Remarks

When compared to other developed countries, the situation regarding destruction of PCBs and other POPs in Australia is an unusual one. Export of POPs materials is difficult and expensive, but the size of the local stockpiles are probably too small to justify the cost of establishing a high temperature incinerator similar to those used in Europe and North America. Some idea of the capacities and costs of establishing and operating these alternative facilities in Australia is given by the data in Table 1. On a unit cost basis, the alternatives are uncompetitive with high temperature incineration, but cost of transport (including insurance) to such a facility, when one is not established in a country which is distant from North America or Western Europe, must be kept in mind when weighing alternatives.

Another factor influencing Australia’s decision to prefer the local development of alternative technologies is the strength of the environment movement in Australia and the opposition by its members to incinerator technology. This view has received bureaucratic and political support, overcoming whatever support existed among holders of industrial waste for the establishment of an incinerator facility. However, these industries have worked within the no-incinerator/no-export framework and have been prepared, with adequate notice, to pay for the destruction of the wastes they hold. In a few cases, shareholder and auditor pres-

<table>
<thead>
<tr>
<th>Technology</th>
<th>Establishment cost $US $10⁶</th>
<th>Capacity tonne/year</th>
<th>Charge $US/tonne</th>
<th>Typical feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incinerator</td>
<td>50</td>
<td>50,000</td>
<td>~300 Europe</td>
<td>Broad range</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>200 – 3000 US</td>
<td></td>
</tr>
<tr>
<td>Plascon (plasma arc)</td>
<td>1</td>
<td>450</td>
<td>&lt;2000</td>
<td>Liquids, gases</td>
</tr>
<tr>
<td>Base-catalysed dechlorination</td>
<td>0.2</td>
<td>2200</td>
<td>~4000</td>
<td>Solution in paraffin</td>
</tr>
<tr>
<td>Ecologic hydrogenation</td>
<td>10</td>
<td>1000</td>
<td>4000 – 6000</td>
<td>PCBs, OCPs</td>
</tr>
<tr>
<td>Sodium alkoxide</td>
<td>?</td>
<td>?</td>
<td>1150 – 1650</td>
<td>PCB solutions reaction (in-line)</td>
</tr>
</tbody>
</table>
sure has begun to be exerted on companies to remove POPs liabilities from their balance sheets. In order for Australia’s experience to be reproduced in other countries, all or most of these features would need to be reproduced.

A number of other alternative technologies may be found in the literature, including those in wide-ranging surveys by the Canadian [13] and Australian [14] governments and by the United Nations Environment Programme [15], as well as in commercial information packages and the open literature. Most are variants of the reductive or nucleophilic substitution types discussed above, but none has yet found on-going commercial application. In continuation of their long crusade, the international Greenpeace organisation has recently endorsed the use of non-incinerator technologies for the destruction of persistent organic pollutants [16].

The most important “alternative” afforded by the alternative technologies is the avoidance of dioxin and furan formation which inevitably results when an oxidative process is applied to waste destruction. It is true that formation of these highly toxic materials may be minimised by choice of appropriate operating conditions, and reduced to extremely low levels in the gases emanating from dioxin-removal systems applied to flue gases. However, as with the old medical adage, “prevention is better than cure”, and only the reductive methods offer this advantage.

Because the alternative technologies are selective, they often lack applicability to a broad physical range of material – solids, liquids, sludges – such as one associates with a hazardous waste incinerator or even a cement kiln. However, there is advantage in this selectivity because materials such as aluminium which are associated with the organochlorine wastes may be recovered for separate recycling.

The trend to destruction rather than mere “disposal” of wastes means that archaeologists of the future will find nothing to remind them of the industrial chemical culture of the late twentieth century. The future’s loss is the present’s gain, however, since many toxic substances are thereby prevented from entering environmental compartments where they are unwelcome. To a present day historian the toxic substances released to air seem to represent a threat to human health like that posed by the miasmas of old and concern over these modern miasmas forces us to look back beyond the germ theory of disease to “something in the air”.

9 References

12. Bukhteyev BM, Grudinin VP, Yufit SS (1999) Dioxin-free technique to dispose harmful and dangerous waste of any type and a commercial reactor for disposing polychlorinated biphenyls (PCBs) and other hazardous substances, personal communication