

C.4. Waste

Management of chlorinated wastes in Australia

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Introduction

Australia provides an excellent case study of the interaction of policy and technology in the management of PCBs and other POPs. By the late 1980s, it was clear that Australia had stockpiles of PCBs and other POPs, arising from their removal from service or - in the case of pesticides - cessation of registration for all or most uses. Although there was interest in the construction of a high temperature incinerator for the destruction of these stockpiles, proposals to do so were met with vigorous resistance from the environment movement in Australia and reluctance by residents to have such an incinerator built at any of the places, which had been tentatively identified as possible sites. The latter opposition was a typical NIMBY response, although matters of substance were raised by the environment movement, concerning the extent to which the incinerator technology of that time could be considered reliable, and - more fundamentally - that it was wrong in principle to employ a destruction technology which produced even small quantities of substances (dioxins and furans) which were more hazardous than the material ostensibly being destroyed.

In 1993, a decision was taken by the national council of environment ministers not to construct a high temperature incinerator - at least for the time being, although many in the environment movement thought it was a categorical ban - but to encourage the development of other facilities capable of destroying particular components of the waste stream. The preference of the national council of ministers for alternative technologies - 'alternative', that is, to high temperature incineration - was reinforced by a Commonwealth decision to adhere to the Basel protocol on transboundary shipment of wastes, thus effectively forcing the development of local technologies. It was expected that commercial destruction facilities would be established and that waste holders would be obliged to meet the cost of destruction of their wastes. This is exactly what has happened.

Management plans

National management plans to form the basis of state and territory regulation, have been prepared for a number of classes of what became known as Scheduled (because of their listing in national Schedule) Wastes. The first of these were the PCBs, which were widely distributed in the electricity generation and supply industry and in equipment contained in older buildings. Further categories of Scheduled Waste were a large stockpile, consisting largely of hexachlorobenzene (HCB) held by a company in Sydney, and unused, unwanted quantities of organochlorine pesticides (OCPs, mostly POPs) that existed mainly on rural properties.

The management plans defined the wastes to be destroyed, set timescales for their removal from service, placed requirements on storage and destruction facilities, and made provision for construction of inventories and for environmental monitoring. No particular destruction technologies were specified but emission limits were placed on any process for destruction of the POPs materials. For example, material containing PCBs was to be treated so that PCB levels fell below 2 mg/kg, and any facility destroying Scheduled Wastes had to meet emission standards under which dioxin and furan emissions were kept below 0.1 ng/m³ (TEQ).

Because the states have jurisdiction over most environmental and many other matters, including health and education, a way has been found to achieve nationally consistent legislation by means of agreements signed off by ministerial councils. The Scheduled Wastes are among a number of environmental matters that have been handled in this way, but states are sometimes slow to turn national agreements into state legislation. For example, the PCB Management Plan, agreed in 1995, has been taken into legislative force by four of the six states (and four two of these only in 2000), although generic legislation is used in the two remaining states to provide interim coverage.

Progress

It was initially estimated that approximately 30,000 tonnes of PCB had been imported into Australia up to 1975. Only about one third of this quantity could be accounted for at the time the PCB management plan was developed, and it was assumed that as much as 20,000 might have found its way into landfills. Subsequent figures, largely obtained from treaters of PCB waste, suggest that there were large quantities held in various industrial sectors, which were not taken into account in the initial reckoning. In the five years 1993-1998, as treatment facilities were developing in Australia, approximately 5,700 tonnes of PCB was destroyed (expressed as concentrated PCB, although

much of the material was in dilute solution in paraffin). The best available information now puts the amount lost to the environment as 3,500-7,000 tonnes, with 5,000-9,000 tonnes still to be accounted for.

The HCB stockpile, derived from industrial processes rather than use as a pesticide, amounts to some 8,000 tonnes, and trials of two destruction technologies (Ecologic hydrogenation, and a version of *in situ* vitrification, which are discussed below) have been undertaken. A decision on the final choice of technology is expected in the (southern) spring of 2000.

Whilst considerable quantities of DDT, and some other POPs have been destroyed by the hydrogenation process (see below), the collection of an estimated 600 tonnes of OCPs (together with 600 tonnes of other unused, unwanted rural chemicals) is being undertaken with joint Commonwealth-state funding. Once this ChemClear program is completed in any region, the manufacturers and suppliers of agricultural and veterinary chemicals have agreed to operate a ChemCollect program, under which holders of unused, unwanted stocks of registered chemicals can return them free of charge to suppliers. This program complements a container return program called DrumMuster, under which small levies are placed on the sale of non-reusable containers, and the proceeds are used by manufacturers and suppliers to collect, recycle or (where appropriate) destroy rinsed containers. Eventually the aim is to move to returnable containers (Envirodrums are already in use), or soluble packaging for as many materials as possible.

Destruction technologies

General

Five quite different technologies are employed to destroy PCBs and other chlorinated substances in Australia. They will be discussed in this section, with some comments offered about their suitability for different waste streams. None, of course, has the versatility of a high temperature incinerator and nor have they been constructed on a scale commensurate with that of northern hemisphere incinerators. Given the size of the Australian market, however, and of those likely to be needed in developing countries, the Australian technologies offer genuine alternatives. In none of them is dioxin/furan formation a concern, so extensive treatment of off-gases is not required. At the end of this section some comparisons of scale and costs are provided.

More details of these processes, and contact details for the proprietors, may be obtained from the report 'Appropriate Technologies for the Treatment of Scheduled Wastes' prepared for the Commonwealth department, Environment Australia, in late 1997. Copies are available on request (pamela.harris@ea.gov.au). Technologies covered by the report, but not implemented in Australia and therefore not covered here, include molten salt treatment, solvated electron technology, supercritical water oxidation, *in situ* vitrification, steam detoxification, and use of cement kilns. Some of these are also covered by a more recent Greenpeace report, 'Technical Criteria for the Destruction of Stockpiled POPs' (October 1998) available from Mrs Pat Costner: (pat.costner@dialb.greenpeace.org). Information is also available in the Inventory of World-wide PCB Destruction Capacity (December 1998) available from UNEP Chemicals.

Since most of the chemistry described in this section is of an industrial nature, there are few reports of it in the scientific literature, although some patents exist and presentations are made at technology conferences.

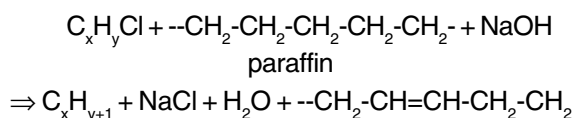
Plasma arc destruction

Conceptually the simplest technology is destruction of the chlorinated material in a plasma, struck in argon gas. Such a facility has been developed in partnership by CSIRO (the Australian government research organisation) and a private company, and marketed by SRL Plasma. The organic molecules are broken down in the plasma to their constituent atoms (carbon, hydrogen and chlorine, in the case of 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. Dioxins and furans known to have been present in some feedstocks have been destroyed in the plasma arc. Liquids from the quenching process contain materials such as hydrochloric acid, which can be disposed of by conventional means. The first Plascon units were installed at a chemical company to destroy a waste stream containing organochlorines, and a separate facility has been established for destruction of the stockpile of CFCs and halons, which have been removed from service in Australia. In early 1998, a Plascon unit was installed in a Brisbane company to destroy concentrated PCB liquids. The plasma arc requires liquid or gaseous feed and is unsuitable for solids, although slurries have been proposed.

Base catalysed decomposition

A Brisbane company, BCD Technologies, has operated for some years the base catalysed decomposition (BCD) process, which was invented some years ago by the US EPA. Hot paraffin (approximately 300°C) in the presence of caustic soda and a proprietary catalyst destroys POPs under reductive conditions, where no dioxins and furans can form (and existing quantities are destroyed). Chemically, the process involves hydride transfer from the paraffin to the chlorinated molecules, with expulsion of chloride ion that ends up as sodium chloride (salt), disposable by

conventional means. Water is also formed. The paraffin is degraded, as double bonds are introduced into the molecules, and the increase in dielectric constant of the bulk material makes it unsuitable for further use in the electricity industry. An equation, which sums up the chemical changes taking place, is:



The process is particularly suitable for dilute solutions of PCB in paraffin, such as those that date from the 1980s when much large electrical equipment was back-filled with paraffin, after removal of PCB. For more concentrated POPs materials, dilution with paraffin is necessary, and this is often achieved by blending, to give the optimum concentrations for the chemical reaction. The distillation of water from the mixture can be measured as a way of following the progress of the reaction. The reaction proceeds by stepwise removal of chlorines, and this has raised some questions about what happens if a run is not completed, but comes to a halt with the most dangerous, moderately chlorinated, biphenyls having been formed during the reaction. No such instances are known, however. The chemistry, as outlined here, does not completely explain the ability of the BCD process to destroy other organochlorine materials, so presumably there are other reactions taking place in the reactor in addition to those described above.

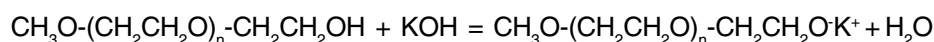
A BCD reaction can take up to eight hours to complete, and this has led to research by another Australian company - ADI, formerly Australian Defence Industries - to speed up the reaction by using a superior catalyst. The result, known as ADOX, is a reaction that can be completed in just a few hours. The process was developed in conjunction with New Zealand government, which has published the results of trials, but the first industrial use of ADOX will be in the clean-up of the Sydney Olympics site. Indirect thermal desorption of a soil-lime mixture results in destruction of much of the organochlorine content. That which desorbs is collected and destroyed in the ADOX process. The ADI story is an interesting one, because the company is a spin-off from the military, and gained its first experience in waste destruction and land decontamination with military sites, which were being released for civilian use. The Biblical reference to swords being beaten into ploughshares seems appropriate in this case, although the chemical technology is rather more subtle.

Ecologic hydrogenation

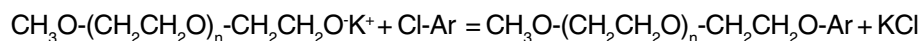
In Kwinana, Western Australia, ELI Ecologic operates a hydrogenation plant using technology invented in Canada. Hydrogen gas at approximately 800°C reduces PCB and other organochlorines with production of hydrochloric acid and methane. These materials may be recovered for use or disposed of by neutralisation and combustion, respectively. The Ecologic process is only superficially similar to hydrogen gas reductions used under laboratory conditions or in other sections of the chemical industry in that (a) no catalyst is used, the rate at high temperatures being sufficiently high, (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. While material may be introduced directly into the reactor, the Ecologic plant also includes an oven (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.

Powerlink reduction process

The Powerlink Company, established just north of Brisbane, uses a proprietary sodium-metal treatment process (licensed from Fluidex, South Africa) to destroy PCBs. The process is especially suitable for dilute solutions of PCB in paraffin oil formed by the refilling of electrical equipment from which PCBs had been drained. The Powerlink facility is relocatable, having been transferred to New Zealand on one occasion but mainly operating in the Brisbane area. No information is available about destruction of other than PCB materials. The processes taking place are likely to be, first, the formation of an alkoxide (in the first published work of this type metallic sodium was used to effect complete conversion to the alkoxide, but more recently the caustic alkalis have been used to provide equilibrium concentrations of the alkoxide):



followed by nucleophilic displacement of one or more aromatic chlorines:

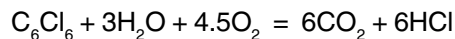


However, it is possible that some hydride transfer from the alkoxide takes place, analogous to that of the Meerwein-Ponndorf-Verley reaction. This would affect hydrodechlorination like that, which takes place in the base-catalysed dechlorinations discussed above. No mention of this is made of this possibility in a recent report of laboratory-scale trials with this system (Chemosphere 1997, 35, 1659-1667).

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 1,100-1,200°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 and ensure that destruction efficiencies reach five to six nines, before the emergent gases are quenched and neutralised. Overall, the destruction reaction may be represented by the equation:



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 8,000 tonnes of HCB that is stored near Sydney awaiting treatment, a much larger facility would need to be constructed.

Concluding remarks

When compared to other developed countries, Australia's is an unusual case. Export of POPs materials is difficult and expensive, but the size of the local stockpiles is probably too small to justify the cost of establishing a high temperature incinerator similar to those used in Europe and North America. 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 pressure 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. In arriving at its management plans, Australia used a consultation process in which three major groups of stakeholders - industry, government and community (as represented by environment groups) - participated, to find solutions acceptable to all.

Treatment facilities for PCBs

Technology	Establishment Cost \$US x 10 ⁶	Capacity tonnes/year	Charge \$US/tonne	Typical Feed
Incinerator	50	50,000	~300 Europe 200-3,000 US	Broad range
Plascon (plasma arc)	1	450	< 2,000	Liquids, gases
Base catalysed dechlorination	0.2	2,200	~ 4,000	Solution in paraffin
Ecologic hydrogenation	10	1,000	4,000 - 6,000	PCBs, OCPs
Sodium metal reduction	?	?		PCB solutions in-line