THE MANAGEMENT OF HAZARDOUS WASTE

Hazardous waste is any unwanted material the disposal of which poses a threat to the environment, i.e. it is explosive, flammable, oxidising, poisonous/infectious, radioactive, corrosive and/or toxic/ecotoxic.

Sources of hazardous waste in New Zealand include hospitals, timber treatment, petrol storage, metal finishing, paint manufacture, vehicle servicing, tanneries, agriculture/horticulture, electricity distribution and dry cleaning.

The waste can be treated chemically (i.e. by neutralisation, oxidation, reduction, hydrolysis, precipitation), physically (encapsulation, separation), biologically (using microorganisms) or thermally (incineration). Most treated waste is then deposited in landfills. To prevent landfills themselves being environmental hazards, conditions of resource consents granted under the Resource Management Act 1991 generally control the types of waste that can be deposited in them and the landfill design.

INTRODUCTION

Life Cycle Management

Many of the materials used or produced in chemical processes possess hazardous properties. As such they require appropriate management throughout their life cycle so as to minimise adverse effects on public health and safety or to the environment generally. For the purposes of this discussion the life cycle of a hazardous substance can be regarded as covering all stages from its recovery from natural resources through to its final disposal as a waste.

Waste

The New Zealand Chemical Industry Council (1991) broadly defined waste as unavoidable materials for which there is currently, or no near future, economic demand and for which treatment and/or disposal may be required.

Hazardous Waste

In New Zealand currently there is no statutory, or generally accepted, definition as to what constitutes a hazardous waste but the Centre for Advanced Engineering, University of Canterbury, (CAE), (1992) proposed that a hazardous waste can be defined as any waste that presents a present or future threat to humans or the environment. More specifically, hazardous wastes are unwanted materials that exhibit hazardous characteristics.

Hazardous Characteristics

A useful listing of hazardous characteristics is that provided by the United Nations (1989) as part of recommendations relating to the transport of dangerous goods. Examples from this listing are given in **Table 1.**

Table 1 - Examples of Hazardous Characteristics: Extracted From U.N. Listing (1989)

U.N. Class Number	Hazardous Characteristic
1	Explosive
3 - 4	Flammable
5	Oxidising
6	Poisonous/Infectious
7	Radioactive
8	Corrosive
9	Toxic (Delayed or Chronic)/Ecotoxic

Hazardous Substances Legislation
In 1996 the Hazardous Substances and New Organisms Act was passed by the New Zealand Parliament. Under this act the Environmental Risk Management Authority is established and the laws controlling hazardous substances are updated and consolidated. Hazardous substancwes are defined as:

> *"any substance which exceeds a threshold level of one or more of the following intrinsic hazardous properties:*
> - *an explosive nature*
> - *flammability*
> - *an oxidising nature*
> - *toxicity*
> - *corrosiveness*
> - *ecotoxicity with or without bioaccumulation*
> - *evolving substances with one or more of the above properties on release into the environment"*

Regulations under the Act describing threshold levels and control details are expected to be promulgated late in 1998.

The Act only applies to hazardous substances which are imported or manufactured in New Zealand. It will not necessarily provide controls for hazardous waste. A Government programme, currently under way by the Ministry of the Environment, is directed at introducing measures under the Resource Management Act 1991 to clearly define hazardous waste, outline responsibilities for its management and to introduce a system for tracking and reporting.

Material Safety Data Sheets
Information relating to hazards and safety precautions appropriate for specific chemical substances should be provided in the Material Safety Data Sheet (MSDS) for that substance. A MSDS is the documented method of transferring this essential information from the supplier of a hazardous substance to the recipient of that substance. It should initially be prepared by the producer of the substance and be available, at the local level, throughout the full life cycle of that substance. Guidelines for MSDS for use in New Zealand have been

produced by the Occupational Health and Safety (OSH) service of the Department of Labour (1995).

International Conventions
Recognising the need for the control of intercountry movement of hazardous wastes the United Nations Environment Programme (1989) developed the Basel Convention. New Zealand ratified this in 1994. This convention does not prohibit the general export of hazardous waste but introduces a system of "prior informed consent" thus ensuring that the wastes involved are properly identified and that appropriate treatment measures are available. The convention emphasises waste minimisation, recovery of resources and the final disposal of the waste as close to the point of generation as possible. Recent amendments to the convention prohibit the export of wastes for disposal from developed to developing countries. From 1997 this prohibition will also apply to hazardous wastes exported to developing countries for recycling.

The Basel Convention is effectively applied throughout the South Pacific region by the Waigani Convention 1995.

Annexes to these conventions also provide useful guidance on the identification and classification of hazardous wastes. These were reproduced for this purpose by the Ministry for the Environment (1994). In these are lists of activities likely to give rise to hazardous wastes, constituents which give rise to hazards, and hazardous characteristics.

Types and Quantities of Wastes Involved
In **Table 2** examples of the types of hazardous waste arising in New Zealand are given. Although surveys have been conducted to try to establish and document the quantities of such waste, these have not been conclusive in the past because of the lack of a uniform definition and classification system. The Ministry for the Environment (1992) moved to address this problem by introducing the Waste Analyses Protocol.

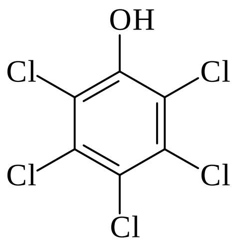

Figure 1 - Pentachlorophenol in waste from sodium pentachlorophenates, previously used for antisapstain treatment of timber

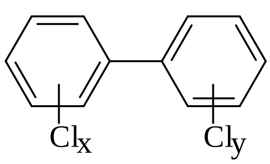

Figure 2 - Polychlorinated biphenyls (PCBs) used in electrical equipment

Table 2 - Examples of Hazardous Wastes Arising in New Zealand

Origin	Waste Type	Constituents	Hazardous Characteristic
Hospitals/clinics	Clinical	Tissues/Cultures	Infectious
Timber Treatment	Sludges/Liquids	Copper, Chromium, Arsenic, Boron, PCP's (see **Figure 1**)	Toxic, Ecotoxic
Petrol Storage	Sludges/Liquids	Hydrocarbons,	Flammable, Toxic
Metal Finishing	Sludges/Liquids	Sulfuric and/or Hydrochloric acids Cyanides Cadmium, Copper Chromium, etc.	Corrosive Toxic Toxic
Paint Manufacture	Sludges/Liquids	Organic solvents	Flammable, Toxic
Vehicle Servicing	Liquids	Lubricating oils	Flammable, Ecotoxic
Tanneries	Sludges/Liquids	Chromium, Sulfides, etc.	Toxic
Electricity Distribution	Oils from capacitors, transformers, etc.	Polychlorinated PCBs (see **Figure 2**)	Toxic, Ecotoxic
Agriculture/ Horticulture	Obsolete herbicides/ pesticides	Organophosphorus pesticides (see **Figure 3**) DDT, Aldrin, Dieldrin, Chlordane, (see **Figure 4**)	Toxic/Ecotoxic
Dry Cleaning	Sludges/Liquids	Perchlorethylene	Toxic

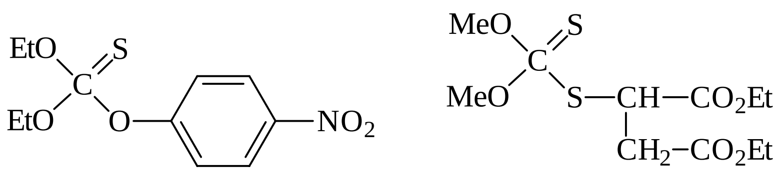

Figure 3 - Organophosphorus pesticides

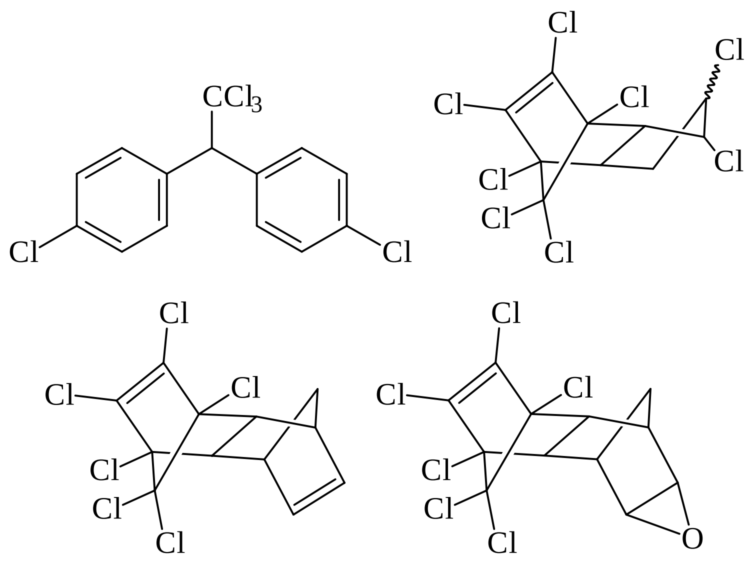

Figure 4 - Examples of organochlorine compounds, mainly obsolete chemicals, from agricultural activities

The total quantity of hazardous waste produced annually in New Zealand has yet to be accurately established. Probably the best estimate is that from the CAE Report (1992) of approximately 100,000 tonnes per year.

MANAGING HAZARDOUS WASTE

The Waste Management Hierarchy

In deciding on the best method for managing any waste there is a hierarchy for decision making which addresses issues such as sustainability, cleaner production, health, safety, and environmental protection. It is applied to existing or proposed practices, examining and testing these at each level, starting at the top of the hierarchy.

For hazardous waste the hierarchy is as follows:

- Eliminate the production of hazardous waste
- Where elimination is not possible apply methods to reduce the quantity or hazard involved
- Minimise amount of waste for disposal by recycling, reuse and/or recovery. This includes the recovery of energy which may be available from the waste.
- Treat waste to stabilise, immobilise, contain or destroy hazardous properties.
- Dispose of residues with a minimum of environmental impact.
- Appropriately contain, isolate and store hazardous waste for which no acceptable treatment or disposal option is currently available.

Cleaner Production

Cleaner production refers to a precautionary approach which includes the goal of preventing the generation of hazardous waste. Minimising the amount of hazardous waste produced would be one of the objectives of a cleaner production programme. In many cases the introduction of cleaner production measures brings economic benefits in addition to savings in waste disposal costs.

The Ministry for the Environment (1994) has produced guidelines on the implementation of such programmes.

Waste Minimisation

Examples of ways in which waste minimisation can be achieved include:

- substituting a hazardous material used in a process with a non-hazardous material
- process changes
- reducing the amount of hazardous materials used
- recovering and reusing materials

Table 3 gives examples indicating how these have been incorporated into activities in New Zealand producing hazardous waste.

Table 3 - Examples of Waste Minimisation Practices

Practice	**Industry**	**Activity**
Substitution	Leather production	Replacement of ammonium salts by carbon dioxide in dehairing operations
Process Change	Manufacture of plastic containers	Labels moulded into lids eliminating need for glues containing organic solvents
Reduction of Waste Quantity by Recycling/ Recovery and Reuse	Wire manufacturing	Recycling by sulfuric acid use for pickling mild steel
	Timber treatment	Recover of copper, chromium and arsenic and/or boron from sludges and reuse in wood treatment process
	Dry cleaning	Improved recovery of perchlorethylene
	Vehicle servicing	Recovery of used lubricating oils for -refining and reuse -use as a supplementary source of fuel in cement kilns

TREATMENT OF HAZARDOUS WASTES

Methods Available

The purpose of treating hazardous waste is to convert it into nonhazardous substances or to stabilise or encapsulate the waste so that it will not migrate and present a hazard when released into the environment. Stabilisation or encapsulating techniques are particularly necessary for inorganic wastes such as those containing toxic heavy metals.

Treatment technologies exist for most if not all hazardous wastes but some are not currently available in New Zealand. Commercial facilities are available locally to effectively treat all hazardous wastes arising except for organochlorines such as PCBs, DDT, Aldrin, Dieldrin etc. This type of hazardous waste is referred to as intractable or problem waste and will be discussed further later.

Treatment methods can be generally classified as chemical, physical and/or biological. Examples of methods currently available in New Zealand will be briefly discussed below. For a more detailed review of treatment technologies appropriate for hazardous wastes arising locally the CAE Report (1992), referred to above, should be consulted.

Chemical Methods

Neutralisation

Waste acid with an alkali e.g. sulfuric acid with sodium carbonate:

$$H_2SO_4 + CO_3^{2-} \rightarrow SO_4^{2-} + CO_2 + H_2O$$

Oxidation

Using common oxidising substances such as hydrogen peroxide or calcium hypochlorite e.g. cyanide waste with calcium hypochlorite:

$$CN^- + OCl^- \rightarrow OCN^- + Cl^-$$

$$OCN^- + H_3O^+ \rightarrow CO_2 + NH_3$$

Reduction

Used to convert inorganic substances to a less mobile and toxic form e.g. reducing Cr(VI) to Cr(III) by the use of ferrous sulphate:

$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Hydrolysis

Decomposition of hazardous organic substances e.g. decomposing certain organophosphorus pesticides with sodium hydroxide.

Precipitation

Particularly useful for converting hazardous heavy metals to a less mobile, insoluble form prior to disposal to a landfill e.g. precipitation of cadmium as its hydroxide by the use of sodium hydroxide:

$$Cd^{2+}(aq) + 2OH^- \rightarrow Cd(OH)_2(s)$$

Physical Methods

Encapsulation

Immobilising hazardous materials by stabilisation and incorporation within a solid matrix such as cement concrete or proprietary organic polymers prior to andfilling. e.g. encapsulating beryllium in concrete

Filtration/Centrifuging/Separation

Physically separating phases containing hazardous substances from other nonhazardous constituents e.g. separation of oils from ship bilge waters.

Biological Methods

These involve the use of microorganisms under optimised conditions to mineralise hazardous organic substances e.g. the use of pseudomonas under aerobic conditions break down phenols.

Thermal Methods

These are the treatment processes which involve the application of heat to convert the waste into less hazardous forms. It also reduces the volume and allows opportunities for the recovery of energy from the waste.

High Temperature Incineration
In North America and Europe the treatment method most commonly used to destroy hazardous organic wastes, including organochlorines such as polychlorinated biphenyls (PCBs), is high temperature incineration. **Figure 5** schematically illustrates the processes involved. Currently in New Zealand incineration is only available for hospital, clinical and quarantine wastes. There is a high temperature incinerator for the destruction chemical wastes in New Plymouth but its use is dedicated solely to those generated on site.

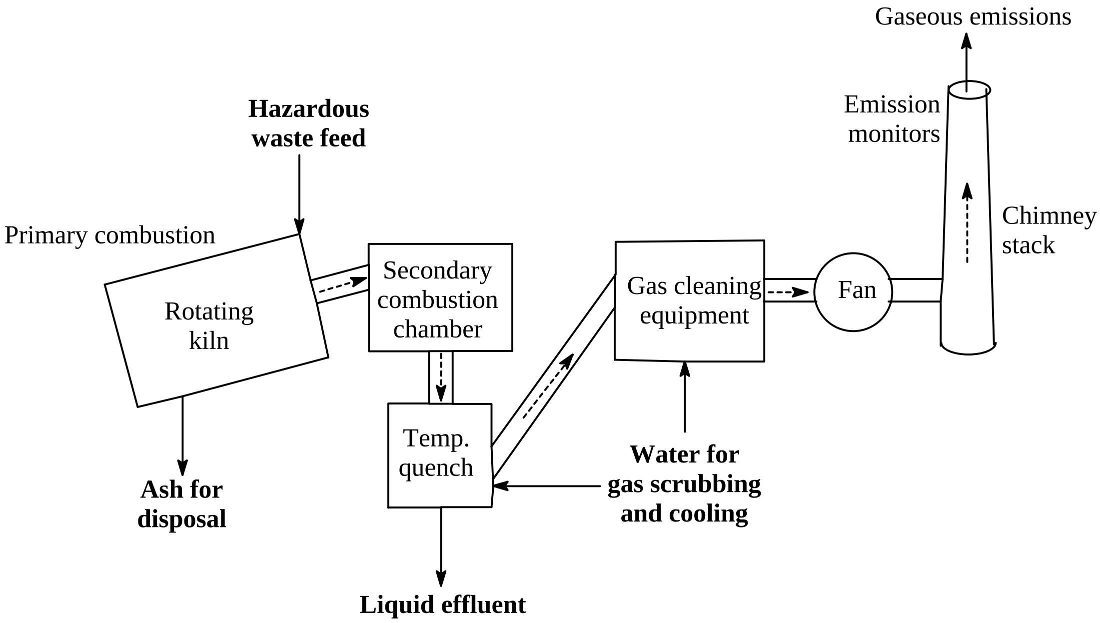

Figure 5 - High Temperature Incineration

Incineration is the controlled combustion process which can be used to degrade organic substances. For a simple hydrocarbon, involving complete combustion, for example the chemical reaction can be illustrated as follows:

$$C_xH_y + (x + \frac{1}{4}y)O_2 \rightarrow xCO_2 + \frac{1}{2}yH_2O$$

In practice, complete combustion is difficult if not impossible to achieve but for hazardous waste 99.99% or greater destruction or removal is required for the process to be generally acceptable.

Combustion Parameters
Incinerators for the treatment of hazardous waste must be carefully designed and operated if they are to achieve the efficiency of destruction required. Combustion of organics occur in two stages. In the primary stage, volatile matter is driven off leaving the remainder to burn to ash. The volatiles are combusted in the secondary stage. Incinerators are designed accordingly. High temperatures are required, for most wastes 800-900^{o}C is sufficient but for materials with high thermal stability 1100^{o}C or higher is required. This temperature must be maintained for sufficient time to allow for complete combustion. For example, two seconds at 1200^{o}C would be suitable for most organic waste. As well as temperature and time, sufficient air must be provided to supply the oxygen required for combustion. The process should be designed to ensure that the air is provided in appropriate locations and in a manner so as to promote the turbulence necessary to achieve effective mixing with the combustible materials.

Toxic Combustion Byproducts.
Public concern relating to the use of incineration for the disposal of hazardous waste relates particularly to emissions of potentially toxic combustion products from the process. Simple examples of such emissions are:

- Carbon monoxide and hydrocarbons resulting from incomplete combustion of organic waste.
- Sulphur dioxide resulting from the combustion of wastes containing sulphur.
- Hydrogen chloride from the combustion of wastes containing chlorinated compunds.
- Heavy metal fume and particulates resulting from the incineration of organic wastes which also contain heavy metals such as lead, cadmium or chromium.

Polychlorinated dibenzodioxins - Dioxins
Polychlorinated dibenzodioxins (PCDDs) are often associated with emissions from waste incinerators. While these are often referred to as dioxin they are in fact a group of 75 compounds with different numbers of chlorine atoms and structures. These are very persistent in the environment and some are established carcinogens or cancer promoters. A closely related family of compounds are the polychlorinated dibenzofurans (PCDFs), a group with 135 members. The structures of PCDDs and PCDFs are given in **Figure 6**.

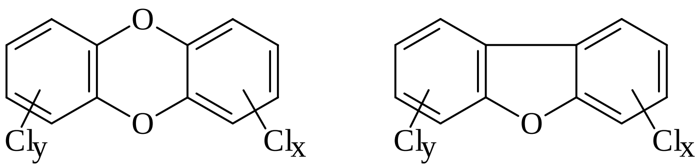

Figure 6 - Chlorinated Dioxins and Furans

PCDDs and PCDFs are formed in trace quantities whenever combustion involving compounds containing chlorine occurs. As such they have been found to be wide spread in the environment but in very low concentrations, normally in nanogram or picogram amounts.

Polycyclic Aromatic Hydrocarbons - PAHs
Another group of compounds that can be found in trace amounts in emissions from the combustion of organic wastes are the polycyclic aromatic hydrocarbons (PAHS). Many of these are established carcinogens. The structure of the most notable, benzo-(a)-pyrene is shown in **Figure 7**.

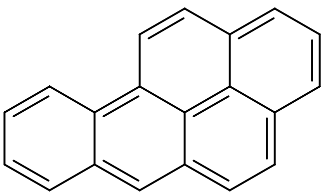

Figure 7 - Benzo-(a)-pyrene

Control of Gaseous Emissions
Emissions of hazardous pollutants resulting from incomplete combustion of wastes can be minimised by good incinerator design and efficient combustion practices. In the case of PCDDs and PCDFs rapid reduction of flue gas temperature immediately following combustion is necessary to prevent the reformation of these compounds. Gas scrubbers using alkaline liquors are used to control acid gases such as sulphur dioxide and hydrochloric acid.

Particulate emissions, including heavy metals in the form of particles, are controlled by the use of bag filters (both wet and dry), high energy scrubbers or, less frequently, electrostatic precipitators.

High temperature incineration of organic hazardous wastes in properly designed and operated facilities can be performed in a manner that complies with stringent standards regulating the emission of gaseous pollutants, such as those enacted in North America and the European Community.

Other Potential Environmental Impacts
The ash resulting from incineration of hazardous waste may itself possess hazardous properties. This is likely to be the case when toxic heavy metals are involved. The ash must therefore be constantly monitored and may require stabilisation and encapsulation before disposal to landfills.

Liquid effluent results where water is used for temperature reduction of gases by quenching, and/or, where wet scrubbers are used for emission control. Some recycling may be incorporated after cooling and chemical treatment, but a quantity of liquid effluent will need to be discharged after appropriate treatment.

Use of Cement Kilns
Kilns used for the production of cement clinker in the manufacturing of Portland cements are designed and operated in a manner that achieves the required parameters for the destruction of hazardous waste, such as time at high temperatures, as discussed under incineration above. In many developed countries overseas such kilns are licensed by authorities for the destruction of appropriate hazardous wastes. Such wastes include PCBs, and recently in Japan, waste chlorofluorocarbons (CFCs). An additional advantage from the use of cement clinker kilns is that the alkaline particulates involved act to neutralise acidic combustion products.

The general use of cement kilns for hazardous waste destruction in New Zealand has not gained favour. Substantial recovery of energy is available however by the use of surplus waste lubricating oils as supplementary fuel for these kilns.

Plasma Arc
A thermal process developed for commercial application in Australia uses the very high temperatures, in excess of 10,000K, which can be attained in arcs formed across high voltage electrodes. This is particularly useful for the destruction of difficult hazardous liquids and gases such as some of the halogenated organics. This process is particularly applicable for the destruction of waste halons and CFCs.

OTHER DEVELOPED TECHNOLOGIES APPROPRIATE FOR NEW ZEALAND

Problem Wastes
As discussed earlier, technologies are already commercially available in New Zealand for the treatment of the vast majority of wastes arising locally. The problem, or intractable, wastes which cannot be treated are organochlorines such as PCBs, and chlorinated pesticides. In the case of PCBs legislative controls have resulted in its withdrawal from use. Contaminated oils containing PCBs have been collected regionally and most exported overseas for destruction

in high temperature incinerators. Other organochlorine wastes must be appropriately stored until treatment options become available.

Two different processes for organochlorine wastes are now commercially available in Australia. Both are based on chemical methods of treatment.

The Base Catalysed Dechlorination (BCD) and the Hydrogen Reduction Processes
The first, referred to as the BCD process, involves catalysed substitution of chlorine by hydrogen atoms under alkaline conditions. The second, operated commercially as the Eco Logic process, is based on complete reduction of organochlorines by hydrogen to carbon monoxide, methane and hydrogen chloride. The Water Shift reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

is used to convert the CH_4 to H_2 thus providing the hydrogen for the process. The CO is used as a supplementary fuel for the process furnaces. Hydrogen chloride is recovered and sold from the process as hydrochloric acid.

Both of the processes are transportable and can be operated without significant environmental impact. They should be appropriate for processing the small quantities of problem wastes arising locally.

LANDFILLS AS A DISPOSAL METHOD

Requirement for Landfills
As discussed above some of the treatment processes discussed above result in residues that themselves require disposal. This disposal is best carried out in properly designed and operated landfills. Controlled quantities of specific hazardous wastes may be broken down to nonhazardous substances, immobilised or adequately diluted by the physical, chemical and biochemical processes which occur in landfills accepting predominantly normal municipal refuse. Such a practice is known as codisposal and entails a degree of management and monitoring usually restricted to the modern larger regional landfills.

New Zealand has been strongly influenced by the practice of codisposal in the United Kingdom. It should be noted however that in 1996 the European Parliament rejected codisposal as it was not convinced that this practice achieved the desirable level of environmental protection. It is therefore likely that this practice will be phased out in the United Kingdom, and its ability to comply with the Resource Management Act in New Zealand will come under review.

Types of Landfills
Most refuse dumps or landfills can be classified into two categories according to the manner in which they have been designed, sited and installed, particularly with regard to leachate management. The principle elements of dilute and disperse, and containment landfills are illustrated in **Figures 8** and **9**. The Ministry for the Environment (1992) has produced guidelines for the siting, design and operation of landfills and these include a review of leachate production, collection, treatment and monitoring measures.

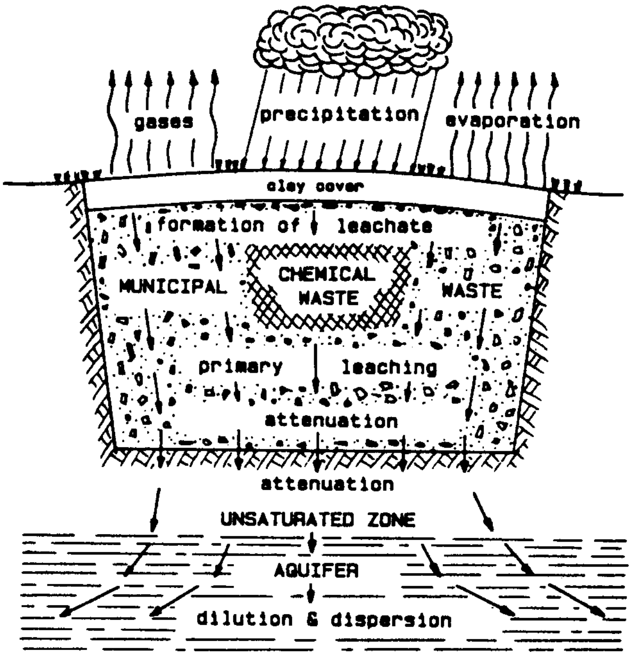

Figure 8 - Dilute and Disperse Landfill

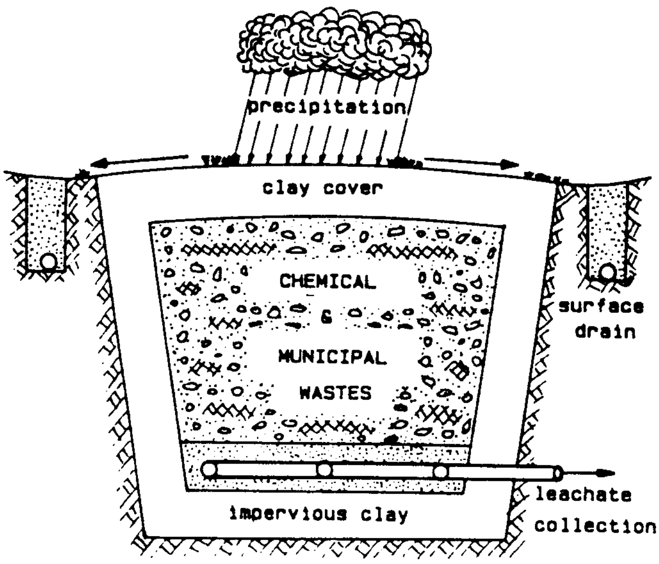

Figure 9 - Containment Landfill

Dedicated Landfills

A further type of landfill is that dedicated solely for the containment of hazardous waste over a long period of time. The hazardous waste may or may not be encapsulated before placement in the landfill. Extra precautions are taken to prevent the formation of leachate from rainfall migration, and to isolate and contain the wastes. This is done by the incorporation of at least a double liner and capping system. At least one of these liners is a thick synthetic material, such as high density polyethylene (HDPE), which must be compatible with the retained waste. Monitor drains underneath and around the landfill are installed so as to illustrate the integrity of containment over time.

To date, only one of this type of landfill has been installed in New Zealand. This is at New Plymouth and contains mainly chlorinated phenolic wastes. A system of solution mining allowing for surface treatment by aerobic biodegradation has been incorporated to breakdown these wastes over time.

The use of landfills dedicated solely for the containment of untreated hazardous wastes is not now widely accepted internationally. There is insufficient experience to allow acceptance of indefinite integrity of clay or synthetic liners. It should be considered to be in the ground long term storage of hazardous waste for which re-excavation and treatment will be required some time in the future.

Classification of Hazardous Wastes for Landfilling.
The CAE Report (1992) recommended that hazardous wastes be classified as follows in respect to acceptability for disposal by landfilling:

Type A. Those wastes unsuitable for landfilling in any quantity or in any type of landfill.

Type B. Wastes which could be suitable for placement in dedicated landfills. See, however, comments above relating to dedicated landfills.

Type C. Those wastes which may be appropriate for codisposal with normal municipal refuse under carefully managed conditions.

Codisposal Limitations
Codisposal was considered appropriate only in containment landfills, sited and operated in compliance with the Ministry for the Environment (1992) guidelines. Care must be taken to ensure that the amount and type of hazardous waste codisposed is compatible with the wastes already in the landfill and the processes occurring. The CAE Report (1992) gives guidance on loading rates for acceptable wastes and recommends that hazardous waste codisposed at a particular landfill should not exceed 1% of the total of all types of wastes accepted into that landfill.

CONCLUSIONS

Some of the waste currently produced by industrial chemical processes possess hazardous properties and require special attention in respect to disposal. Concern relating to these wastes has resulted in the development of international conventions aimed at controlling their intercountry movement. These conventions also assist in the management of these waste by providing listings that can be used as the basis for a identification and classification scheme. A hierarchy to assist decision making is available to promote sustainability from waste management and this places emphasis on the elimination or minimisation of the production of hazardous waste.

Established chemical, physical, and or biological methods are available to stabilise or break down most hazardous waste to a form which will have minimal adverse effect on health, safety and or the environment. Methods available in New Zealand are appropriate for all but a few problem wastes which are mainly the organochlorine based. Technologies for these are, however, becoming more readily available.

Modern refuse landfills have a role in the disposal of residuals from treatment processes and possibly for limited codisposal of hazardous waste with normal refuse. This requires a level of management of these landfills considerably in excess of that practised at refuse dumps in the past.

The quantities and types of hazardous wastes arising in New Zealand and the methods available for elimination, minimisation, treatment and disposal of residues are such that, with proper management, hazardous waste need not present a long term problem in New Zealand in the future.

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