

METHODS FOR THE DESTRUCTION OF HAZARDOUS CHEMICALS:
A SHORT REVIEW OF CURRENT RESEARCH

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INTRODUCTION

In the past, the major ways of disposing of toxic chemicals have been dumping, landfill, deep-well injection or incineration. The first three methods do not actually destroy the chemicals, merely remove them from sight. The problems associated with incineration are now widely known, including their toxic discharges to atmosphere and the generation of contaminated ash and scrubber wastes. Yet, because of the widespread availability and low cost of incineration technology, research into alternative methods of detoxification of wastes has been largely neglected by industry.

This document sets out and briefly describes some current research into the destruction of a variety of intractable chemicals. Whilst most of the literature cited deals with halogenated hydrocarbons this is merely indicative of current research priorities. Many of the techniques described below are equally suitable for other types of waste. Indeed, most waste streams are more easily detoxified than the HHCs. Some of these destruction technologies are already operational at the pilot plant level. The variety of methods described belie the frequent assertions by industry and other interested parties that incineration is the only viable method for waste destruction. It must be remembered that none of the methods have been proven to be totally free of toxic emissions but some may prove, after further research, to be amenable to operation as a closed loop system with great advantages over the an open-ended incineration process.

The research currently under way can be divided into four major headings; biodegradation, photolysis, chemical degradation and electrochemical degradation.

BIODEGRADATION

There is a plethora of information on the subject of biodegradation, which is in some cases already under operational conditions. (See, for example, Boyer *et al* 1988, Krumme & Boyd, 1988). Some general reviews of the subject include: Visscher & Brinkman 1989, Ghosal *et al* 1985, Alexander 1981. The majority of systems are anaerobic and they vary between monocultures of specifically chosen species (Oldenhuis *et al* 1989a) to consortia of naturally occurring bacteria taken from contaminated areas (Neilson *et al* 1988, Dean-Ross 1989 and Genthner *et al* 1989a & b). Degradation of the less toxic and persistent chemicals has frequently been achieved, for example, the alkanes (Onodera & Ogasawara 1989) and the chlorinated solvents (Boyer *et al* 1988, Oldenhuis *et al*, 1989b Galli & McCarty 1989, Mayer *et al* 1988, Vogel & McCarty 1985). Other chemicals and classes of chemicals for which degrading microorganisms have been identified include chloroguaiacols, chloroveratroles, chlorocatechols (Neilson *et al* 1987), chlorobenzenes (Bosma *et al* 1988), substituted benzenes (Goulding *et al* 1988), pentachlorophenol (Topp & Hanson 1990), 2,4-D (Kelly *et al* 1989) and dioxin (Klecka & Gibson 1980). Some groups of species, notably the *Pseudomonas* species and fungal species such as white rot fungus, have been found to have potential for degradation of a variety of groups of chemicals and are the subject of considerable research. *Pseudomonas* species have been found to break down

chlorobenzenes (Haigler *et al* 1988, Spain & Nishino 1987), chlorotoluene (Haigler & Spain 1989), lindane (Imai *et al* 1989) and PCBs (Parsons & Sijm 1988). The fungus *Aspergillus niger* is reported to be able to degrade the lower chlorinated technical mixtures of PCBs (Dmochewitz & Ballschmiter 1988). The white rot fungus *Phanerochaete chrysosporium* can degrade DDT (Bumpus and Aust 1987) crystal violet (Bumpus & Brock 1988) and pentachlorophenol (Mileski *et al* 1988). The enzyme employed by the fungus is a ligninase, and this has been extracted from the fungus and used to oxidise PAHs and dioxins (Hammel *et al* 1986). This is an alternate method to adding pollutants to a culture of the appropriate microorganisms, although less flexible because natural selection in a pollutant-exposed culture will continually be improving its resistance and catabolic capabilities.

While it appears that microorganisms may be isolated which are capable of degrading almost any group of organic compounds, care must still be exercised when choosing applications. Not all compounds are fully broken down and metabolites such as trichloroethylene, dichloroethylene or vinyl chloride can accumulate (Vogel & McCarty 1985, Oldenhuis *et al* 1989b). Sholz-Muramatsu *et al* (1988) and Gibson & Suflita (1986) also note the difficulties of degrading a leachate of complex character as compared with the simple mixtures used in the majority of laboratory studies.

PHOTOCHEMICAL DEGRADATION

This is a class of reactions where the requisite energy is provided by photons of light. This is a natural route of degradation which takes place extremely slowly in the atmosphere (Bunce *et al* 1989) and aquatic systems (Choudry & Webster, 1988 & 1989; Dulin *et al* 1986). This type of reaction has been investigated for a wide variety of compounds, using different light sources and catalysts.

For example, in static experimental systems, Wang & Tan (1988) report photolysis of chlorinated solvents in a platinum-catalysed system using natural sunlight as the energy source. Brominated and bromochlorinated dioxins and furans have been degraded by natural sunlight or artificial light either in hydrocarbon solution or as dispersed films (Buser 1988). Campanella *et al* (1989) have used iodine doped membranes of polyphenylacetylene to catalyse the breakdown of monochlorophenols and butylcellosolve. Stallard *et al* (1988) achieved dechlorination of PCBs using visible light and a common dye, methylene blue, to promote the substitution of chlorine in the PCB molecule with hydrogen from a source such as propane.

Gamma-radiation has also been used as the energy source for the breakdown of pollutants. Gehringer *et al* (1988) used gamma-irradiation combined with ozone to remove trichloroethylene and tetrachloroethylene from drinking water. Similarly, UV light, which has only slightly less energy, has been used to dehydrochlorinate dioxins (Exner *et al* 1982).

A potentially powerful catalyst for photodegradation of toxic organics is sodium borohydride. Using irradiation from low pres-

sure mercury lamps researchers have shown that it is possible to degrade PCBs (Epling et al 1988a), PBBs (Epling et al 1987) and chlorotoluenes (Epling & Florio 1986). As with titanium dioxide-catalysed reactions, degradation can in some cases be accelerated by the addition of enhancers (Epling et al 1988b).

Researchers have also been investigating the use of sunlight with titanium dioxide as a catalyst. The pollutant in aqueous solution with suspended titanium dioxide particles is passed through glass tubes exposed to concentrated sunlight. The sunlight, concentrated by a mirror trough system, excites the titanium dioxide to release electrons which combine with dissolved oxygen and other oxidants in the water to provide strongly oxidising hydroxide radicals and superoxide ions. This has proved effective for the destruction of trichloroethylene at low concentrations in water (Pacheco et al 1990), and these researchers cite the method as capable also of completely oxidising chemicals such as chlorinated solvents, PCBs, dioxins, pesticides and dyes. In some cases it has been found that the addition of sensitisers as well as the titanium dioxide catalyst can enhance the degradation of the less reactive substances such as the PCBs (Menassa et al 1988). A pilot plant, operating a flow-through system is currently in operation in the United States (Pacheco et al 1990).

There therefore appears to be considerable capacity for the optimisation of a photodegradation system for particular waste streams. The demonstrated ability of photochemical methods to rapidly degrade extremely thermodynamically stable compounds bodes well for their application to waste streams containing more reactive components. There remains, however, for any in depth investigation of efficiency of photodegradation systems with mixed wastes. One attraction of this type of destruction method is that it could easily be adapted to operate as a closed loop without discharge to the environment.

CHEMICAL DEGRADATION

The literature on this area is less extensive than that for biodegradation or photochemical degradation. This is an field where, perhaps, it is more necessary to exactly tailor the treatment to the waste. Dechlorinating reagents such as liquid sodium are very effective, but are expensive and must be handled with care to ensure a controlled reaction. For less intractable wastes, a less vigorous method may be appropriate and should be evaluated on a case-by-case basis. Sodium sulphite, for example, is widely used as a mild dechlorinating agent (Fam & Senstrom 1988); in the case of non-chlorinated wastes, simple oxidising or reducing agents may be able to detoxify them effectively. In many cases, chemical methods for waste destruction suffer from the problem that the detoxifying agent is destroyed in the process. It is therefore more difficult to adapt chemical methods the kind of continuous flow, closed-loop system which would be necessary to achieve total destruction of toxic agents with zero discharge.

Alkali metal polyethylene glycolate complexes (APEGs) are a group of compounds capable of dehalogenating PCBs, working most effi-

ciently at 60-100°C. It has been suggested that these could be used to decontaminate soils, though toxicity of the reaction products of the APEG and the need for a nonpolar solvent may preclude this. However, a modified reagent, APEGM, has been developed which does not have these solvation problems (Kornel & Rogers 1985). The reaction takes place in solution of the reagent itself. Toxicity of remaining reagent still needs to be assessed before it could be used *in situ*.

Molten nitrate salts have also been suggested as oxidising agents for a wide range of wastes (Tyner *et al* 1990). Potassium and sodium nitrates would be heated to 500°C, at which they would be very strongly oxidising. The major reaction products would be carbon dioxide and water vapour, and liberated halogens would precipitate out as sodium or potassium halides. Similarly any metals in the feedstock could be separated as simple salts. One advantage of this proposed method over some other chemical methods is that the nitrate reagent can be regenerated by the injection of oxygen and does not have to be discarded.

Ruthenium tetroxide is a very strong oxidising agent which has been used for applications such as the destruction of dioxins (Ayres *et al* 1985). It or its hydrated dioxide or trichloride may be applied either on its own or with a secondary oxidant such as potassium permanganate or sodium hypochlorite. In the latter case, it is the secondary oxidant which is consumed. This process is very vigorous and capable of destroying most classes of organic compounds at room temperature.

ELECTROCHEMICAL DEGRADATION

The electrochemical destruction of wastes has so far only been investigated by a few groups of workers. The energy necessary to break down the chemicals is supplied as electricity. The electric power is used to generate highly reactive moieties which break down the added waste.

In one process, for example, the current reduces dissolved oxygen to superoxide ion which then attacks the waste molecules by nucleophilic substitution (Sugimoto *et al* 1988). In another (Steele 1989), the current is used to generate strongly oxidising silver II ions which then react with water to form species such as hydroxide radicals which oxidise the waste.

Thus it can be seen that although no destruction method has yet been developed which has been proven to destroy chemical wastes in a totally safe manner, a number of areas have been identified that warrant further research. There are also undoubtedly further potential detoxification routes that have not been investigated. It is simply not possible therefore to hold up an open-ended process such as incineration as the best available technology until all other avenues have been fully explored.

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