

**PRELIMINARY INVESTIGATION OF NUTRIENT SUPPLEMENTATION
OF, AND HEAVY METAL MOBILIZATION BY, DUAL
(PHENOL/ACTIVATED SEWAGE SLUDGE) CO-DISPOSAL
WITH REFUSE**

by

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Abstract

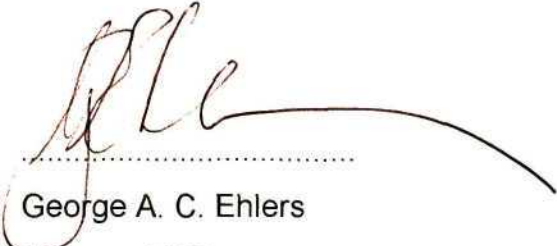
Investigation of landfill co-disposal technology, with emphasis on nutrient supplementation and heavy metal mobilization, was made. For the purpose of this study, co-disposal is defined as the combined disposal of wastewaters and/or sludges with refuse. It is, currently, the most cost-effective method of waste treatment and disposal. To assess whether refuse could be characterized as nutrient limited and to determine the effects of nutrient additions on the refuse solid-state methanogenic fermentation, nutrient supplementations were made to refuse (control), co-disposal (activated sewage sludge with refuse) and dual co-disposal (activated sewage sludge plus phenol with refuse) microcosms. The results showed that the domestic refuse used was not nutrient limited. For the controls, previously reported solid-state fermentation patterns resulted. Self-generating redox gradients were established with concomitant reductions in leachate Chemical Oxygen Demand and initiation of sulphate reduction. Thus, hydrogen sulphide and methane were both evolved. In contrast, nutrient supplementation, particularly with macronutrients and macronutrients plus trace elements, effected fermentation imbalances such that protracted low pH values and high volatile fatty acid concentrations were apparent. Redox gradient generation was slowed which militated against sulphate reduction and the onset of methanogenesis. In the absence of nutrient supplementation, low residual phenol concentrations characterized the dual co-disposal microcosms whereas elevated concentrations persisted in the equivalent nutrient supplemented microcosms.

To investigate the implications of heavy metal retention / mobility during landfill co-disposal operation, microcosms were packed with "young" synthetic refuse and/or activated sewage sludge at packing ratios of 4.1:1 (1) or 4.1:2 (2). The sludge was "spiked" with each of four heavy metals, Cr^{3+} , Cu^{2+} , Ni^{2+} and Zn^{2+} , to a concentration of 100 mg l^{-1} (refuse/sludge ratio 1) or 200 mg l^{-1} (ratio 2) while the control received the same concentrations of metals dissolved in distilled water.

The heavy metal concentrations were increased progressively to 800 mg l^{-1} (ratio 1) and 1 600 mg l^{-1} (ratio 2). For all the microcosms, including an unperturbed control, unbalanced fermentations (acidogenesis > acidotrophy) resulted as evidenced by the low pH values. Thus, heavy metal toxicity was not the sole cause. The leached metal concentrations were in a consistent order with high Zn and Ni concentrations detected compared with immobilized Cr and Cu. After 15 weeks of operation with the higher applied loading, despite extensive retention, increases in Cr, Ni and Zn were detected in the microcosm leachates. Due to the elevated redox potentials, precipitation of the metals as insoluble sulphides was not operable. After 28 weeks of operation, microcosm depth samples (15, 25 and 40 cm) were collected and analysed for immobilized metals. Chromium was characterized by maximum retention at a depth of 15 cm. In contrast, nickel concentrations were comparable throughout the refuse/sludge profile while no specific adsorption patterns emerged for Cu and Zn. The implications of these findings in relation to co-disposal landfill site operation are discussed.

Declaration

I hereby certify that this research, unless specifically indicated in the text, is the result of my own investigations.



George A. C. Ehlers
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CHAPTER 1

Introduction

1.1 Waste Disposal with Emphasis on Landfilling

The disposal of refuse to land was practised for more than 7 millennia with little regard to the environmental consequences and was merely seen as a low-cost disposal option (White-Hunt, 1981a). Exploitation of refuse by solid-state fermentation also has a long history. Archaeological evidence has demonstrated that the disposal of domestic refuse to excavated areas (landfills) has been practised for more than 5 000 years (White-Hunt, 1980). In Northern European Stone Age communities examples have been found of waste deposited in middens by emplacement strategies similar to those employed today. Exploitations of the solid-state fermentation were found in Minoan Crete (1900 BC) and Tudor England (1530) (White-Hunt, 1981a) with the products used for agricultural and military purposes, respectively. At the turn of the 20th century, the emphasis changed to energy, with refuse incinerated to generate heat and electricity in France and Brazil (White-Hunt, 1981b). Today, a number of possibilities are under consideration including the production of energy (direct incineration, CH_4) (Humphrey, 1978), chemical feedstock (Senior, Watson-Craik and Kasali, 1990), value-added chemicals (by low-energy pyrolysis or acid hydrolysis) (Humphrey, 1978) and protein (by Single Cell Protein or vermiculture technologies) (Senior *et al.*, 1990). The use of refuse as an anaerobic filter for the combined disposal of industrial wastewaters and sludges (co-disposal) is also a possible strategy for chemical energy (CH_4) generation (Pauss, Nyns and Naveau, 1984). Finally, the restoration of impoverished soils by fresh or composted refuse additions has also been identified (Anderson, 1990).

Despite the long history, it was not until 1930 that Codes of Practice for controlled tipping were enforced with directives from the Ministry of Health (UK) on emplacement methods, use of intermediate cover and erection of screens (White-Hunt, 1981a).

With the rise in the world's population and the rapid development of industry, together with the accompanying increase in the volume and complexity of waste material, landfill sites have become, and continue to be, the ultimate disposal option (Sinclair, 1994). Currently, the world faces the, so-called, "garbage crisis". Wastes are generated in enormous quantities with refuse volumes approaching 150-200 million tonnes per annum (USA) with the hazardous wastes (1.2) accounting for around 10-100 million tonnes per annum. The latter includes industrial wastes, hospital wastes and chemical wastes (Cheremisinoff, 1975; USEPA, 1984). It is also well established that more sewage sludges are generated each year and convenient places to dispose of them are becoming increasingly scarce (Sufliya, Gerba, Ham, Palmisano, Rathje and Robinson, 1992). Some of them are accounted for by ocean dumping or incineration although the major portion (around 60-70%) is land disposed, by land farming or sanitary landfilling, or composted (Cheremisinoff, 1990; Anon, 1991).

The philosophy of sanitary landfilling, wherein the waste is compacted to the smallest volume, by excluding as many voids as possible, and covered each day with soil to exclude wind blown litter, rats, flies and other health problems, has been applied successfully throughout the world. In biological terms, a landfill can be described as a stationary fixed-film reactor with hydraulic characteristics which range from saturated to unsaturated conditions and include downflow, upflow, lateral flow, single pass and recycle modes. The mean hydraulic retention time (HRT) is often several years (Knox and Gronow, 1989). The fates and behaviour of specific organic compounds are directed by numerous transport and transformation pathways which are active within the landfill. These include advection (as moisture percolates through the landfill), sorption on solid waste surfaces, biodegradation and volatilization and transport by gaseous degradation end products (Reinhart and Pohland, 1991). Unusable waste lands exploited through landfilling have been transformed into city parks, sport fields and recreation areas (Novella, Ross, Lord, Stow, Fawcett and Greenhalgh, 1996).

Increasing social and environmental concerns around the world have resulted in the implementation of tighter controls on landfilling solid wastes and these have necessitated a comprehensive knowledge of the scientific and engineering processes involved (Sinclair, 1994).

1.2 Hazardous Waste

1.2.1 Nature of Hazardous Waste

The term "hazardous" has proved difficult to define legally. In the UK hazardous waste is not defined in the legislation but many industrial wastes, which are considered under Section 17 of the UK Control of Pollution Act (1974) to be "dangerous" or "difficult to dispose of", are referred to as "special waste". The Control of Pollution Act (Special Waste) Regulations (1980) were established to make provision for tighter control over the carriage of wastes which could threaten life. Inclusions made to the Regulations were toxicity, carcinogenicity, corrosivity, medical products and listed products of low (<21°C) flash point (Cope, Fuller and Willets, 1983; Watson-Craik and Sinclair, 1995).

Tchobanglous, Theisen and Vigil (1993) defined a hazardous waste as being non-degradable or persistent in nature and one which can be biologically magnified. Properties which have been used to assess whether a waste is hazardous are related to options of safety and health:

Safety-related properties:

Corrosivity
Explosivity
Flammability
Ignitability
Reactivity

Health-related properties:

Carcinogenicity
Infectivity
Irritant
Mutagenicity
Toxicity (Acute/Chronic)
Radioactivity
Tetratogenicity

(Tchobanoglous *et al.*, 1993).

In the USA, two approaches are taken to define hazardous waste: by listing; and by identification of characteristics. A third approach using toxicological standards for defining hazardous waste has been described (Bagchi, 1994).

Hazardous waste in South Africa is classified according to the South African Bureau of Standards (SABS) Code 0228 which uses the International Maritime Dangerous Goods Code as its base. Hazardous wastes are then hazard rated for disposal by considering their acute and chronic toxicities and their environmental fates. The classification also provides a hazardous rating for the transport of waste material (KwaZulu-Natal Department of Traditional and Environmental Affairs, 1997).

A report by the Council for Scientific and Industrial Research (1991) and the subsequent Minimum Requirements for the Handling and Disposal of Hazardous Waste proposed the following definition: "hazardous waste" is any waste that directly or indirectly presents a threat to human health or to the environment by introducing one or more of the following risks:

1. Explosion or fire;
2. Infection, pathogens, parasites;
3. Chemical instability, reactions or corrosion;
4. Acute or chronic toxicity;
5. Cancer, mutations, tumours or birth defects;
6. Ecotoxicity or damage to ecosystems; and
7. Accumulation in biological food chains, persistence in the environment or multiple effects so that it requires special attention and cannot be released into the environment

(Department of Environment Affairs, 1992a; Peckham, 1994; Department of Water Affairs and Forestry, 1998b).

1.2.2 Quantities Produced

It was estimated by the World Health Organisation that before 1980 some 4 million chemicals had been either isolated from natural products or had been synthesized. Of these some 60 000 were in daily use (Senior and Balba, 1984) and > 1250 new chemicals were marketed each year (E. Senior, personal communication). The USA is the highest producer of hazardous waste and generates 10 times as much as the whole of western Europe. During 1991 the USA total was estimated to be 500 million tonnes (Moyers, 1991).

Since quantities of hazardous waste are shipped from industrialized nations to less developed countries, estimates of wastes for disposal are not representative of the true situation. Between 1986 and 1988, for example, European industrialized countries shipped more than 3 million tonnes of hazardous waste to less developed nations (Anon, 1991; Moyers, 1991).

Due to the tightening of already stringent controls that govern the disposal of waste in European nations as well as the USA, increased interest in the Third World as a disposal option resulted (Koch, Cooper and Coetzee, 1990).

Prior to 1990, very little was known about the total waste stream and, in particular, the hazardous waste generated in South Africa. The Council for Scientific and Industrial Research, therefore, initiated a survey during which interviews were conducted with representatives of many major waste generators from different sectors of industry. It was clear, however, that reliable data on hazardous waste generation would be difficult to obtain. This was attributed to the fact that very few of the industries determined the quantities and compositions of their waste streams (Daneel, 1996).

1.2.3 Hazardous Waste Minimization and Recovery

With the global increase in industrial (hazardous) waste it has become essential to reduce the waste produced and to give priority to the recovery of valuable materials by use of appropriate process recovery techniques in integrated waste management strategies.

The inclusion of this module (resource recovery) into a solid waste management protocol means that the inherent value of a waste stream could be realised and thus minimize its mass or volume thereby extending the life of a landfill site (Nel, 1997). The evaluation of waste management alternatives by the multiple criteria approach (MCA) is becoming increasingly popular (Chung and Poon, 1996). The MCA model has been used to determine the overall performance of different waste management tools. The approach not only accommodates quantitative data but also handles qualitative information with less subjectivity. The MCA identifies alternative courses of action and appropriate evaluation criteria for waste management (Chung and Poon, 1996).

1.2.4 Hazardous Waste Disposal

The high cost of waste disposal and the potential long-term legal liabilities of unlawful waste disposal schemes are likely to provide the necessary economic incentives to increase the disparities between the volumes of hazardous wastes generated and the those requiring disposal (Watson-Craik and Sinclair, 1995). As an issue of resource use, hazardous waste disposal represents a problem of two dimensions. In the first, the waste represents a misallocation of resources since most waste can be either reused or recycled. Secondly, it may contaminate air, land and water (Harris, 1985).

Hazardous waste is also an issue of public health since its disposal often poses a threat to the safety and well-being of people. For example, it has been estimated that between 60 and 90% of all cancers are of environmental origin (Senior, 1991). Many of these cancers are associated with hazardous waste through the contamination of surface- and groundwater. Hazardous waste can also invoke acute reaction from periodic exposure, subtle impacts, such as birth defects, and genetic damage (Harris, 1985).

For industrialised nations such as the UK, the largest portion (65%) of hazardous waste generated is recycled or reclaimed by industry (UK Department of the Environment, 1990).

Fortunately, there is a wide range of technologies available for the treatment and disposal of hazardous waste including thermal (pyrolysis, incineration), chemical (oxidation, ion exchange), physical (including carbon sorption, filtration) and biological (including activated sludges, trickling filters) (Lederman and LaGrega, 1981; Watson-Craik and Sinclair, 1995) approaches. Landfilling is the most popular disposal route for hazardous waste in the UK since only low volumes are treated (Watson-Craik, Sinclair and Senior, 1992a). According to Lederman and LaGrega (1981) landfilling should be the method of last resort. If landfilling is the only viable option, careful site selection/construction and good operation practice are compulsory.

1.3 Landfilling in South Africa

South Africa's population is expected to grow from 29.1 millions in 1985 to 59.7 millions by the year 2010. This rapid population growth, accompanied by expansions of industry and urbanization, will continue to result in a dramatic increase in the mass of waste generated. In 1997, the production of domestic refuse in South Africa was approximately 40 million tonnes and was accompanied by 12 million tonnes of wastewater sludge from biological treatment processes. About 95% (m/m) of all solid waste generated is disposed of in South Africa's 1 400 landfills (Council for Scientific and Industrial Research, 1991; Ninham Shand Inc., 1993). The possible infiltration of leachate from these sites into groundwater bodies is, hence, of major concern. Even though groundwater accounts for only some 13% of the total potable national water supply, approximately 65% of the area of the country relies on this to one degree or another (Parsons and Jolly, 1994).

In 1995, South Africa did not have a comprehensive national statute covering waste management. Provisions for dealing with waste were fragmented among 37 national statutes, 16 provincial ordinances and numerous by-laws (Department of Environment Affairs, 1992a).

The important Acts were:

- 1.Environment Conservation Act No. 73 (1989). This was the only act which dealt specifically with waste management. It empowered the Minister to determine what will and will not constitute waste;

2. Water Act No.54 (1956). This act, including the amendments of 1991, dealt primarily with the utilization of water and contained important provisions with regard to the prevention of water pollution; and

3. Health Act No.63 (1977). Since waste disposal can under certain circumstances develop into a health hazard, certain provisions of the Health Act, including the 1992 amendments, had important relevance.

The Minimum Requirements for Waste Disposal Sites

The Department of Water Affairs and Forestry developed the Minimum Requirements for Waste Disposal by Landfill (Department of Water Affairs and Forestry, 1998a), for the Handling, Classification and Disposal of Hazardous Waste (1998b) and for Monitoring at Waste Management Facilities (1998c). Minimum Requirements may be defined as the norms used to distinguish between acceptable and non-acceptable waste management practices and are essential for the enforcement of legislation (Bredenhann, Abbott and Van Driel, 1991).

1.4 1997 Overseas Legislation

In some countries, for example the USA, landfill siting, design and operation are highly regulated. The United States Environmental Protection Agency (USEPA) published general requirements for operating a sanitary landfill site. These included:

1. Wastes for which the specific facility has been designed to hold are the only ones to be accepted; and
2. Certain hazardous wastes should be excluded from municipal landfills. These include toxic chemicals (such as pesticides and radioactive waste) or any other that may contaminate groundwater (USEPA, 1991).

In the USA the engineering requirements stipulate that rainfall infiltration into household waste sites will be minimized by the use of capping layers (USEPA, 1991). (Stegmann, 1989a).

In contrast, in Australia regulatory requirements are poorly developed and the engineer has the opportunity to use leachate control and landfill design measures to suit the hydrogeological setting in which the landfill is to be constructed (Parker, Bateman and Williams, 1993).

Current landfill practice in the UK and mainland Europe has evolved to an international standard which is designed to provide engineered containment of waste breakdown products to prevent pollution of water. This approach was directed by the Council of the European Communities.

1.5 Waste Classification and Site Selection

There is a wide range of issues which affect the selection of landfill sites. In addition to the technical issues, such as the hydrogeological setting, matters including social impact, environmental impact, strategic position, etc. play major roles. In dealing with the issues that must be faced it may be necessary to call on a wide range of experts including: engineers; planners; hydrogeologists; biologists; agriculturalists; hydrologists; climatologists; chemists; and others (Parker *et al.*, 1993).

The physical and chemical characteristics of the waste materials and the environmental and ecological impacts at and around the proposed site also play important roles (Cheremisinoff, 1990). Information and data on the physical composition of the solid wastes are important in the selection and operation of equipment and facilities, in assessing the feasibility of resource and energy recovery and in the analysis of landfill disposal facilities (Tchobanglous *et al.*, 1993).

Waste may be classified as:

1. Municipal solid waste that may change in the future due to separate collection activities;
2. Mass waste (e.g. residues from gas treatment activities, mine wastes and industrial sludges);
3. Demolition waste or residues from demolition waste recycling plants;
4. Soil;
5. Wastewater sludges; and
6. Bulky waste

1.5.1 Municipal Solid Waste (Refuse) Composition

Municipal solid waste deposited in landfills is a heterogeneous mixture of paper products, food residues, vegetable matter, textiles, plastics, leather, rubber, metals, glass and ash which originate from industrial, residential and commercial sources (Ross, 1990). The composition of waste is variable and is a function of climate, population, demographics and geographical location (Reinhart and Pohland, 1991). The organic content of refuse is approximately 75 - 80% (dry mass) and includes lipids, proteins, carbohydrates and lignins (Ross, 1990).

Municipal waste, typically, contains 40 - 50%(m/m) cellulose, 10 - 15%(m/m) lignin, 12%(m/m) hemicellulose and 4% (m/m)protein (Bookter and Ham, 1982). About two-thirds of this material is biodegradable with the remainder recalcitrant. The biodegradable portion can be further classified into a labile fraction (food materials) and a moderately biodegradable fraction (paper, wood and textiles) (Tchobanoglous *et al.*, 1993).

For the purposes of comparison, typical data on the distribution of the components in residential municipal solid waste (MSW) from low, middle and upper income countries are presented in Table 1.1. It is interesting to note the high percentage of food waste in the refuse of less developed countries since the vegetables and fruits are not pre-trimmed and there are, essentially, no kitchen food waste grinders (Tchobanoglous *et al.*, 1993).

The organic materials found in a landfill decompose as a result of exothermic aerobic microbiological action and, as a result, the temperature increases. The oxygen is quickly depleted and anaerobic bacteria continue the degradation process. Anaerobic degradation gives rise to soluble and gaseous compounds (Barlaz, Shaefer and Ham, 1989a) of which landfill gas (1.9) comprises various molecules. Methane and carbon dioxide are produced in the largest quantities although carbon monoxide, nitrogen, hydrogen sulphide and ethylene are also produced in trace concentrations (Parry, 1981).

The transformation processes which can affect the form and composition of MSW and which can be used for the management of MSW are as follows:

1. Physical. These transformations include component separation, mechanical volume reduction and mechanical size reduction;
2. Chemical. These involve a change of phase. The principal chemical processes used to transform MSW include combustion (chemical oxidation), pyrolysis and gasification; and
3. Biological. Transformation of the organic fraction of MSW may be used to reduce the volume and weight of the material, produce compost and produce methane. These transformations may be accomplished aerobically or anaerobically (Tchobanoglous *et al.*, 1993).

Table 1.1. Typical distribution (% m/m) of components, excluding recycled materials, in residential MSW for low-, middle- and upper-income countries^a (Cointreau, Gunnerson, Huls and Seldman, 1985)

Component	Low-income	Middle-income	Upper-income
Organic			
Food wastes	40-85 ^b	20-65	6-30
Paper	1-10	8-30	20-45
Cardboard			5-15
Plastics	1-5	2-6	2-8
Textiles	1-5	2-10	2-6
Rubber	1-5	1-4	0-2
Leather			0-2
Garden wastes			10-20
Wood	1-5	1-10	1-4
Misc. organics	-	-	-
Inorganic			
Glass	1-10	1-10	4-12
Tin cans			2-8
Aluminium	1-5	1-5	0-1
Other metal			1-4
Dirt, ash, etc.	1-40	1-30	0-10

^aLow-income countries: per capita income < US \$750.

Middle-income countries: per capita income > US \$750 and < US \$5 000.

Upper-income countries: per capita income > US \$5 000.

^bFood waste composed predominantly of waste from the preparation of food.

1.5.2 Hazardous Waste Classification

The Council for Scientific and Industrial Research (1991) classified hazardous waste in five groups.

1. High hazard group (Group 1) of first priority concern, containing significant concentrations of highly toxic constituents which are easily accessible, mobile or persistent in the environment and bio-accumulative;
2. Moderately hazardous waste (Group 2) of secondary priority concern include molecules with highly dangerous characteristics which could be explosive, corrosive or reactive, or which are infective, or which contain significant concentrations of constituents that are potentially highly toxic but only moderately mobile, persistent or bio-accumulative, or that are moderately toxic but are highly mobile, or persistent in the environment, or bio-accumulative;
3. Low hazard waste (Group 3) of third priority concern, which is moderately explosive, flammable, corrosive or reactive, or contains significant concentrations of constituents that are potentially harmful to human health or to the environment;
4. Potentially hazardous waste (Group 4) which often occurs in large quantities and which contains potentially harmful constituents in concentrations that in most instances would represent only a limited threat to human health or the environment; and
5. Non-hazardous waste (Group 5) which, at most, contains only significant concentrations of harmful constituents.

According to a survey by the Council for Scientific and Industrial Research (1991), the total waste produced in South Africa is dominated by a few large and relatively non-hazardous waste streams. Further, it was found that 59% of the hazardous waste stream was carried in wastewater with 93.6% of this figure accounted for by the cyanide-containing effluents from gold extraction (Department of Environment Affairs, 1992b).

1.5.3 Site Selection and Characterization

Site selection for a landfill is constrained by the geological structure and the hydrological conditions of the site. A hydrological study should be made of the quality of the ground- and surface water prior to the establishment of a landfill. Water conditions should be quantified including the direction, volume and velocity of groundwater flow (Carra and Cossu, 1990). The structure of the site depends largely on the geological events which produced the association of rock types. Knowledge of the proportion and location of bedrock and other deposits is necessary to determine the economic advantages and disadvantages of a particular site (Cheremisinoff, 1990).

Landfills can be constructed as "below ground" sites, such as in former extraction industry sites (quarries), in purpose built excavations and as "above ground" sites, including valley-fill landfills (Parker *et al.*, 1993). In assessing a site for location of a landfill facility, the engineers and hydrogeologists have three primary concerns (Howard, 1987):

1. Is the site structurally sound and free from potential problems such as active faulting and landslides?;
2. Are suitable materials available close to the site for construction?; and
3. What impact will the landfill have on the quality of ground- and surface water?

Soil at the site should be analyzed to determine its permeability, pH value and cation exchange capacity. The permeability should be low enough to provide a barrier to the flow of hazardous leachates. The accepted value for permeability is $1 \times 10^{-7} \text{ cm sec}^{-1}$ (Environment Resources Management, Inc., 1981).

Site characterization is the key to the development of a monitoring plan for a landfill and can be broadly considered in terms of the physical properties of the waste facility itself and the environment in which it is placed. A monitoring plan is compulsory to determine the impacts a landfill has on the water quality of the area (Rosin and Avalue, 1993).

Landfill sites are usually classified into three groups:

Class I landfills hold refuse and leachate within the site by the use of a synthetic liner, such as butyl rubber and PVC, or a natural layer, such as clay;

Class II sites are not lined and allow gradual release of leachate from the refuse into underlying strata; and

Class III sites offer little or no protection to the surrounding earth and water table, thus leachate rapidly migrates from the refuse (Senior, 1990; Percival, 1996).

In industrialized nations the trend is towards fewer but larger operational landfills and, more importantly, scientifically designed sites (Senior, Watson-Craik, Sinclair and Jones, 1991). Thus, traditional Class 3 sites are no longer an acceptable option. Even Class 2 sites are becoming less common particularly in countries which are heavily dependent on groundwater for drinking water supply. Increasingly, Class 1 sites are becoming the norm (Senior, 1990).

In South Africa, a replacement of the classification system was introduced as part of the "Minimum Requirements" (Department of Water Affairs and Forestry, 1998a,b,c) document. Landfill sites are, thus, classified according to the waste type (hazardous or general) received. General waste landfill sites are sub-classified into four categories (Communal, Small, Medium and Large). These classes are further sub-divided on climatic water balance (B^+ indicates a water surplus; B^- a water deficiency).

Hazardous waste landfill sites must be containment sites which are equipped with a liner and a leachate collection facility. Hazardous waste is classified into four different ratings, with rating 1 signifying an extreme hazard. If waste with a hazard rating of 1 or 2 is disposed of to landfill, the site has to be classified as an H:H site. Sites accepting wastes with a rating of 3 or 4 are classified as H:h sites (DWAF, 1998a;b;c).

The principal components of a lining system are the liner material and the leachate collection network. The liner must minimize the migration of contaminated leachate into the environment.

The leachate collection network removes leachate from the landfill and in doing so maintains a low hydraulic head on the liner (Parker *et al.*, 1993). A liner consists of one or more of the following components: compacted soil; geomembranes; geotextiles; and composites of soil and membrane. Other materials such as asphalt and concrete can also be used for lining purposes (Stegmann, 1989a).

In the absence of suitable natural materials such as 2 metre depths of clay with hydraulic conductivities of $\leq 10^{-7} \text{ cm s}^{-1}$, liners (natural or synthetic) have to be constructed, often at great expense. Considerable cost saving could, however, be made by reducing the conductivity of country soil to substitute for the expensive synthetic materials. This might be achieved by either compaction or chemical addition. Thus, it is possible to significantly reduce the permeability of sandy soils which contain as little as 5% (m/m) clay (kaolinitic or bentonitic) (Senior *et al.*, 1991).

Geomembranes provide an alternative to clay lining, particularly where there are limited sources of clay soils. It is, however, preferable that geomembranes are used in combination with clay liners to form what is referred to as a composite liner (Parker *et al.*, 1993). The advantages and disadvantages of clay liners and geomembrane liners are presented in Table 1.2.

Landfill site selection and management in the USA are controlled under the Resource Conservation and Resource Act (RCRA) of 1976 and the Hazardous and Solid Waste Amendments (HSWA) of 1984. A requirement of the HSWA was that hazardous waste landfills were to be lined with a double membrane (Figure 1.1).

Two synthetic liners overlain by a primary leachate collection system and separated by a secondary leachate collection system, together with at least 0.6 m of clay liner with hydraulic conductivity of $1 \times 10^{-9} \text{ m s}^{-1}$ below the lower synthetic liner must be used. The minimum synthetic liner thickness is 0.75 mm or 1.5 mm in the case of high density polyethylene (HDPE) (Parker *et al.*, 1993).

Table 1.2. Comparison of clay and geomembrane liners (Parker *et al.*, 1993)

	Compacted Clay Liners	Geomembrane Liners
Advantages	High sorptive capacity	Easily installed
	Low leakage rate	Very low leakage rate if no punctures
	Thick	Flexible - can accommodate settlement
	Long life	
Disadvantages	Construction difficult	UV light degradation
	Thickness - reduced airspace	Slope stability
	Desiccation	High leakage if punctured
	Degraded by high concentrations of organics	Minimum thickness
		No sorptive capacity

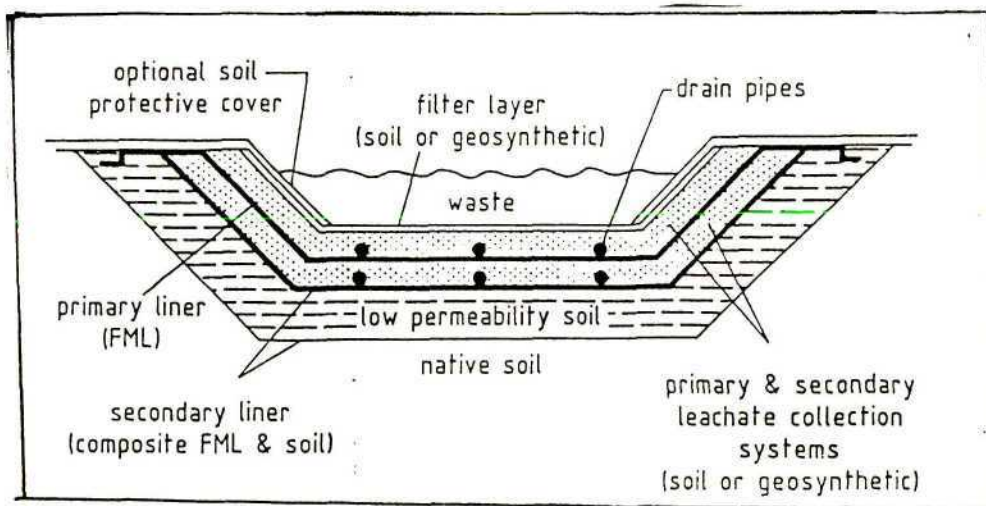


Figure 1.1 Hazardous waste landfill lining requirements (Parker *et al.*, 1993).

1.6 Methods of Landfill Operation

A landfill cell is the basic building mechanism of a landfill. Waste is spread and compacted in layers in a confined area. Cover material, usually soil, is then applied to the emplaced refuse. The compacted waste and soil layers constitute a cell (Senior, 1990).

Two basic methods are employed in the operation of a sanitary landfill. These methods are called the trench method and the area method (Cope *et al.*, 1983). In the trench method waste is spread and compacted into an excavated trench. Cover material, which is taken from the excavation, is then spread thinly over the waste mass.

The area method is usually used when waste is spread and compacted on the natural surface of the ground and cover material is spread and compacted over it (Novella *et al.*, 1996). A third approach, the ramp method, was described by Cheremisinoff (1990). This method is used when new refuse is pushed against preceding refuse cells and a cover material is applied.

The results obtained from German experiments on the enhancement of refuse degradation processes indicated that the following operation techniques should be beneficial for full-scale landfills (Stegmann and Spendlin, 1986):

1. A liner of uncompacted refuse should be placed at the bottom of the landfill. The height of the layer depends upon whether the subsequent aeration is supported by perforated pipes and induced aeration (2-3m) or loosely placed refuse (2 layers of 1m);
2. After the Biological Oxygen Demand (BOD_5) concentration of the leachate has decreased to a low percentage ($\pm 6 - 12$ months) the MSW should be landfilled in thin, highly compacted layers (30-40 cm) over large areas on top of these uncompacted layers and no daily cover should be used; and
3. Controlled leachate recirculation should be practised to increase the moisture content of the MSW but only if precipitation is $< 750 - 800 \text{ mm year}^{-1}$.

1.7 Digestion Processes in a Landfill Ecosystem

1.7.1 Degradation of Refuse

Within a landfill a complex sequence of physically-, chemically- and biologically-mediated events occurs. As a consequence of these processes, refuse is degraded or transformed (Reinhart and Pohland, 1991).

Aerobic Processes

Initially, air occupies the pores of the deposited waste but the O₂ is quickly used by aerobic microorganisms. Nitrate is also used but there is little change in the populations of cellulolytic, acetogenic and methanogenic bacteria (Barlaz *et al.*, 1989a). The products are heat, carbon dioxide and water. Soluble sugars serve as the carbon source for microbial activity. The rate of oxygen consumption depends on the nature and composition of waste and on the rate of oxygen supply (Beker, 1987).

Anaerobic Processes

The anaerobic phase is characterized some successive processes (Figure 1.2).

During the hydrolysis phase, organic materials such as polysaccharides, proteins and fats are hydrolyzed to monomers such as sugars, amino acids and fatty acids. During the acid fermentation, mainly volatile fatty acids (short-chained fatty acids) are produced (Barlaz *et al.*, 1989a). The more reduced products of the acid fermentation must be oxidized under anaerobic conditions to acetic acid, carbon dioxide and hydrogen. These intermediates can then be used by methanogenic bacteria. The methanogenic population begins to increase and methane is detected in the landfill gas. A methane concentration of 50-60% (v/v) may be measured at this stage with a concomitant decrease in total carboxylic acid concentration and an increase in pH (Beker, 1987).

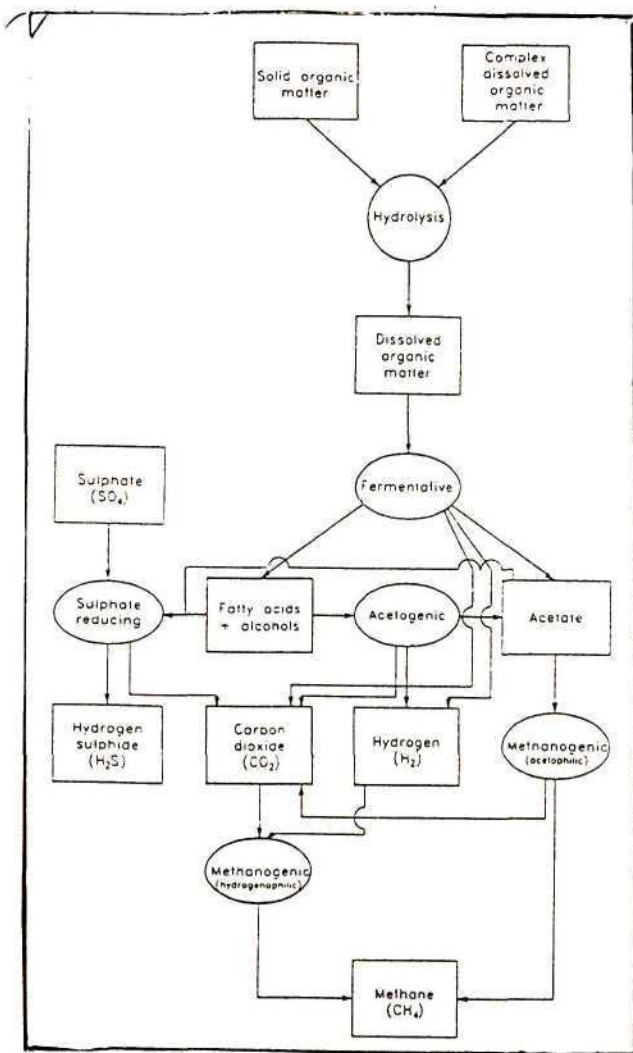


Figure 1.2 Substrates and major bacterial groups involved in the methane generating ecosystem (Christensen and Kjeldsen, 1989).

There is a final phase which is referred to as the stabilization or decelerated methane production phase or the maturation of the landfill. The methane concentration, pH and methanogenic populations remain at least similar to those in the previous phase (Barlaz, Schaefer and Ham, 1989b). Landfill stabilization (Figure 1.3) is a dynamic, microbially mediated process which is primarily influenced by the waste characteristics and the availability of moisture and nutrients. By controlling leachate accumulation, containment, collection and recirculation back through the landfill, stabilization may be accelerated (Pohland and Al-Yousfi, 1994).

By accelerating the stabilization of a landfill, the site life is extended so that 2 -3 times more refuse can be placed in the site which makes it very cost effective (Chapman and Ekama, 1992).

Rees and Grainger (1982) suggested that the refuse fermentation can be controlled and directed so that the carbon compounds are mineralized to methane and carbon dioxide. The potential benefits of this are an improved yield of methane for use as an energy source or chemical feedstock, stimulated gas production leading to more predictable rates of land stabilization and a shortened acid phase in anaerobic catabolism during which high strength leachates are produced.

Refuse Decomposition Indication

Bookter and Ham (1982) used the ratio of cellulose to lignin as an indicator of refuse decomposition by relating this ratio to time. They used this ratio instead of cellulose concentration *per se* because cellulose and lignin occur together in wood, paper and other wood products in refuse. Cellulose is labile under anaerobic conditions whereas lignin is not.

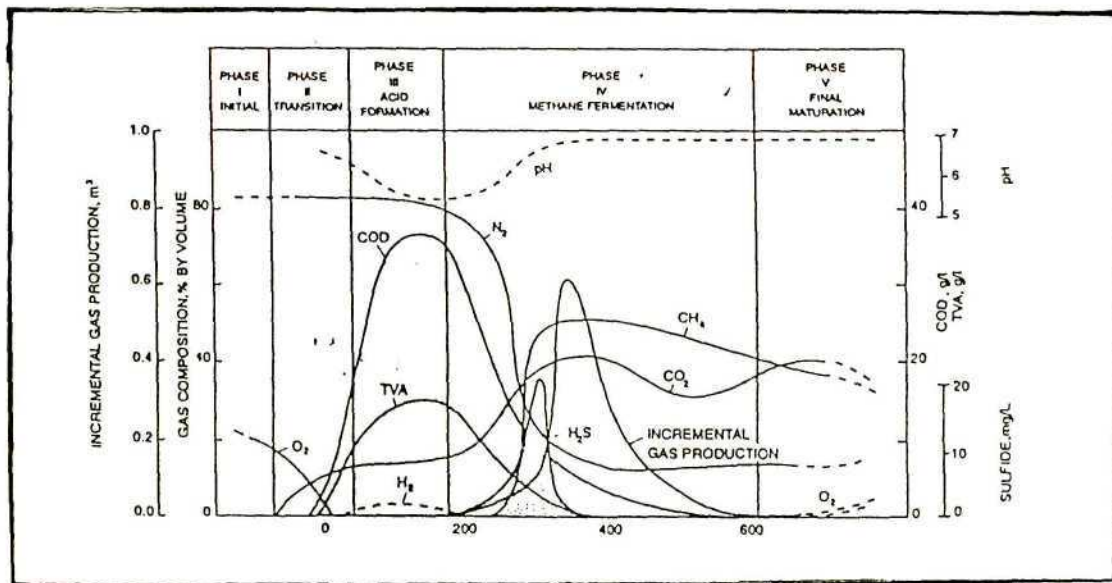


Figure 1.3 Illustration of developments in gas and leachate composition in a landfill cell (Pohland and Al-Yousfi, 1994).

1.7.2 Biochemical Interactions in Anaerobic Processes

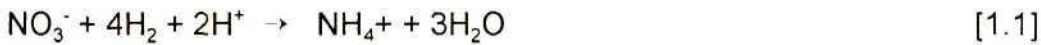
To gain an insight of the complex anaerobic digestion processes that operate in a landfill ecosystem it is necessary to study the interactions between electron donors and the predominant electron acceptors that occur in solid and liquid waste digestion processes.

Nitrogen Metabolism

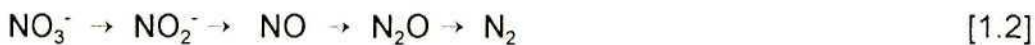
(i) Nitrate Reduction and Denitrification

The physiological group of bacteria which carries out nitrate respiration can transfer substrate hydrogen to nitrate which becomes reduced with the free energy used for electron transport phosphorylation. The process is called nitrate respiration or dissimilatory nitrate reduction (Schlegel, 1992). During dissimilatory nitrate reduction, nitrate is converted to a variety of reduced products while organic matter is simultaneously oxidized (Focht and Verstraete, 1977).

The complex reaction (dissimilatory reduction) may be presented as follows:



Denitrification is the conversion of bound nitrogen (nitrate) to free N_2 . Denitrifying nitrate reducers such as *Thiobacillus denitrificans* and *Paracoccus denitrificans* and various pseudomonads convert nitrate through nitrite to nitric oxide (NO) and nitrous oxide (N_2O) to molecular nitrogen (Atlas and Bartha, 1993) as follows:



The role of the dissimilatory pathway for nitrate reduction, like denitrification, has been speculated. The partitioning of nitrate between these two pathways was discussed by Tiedje (1988). The ratio of available carbon to electron acceptors was thought to influence the partitioning.

In anaerobic environments, the concentrations of electron acceptors are fundamentally important and as dissimilatory nitrate reduction has the capacity to receive a total of 8 electrons rather than 5 in denitrification, it was suggested (Tiedje, 1988) that the pathway may be favoured.

Several facultatively anaerobic bacteria which can grow with fermentative energy under anaerobic conditions (for example *Escherichia coli* and *Enterobacter aerogenes*) are able to transfer the substrate derived-electrons to nitrate to produce nitrite. Nitrite may accumulate but there is no evolution of N₂. Instead, the nitrate can be reduced to ammonium by assimilatory nitrate reduction. Assimilatory nitrate reduction does not result in the accumulation of high concentrations of extracellular ammonium ions as they are incorporated into organic nitrogen (Gottschalk, 1977; Schlegel, 1992).

Assimilatory nitrate reduction is tightly regulated and normally proceeds only at the rate at which ammonia is required for growth. Nitrate, therefore, rarely accumulates during assimilation. Unlike assimilatory nitrate reduction, dissimilatory nitrate reduction is not inhibited by ammonia even if substantial quantities of ammonia have accumulated (Sinclair, 1994).

(ii) Nitrogen Metabolism in the Landfill Ecosystem

In a study on the landfill environment, Barlaz *et al.* (1989a) assumed that any nitrate present in fresh refuse would be utilized solely for carbohydrate oxidation via denitrification. The possibility does exist, however, that assimilatory reduction to ammonia could account for a substantial proportion of nitrate utilization.

Tiedje (1988) hypothesized that a landfill, which is characterized by a high organic content and limited nitrate concentration, would be expected to favour dissimilatory nitrate reduction to ammonia. However, since considerable spatial variations can exist within a landfill, the possibility exists that during different stages of the refuse fermentation added nitrate may undergo a variety of fates depending on the conditions within the environment.

Based on Cole's (1988) investigation, it would appear that a population of viable nitrate-reducing bacteria could be maintained in the refuse mass particularly when sewage sludge co-disposal is practised.

Denitrification could be the fate of any added nitrate leading to N_2 as the terminal product (Sinclair, 1994).

The primary source of ammonia generated in landfills, particularly those which have accepted sludge waste, is from ammonification. The degradation of proteins accompanied by the formation of ammonia is referred to as ammonification (Schlegel, 1992). The organic nitrogen source in landfills is primarily from putrescible material such as vegetable and garden-type wastes while co-disposed sewage sludge also contributes to the organic nitrogen concentration which, in turn, leads to increased NH_3/NH_4^+ generation (Craft and Blakey, 1988).

Sulphur Metabolism

(i) Dissimilatory and Assimilatory Sulphate Reduction

When obligately anaerobic bacteria carry out dissimilatory sulphate reduction, they are referred to as sulphate reducers (Postgate, 1984). The sulphate-reducing bacteria (SRB) are characterized by their ability to transfer substrate hydrogen to sulphate as the terminal acceptor with the reduction of sulphate to sulphide (Schlegel, 1992). The most common electron donors are pyruvate, lactate, succinate and molecular H_2 (Figure 1.4). The traditional sulphate-reducing genera *Desulfovibrio* and *Desulfotomaculum* were joined by several morphological and physiological types such as *Desulfobacter*, *Desulfococcus*, *Desulfonema* and *Desulfosarcina* (Pfennig and Biebl, 1981).

The reduction of sulphate results in production of hydrogen sulphide according to the following equation:



Assimilatory sulphate reduction differs from dissimilatory sulphate reduction in that a second sulphate activation step is necessary. Assimilatory sulphate reduction produces H_2S in low concentrations which is immediately incorporated into organic compounds (Atlas and Bartha, 1993).

(ii) Sulphate in Anaerobic Degradation Processes

The presence of sulphate and sulphide are necessary but may be problematic. The presence of sulphide has been shown to precipitate toxic heavy metals such as chromium, nickel, iron and zinc (Lawrence and McCarty, 1965). For the cultivation of anaerobes, sulphur-containing compounds have been employed to maintain reducing environments which are essential (Bryant, Robinson and Chu, 1959). The same compounds are also integral to the formation of ferredoxin (Valentine, 1964) and other compounds involved in electron transport. In contrast, sulphide has been shown to inhibit methanogens (MacGregor and Keeny, 1973; Winfrey and Zeikus, 1977).

In a study undertaken by Khan and Trottier (1978) of the effects of sulphur-containing compounds on the anaerobic degradation of cellulose to methane by mixed cultures obtained from digested sewage sludge, the results indicated that the presence of sulphur in defined medium was essential for cellulose mineralization. In concentrations > 1.75 mM the inhibition of cellulose degradation depended on the type of sulphur-containing compound (sulphate, thiosulphate, sulphite, sulphide and H_2S). Of these, H_2S had the greatest inhibitory effect on cellulose mineralization.

Hilton and Olezkiewicz (1988) studied sulphide inhibition of anaerobic digestion processes and concluded that the prime factors involved in the inhibition of methanogenesis were competition for hydrogen by the different trophic groups, dynamic population shifts induced by substrate selection pressures and different tolerance levels to the H_2S - HS^- system. The authors also concluded that acetate utilization was inhibited by un-ionized H_2S more than total sulphide and that lactose and acetate utilization in the presence of high concentrations of sulphide required a prolonged retention time.

The application of anaerobic digestion to the treatment of high sulphate content effluents is complicated by competition between the sulphate-reducing bacteria (SRB) and methane-producing bacteria for electrons from H₂ and acetate and by competition between the SRB and obligate hydrogen-producing bacteria for electrons from acetate precursors, such as propionate and butyrate (Hilton and Oleszkiewicz, 1988). Qatibi, Borris and Garcia (1990) and Sai Ram, Singh, Suryanarayana and Alam (1995) found an enhanced propionate/butyrate/valerate oxidation with acetate accumulation resulting after sulphate addition while acetotrophy was found to be independent of the sulphate concentration.

In environments with a plentiful supply of sulphate, it is during the terminal stages of anaerobic degradation that SRB have a major role to play. If low molecular weight components, such as acetate and hydrogen, are allowed to accumulate, initial oxidation processes higher in the catabolic pathway are inhibited (Bryant, 1976).

Until the discovery of sulphate-reducing bacteria which utilized acetate, it was thought that acetate oxidation occurred by methanogenic and sulphate-reducing bacteria in syntrophy (Cappenberg, 1974). In the presence of sulphate, however, it is clear that methanogenesis is inhibited (Winfrey and Zeikus, 1977; Oremland and Taylor, 1978; Mountford, Asher, Mays and Tiedje, 1980). The sulphate reducers are able to out-compete the methanogens for the common growth substrates of hydrogen and acetate since they have a higher affinity for these substrates (Robinson and Tiedje, 1984).

VFA Accumulation and Utilization

Analysis of volatile fatty acids (VFA) has proven to be one of the most important control tests for anaerobic digestion. It is recognized that an increase in the VFA concentration in a digester is one of the first signs of an unbalanced fermentation and identifies the need for control measures. Many different factors may effect this.

These include changes in temperature, changes in organic loading or addition of some toxic substance. Under unbalanced conditions acidogenesis may exceed acidotrophy. If this increase exceeds the buffering capacity of the fermentation, the pH will drop and the hydrogen ion concentration will increase. As H^+ is known to be one of the most toxic cations to biological systems it must be removed by the addition of an alkaline material which replaces the H^+ with another cation (McCarty and McKinney, 1961).

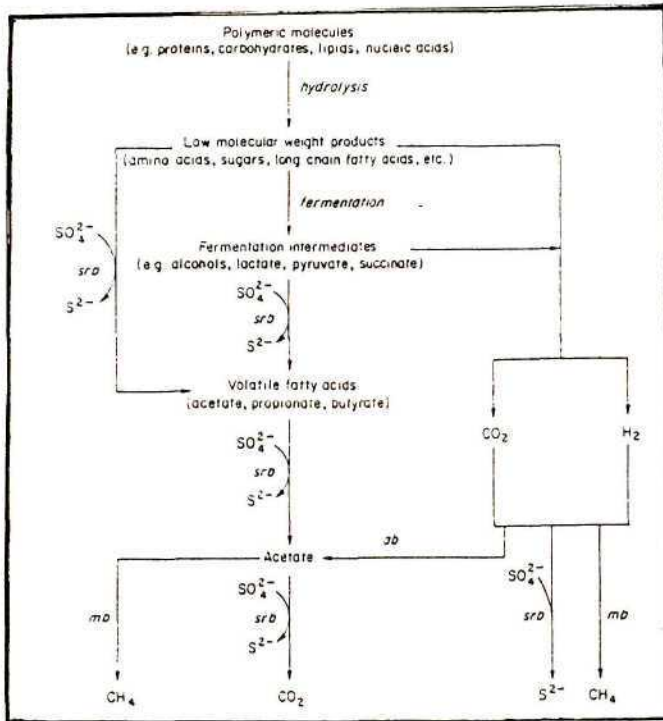


Figure 1.4 Anaerobic degradation of organic matter showing the potential interactions of sulphate-reducing bacteria (srb = sulphate-reducing bacteria; mb = methanogenic bacteria; ab = acetogenic bacteria) (Gibson, 1990).

1.7.3 Toxic Phenomena in Anaerobic Digestion

As a biological process, certain substances can affect the growth and function of microorganisms in anaerobic digestion. Three basic effects of toxic phenomena in anaerobic processes were observed by Cheremisinoff (1994): toxicity; antagonism; and stimulation. Toxic effects can be expected from substances which are not normally found in biological environments. Retardation of methane formation is the starting point for unbalancing the process (Kugelman and Chin, 1971; Barnard, 1985).

According to Robinson (1989), the methanogenic stage in refuse decomposition is probably not the rate-limiting step as methanogens can sustain themselves in adverse environmental conditions such as high substrate concentrations.

Any cation can be inhibitory in high enough concentrations. Heavy metals, for example, are, primarily, non-specific, reversible, non-competitive inhibitors. Increased concentrations decrease proportionately the maximum specific growth rate (μ_{max}) of the bacteria and increase the minimum solids retention time (SRT) required for digestion (Watson-Craik and Senior, 1990). Variations in the degree of toxicity exerted by metal ions are coupled to the valency and atomic weight. The important role that sulphide plays in precipitation of metal ions in anaerobic digestion processes has been demonstrated for copper, nickel, zinc and iron (Lawrence and McCarty, 1965). In a study made with monocultures of the inhibitory effects of heavy metals, nickel was found to be less toxic than either zinc or copper (Jarrell, Saulnier and Ley, 1987).

The inhibitory effects of a range of organic molecules such as formaldehyde, ethanol, benzene, aniline, chloroform and phenols to microorganisms in anaerobic digestion have been assessed (Wang, Suidan, Pfeffer and Najam, 1989; Gerike and Gode, 1990; Vaishnov and Korthols, 1990). Volatile fatty acids (VFA) and ammonia toxicity to methanogenesis have also been studied (McCarty, 1964; Lawrence and McCarty 1965).

Understanding inhibitory factors is a necessary prerequisite for improving the efficiencies of degradation processes.

1.8 Landfill Leachate

1.8.1 Landfill Moisture Content and Water Flux

Lema, Mendez and Blazquez (1988) reported that anaerobic degradation of organic material is usually stimulated when a landfill has a water content of 50 - 70% (m/m), a content which is unlikely to be reached in dry areas or during dry periods elsewhere.

The moisture content of refuse is derived from three sources: the moisture content at emplacement, which can be as high as 60% (m/m) (Pfeffer, 1980); the infiltrated moisture; and moisture generated by microbial activity which is considered minor compared to infiltrated water (Holmes, 1980). Moisture is of prime importance in solid-state anaerobic decomposition. It serves as a solvent in which chemical reactions can take place and for transporting microbial metabolites in the degradation process (Ross, 1990).

Water has many effects in the landfill ecosystem including the solubilization and distribution of substrates and nutrients and the dilution of toxic substances. Studies on moisture content have indicated that an elevated initial moisture content in a landfill helped to accelerate methane formation (Farquhar and Rovers, 1973). A later study proved that a high initial moisture content appeared to stimulate the hydrolysis of cellulose to a greater extent than it stimulated the methanogens and the acidogens (Barlaz, Milke and Ham, 1987).

Jones, Rees and Grainger (1983) investigated the position of the water table on biogas production and enzyme activity in domestic refuse. They showed that extracellular enzyme activities were dependent on the refuse moisture content. The enzyme activities were minimal at depths of 10-11 m and gas production also ceased since the moisture content was minimal. They concluded that enzyme activity measurements were indicative of landfill reactivity.

Holmes (1980) developed an equation to describe the landfill site water balance as follows:

$$P = R + E + \Delta W \quad [1.4]$$

where: P is the mean site catchment precipitation; R is the mean site runoff which may be maximized by emplacement and restoration strategies; E is the mean site actual evaporation and transpiration (facilitated by vegetative cover and refuse temperature); and ΔW is the mean storage change over the site.

Waste transported to most landfills has a much lower water content than its sorption capacity (Straka, Chra and Kbrova, 1993).

Various data place the initial water content in the range of 17 - 35% (v/m), while the value of the percolation limit is in the range of 45 - 55% (v/m) or higher (Leckie, Pacey and Halvadakis, 1979; Rees, 1980). The differences in these values correspond in some cases to the high volume of water that the landfill is capable of absorbing before percolation begins.

Leachate production is often observed within a few months of a new site being commissioned. This happens when the absorptive capacity of the emplaced waste is exceeded and the waste becomes saturated (the field capacity of the waste) with water (Maris, Harrington, Biol and Chismon, 1984). The field capacity of refuse is the water content, expressed as a percentage of the dry mass of the refuse, that will be held in the refuse by capillarity when allowed to drain by gravity (Ross, 1990). The rate of saturation depends upon the presence or absence of a liner, the degree of compaction, the cover material, the climatic conditions and the initial water content of the waste material (Maris *et al.*, 1984).

The immobilization of liquid waste in the refuse mass can only be achieved in sites with a significant absorptive capacity. Various interacting forces influence this (Watson-Craik, 1990):

1. Type of site, area and depth, permeability of the sides and base;
2. Ground- and surface-water infiltration;
3. Extent and pattern of rainfall;
4. Evaporation and evapotranspiration;
5. Input refuse rates;
6. Moisture content of both emplaced refuse and the waste to be deposited; and
7. Extent of channelling.

The time taken for the theoretical saturation of the landfill body by water is dependent, primarily, on the climatic conditions at the site and the shape of the site body.

A simple relationship can be derived to determine the effects of climatic conditions and refuse mass capacity on the saturation time if it is assumed that the wastes are filled evenly over the whole given area (Straka *et al.*, 1993).

The relationship simultaneously assumes that all percolated water is recycled:

$$t_s = \frac{T - 1}{A} \cdot \frac{(W_p - W_o)}{(\mu \cdot Y - W)} \cdot 100 \quad [1.5]$$

where: t_s is the landfill saturation time (years);

T is the total capacity of the landfill (kt);

W_p is the "percolation" water content of the waste (mass fraction);

W_o is the input water content of the waste (mass fraction);

A is the landfill area (ha);

μ is the fraction of precipitation percolating in the landfill (volume fraction);

Y is the annual precipitation (mm) = (litres/(m² y¹)); and

W is the average annual evaporation (litres/(m² y¹)).

1.8.2 Leachate Composition and Characterization

Prior to 1965, it was not widely recognized that water passing through refuse in a landfill would become highly contaminated. There are wide differences in the compositions of leachates from different sites (Smith and Weber, 1990). Various factors are responsible for these differences: refuse composition; site hydrogeology; climate; site age; seasonal weather fluctuations; and moisture routing through the refuse mass (Boyle and Ham, 1974). Climatic conditions and the rainfall patterns are important particularly in relation to the leachate volume and quality (Knox, 1985). Following heavy rainfall, peak volumes may result. In contrast, in very dry seasons flow may cease altogether.

Leachate from recently emplaced waste contains a high concentration of dissolved organic matter and the largest portion of the total organic carbon may be accounted for as short-chain volatile acids (Maris *et al.*, 1984; Doedens and Cord-Landwehr, 1987). Untreated or raw leachate from "young" refuse is labile and, traditionally, biological processes have been used to treat this (Birchler, Milke, Marks and Luthy, 1994). Leachate generated by "aged" waste (>5 years) generally has a lower concentration of volatile acids and a lower Biological Oxygen Demand (BOD) value. Studies have shown that physical-chemical treatment methods, such as activated carbon, chemical precipitation, chemical oxidation and reverse osmosis are more applicable to stabilized leachates or leachates from "aged" waste (Venkataramani, Ahlert and Corbo, 1984). The relationship between the BOD and Chemical Oxygen Demand (COD) values is an important factor in determining degradability. A high ratio (> 4) indicates good biodegradability. As waste matures and stabilizes, biologically more refractory compounds become dominant (Ehrig, 1984).

The physical and chemical analyses of sanitary landfill leachate are important since they provide information on degradation processes, the major pollutants present and which treatment option will be necessary (biological or physical-chemical or a combination) (Knox, 1983). In co-disposal landfills hazardous constituents of industrial wastewaters may appear in the leachate which, in turn, may inhibit treatment (biological).

Thus, when a biological system is part of the leachate treatment process, toxic compounds in the leachate might have a detrimental effect on the microbial population in, for example, an anaerobic digester (Britz, Van der Merwe and Riedel, 1992).

Leachate can be classified into two broad categories: non-hazardous leachate; and hazardous leachate. Hazardous leachates are generated from hazardous wastes or co-disposal landfills. Non-hazardous leachates result from non-hazardous solid waste landfills (Liu, Li, Henry and Kruckel, 1991). Leachate, typically, exhibits low pH, low dissolved oxygen, and high iron, heavy metal ion and toxic chemical concentrations (Venkataramani *et al.*, 1984).

Analysis of the major chemical parameters (e.g. COD, nitrogen and phosphorus) not only gives information on the progress of biological processes within the landfill but also indicates the presence of pollutants which must be removed before the leachate can be discharged (Chu, Cheung and Wong, 1994). Typical toxic compounds in leachate which pose contamination threats to ground- and surface water are pesticides, trace metals, cyanide, phenols, reactive wastes, solvents and hydrocarbons (Smith and Weber, 1990).

As South Africa is a semi-arid country with limited resources, we cannot afford to compromise water by unnecessary pollution (Myburg and Britz, 1993) from landfill leachate.

1.8.3 Leachate Treatment

As more than 90% of domestic and commercial solid wastes plus > 95% of all industrial wastes are disposed of by landfilling in the UK, the country places emphasis on natural treatment and attenuation of leachate by permeable strata beneath sites (Robinson and Maris, 1985). The UK policy with regards to leachate dispersal is "dilute and dispose". In other European countries and the USA, containment and, subsequent, collection and treatment of leachate are practised. The most direct method of disposal is via pipelines to the local sewage treatment works or sea outflow. On-site treatments are increasingly being considered as viable options (Maris *et al.*, 1984) although careful site operation can minimize leachate production by sealing and containing the waste materials to encourage rainfall runoff.

With increasingly stringent standards, additional treatment processes may be required to attenuate leachate. In Germany and Switzerland full-scale facilities are in place to treat raw landfill leachate by evaporation (Birchler *et al.*, 1994). Another treatment option is the use of poplar trees (Licht and Madison, 1994).

Recycling

The most promising methods for reducing polluting strengths of leachates were, according to Robinson and Maris (1979; 1985), a combination of aerobic biological treatment and recirculation through the landfill. Pohland (1989) stated that evidence was mounting that leachate recycling for *in situ* treatment is the preferred technique when both practicality and economics are considered.

According to Robinson (1980), the treatment of leachate during the recirculation process has various benefits. For example, ammoniacal-N could be converted to nitrate-N in an on-site plant and then recycled to undergo denitrification to nitrogen gas within the landfill and flush out ammoniacal-N. Robinson and Maris (1985) and Knox and Gronow (1993) addressed these possibilities in pilot-scale studies.

Leachate recycling back into the refuse could also be counter-productive. Chapman and Ekama (1992) studied the effects of sewage sludge co-disposal and leachate recycle on the onset of methanogenesis in municipal refuse in pilot-scale lysimeters. They found that leachate recycling during the acid phase resulted in a 10% (m/v) increase in short-chain fatty acid and COD concentrations. It was suggested that leachate produced from the "fresh" part of the landfill should be recycled to an "aged" zone in its methanogenic stage of decomposition so that the short-chain fatty acid concentration could then be reduced via methanogenesis.

Biological Treatment

(i) Aerobic Treatment

The use of aerated lagoons (Maris *et al.*, 1984; Venkataramani *et al.*, 1984; Robinson, 1995), activated sludge (Boyle and Ham, 1974; Knox, 1983; Venkataramani *et al.*, 1984; Knox, 1985), biological filters and rotating biological contactors (RBC) (Ehrig, 1984; Maris *et al.*, 1984; Robinson and Maris, 1985) can be included in the aerobic biological treatment strategy. Internationally, aerobic biological processes have provided the most successful and reliable treatments of landfill leachate (Robinson, 1995).

(ii) Anaerobic Treatment

The advantages of anaerobic digestion include its high treatment efficiency and the production of methane as a potential energy source (Kroeker, Schulte, Sparling and Lapp, 1979; Lin, 1991). Disadvantages such as heat input, longer residence time compared to aerobic treatment, the long start-up period and sensitivity to toxic substances should be taken into consideration when a treatment strategy is planned (Grady and Lim, 1980).

Anaerobic biological treatment processes include the use of pond treatment which is not a complete method of treatment but could be used for storage, balancing and as a possible pretreatment stage. Alternative biological reactors include the up-flow anaerobic sludge blanket (UASB) (Kennedy, Hamoda and Guiot, 1988; Britz, Venter and Tracey, 1990; Britz *et al.*, 1992; Myburg and Britz, 1993), the anaerobic filter (Chian and Dewalle, 1977; Henry, Prasad and Young, 1987) and bench-scale digesters (Boyle and Ham, 1974; Lin, 1991).

Various supports have been used for the immobilization of microorganisms in anaerobic filters. Among those are sand, plastic, activated carbon, stone and metal mesh particles (Black, Webb, Matthews and Atkinson, 1984; Worden and Donaldson, 1987; Shieh and Li, 1989; Puhakka and Jarvinen, 1992). Microorganisms grow either on support particles or inside porous structures in the form of a biofilm. Fluidized bed bioreactors (FBBR) have been used by various investigators for biological wastewater treatment (Cooper and Wheeldon, 1980; Kargi and Park, 1982; Kargi and Eyiisleyen, 1995).

Physico-Chemical Treatment

Evaluation of physico-chemical treatments of sanitary landfill leachate has shown that with "young" leachate the degree of organic removal is lower than can be accomplished with biological processes. In contrast, effective removals resulted with stabilized leachate from "aged" landfill sites (Venkataramani *et al.*, 1984).

Various physico-chemical treatment methods have been evaluated to determine their efficiencies. These include: chemical precipitation and oxidation (Thorton and Blanc, 1973; Ho, Boyle and Ham, 1974; Chian and Dewalle, 1977; Knox, 1983; Sletten, Benjamin, Horng and Ferguson, 1995); activated carbon adsorption (Ho *et al.*, 1974; Liu *et al.*, 1991); and reverse osmosis (Kinman and Nutini, 1991).

1.9 Landfill Gas

1.9.1 Landfill Gas Production and Composition

Typically, landfill gas contains two volumes of methane per volume of carbon dioxide, together with a solid residue that is virtually odourless but is rich in nitrogen, phosphorus and metal ions (Large, 1983). Landfill gas generation is the major route for the decomposition products to leave the landfill and up to 30% by weight of the waste can be lost as gas, a much larger amount that leaves via leachate (Parker *et al.*, 1993).

Landfill gas contains more than 80 different molecules of which hydrogen, carbon dioxide (CO₂) and methane (CH₄) are the key compounds (Kasali, Senior and Watson-Craik, 1990b). Beside H₂S, the chlorinated hydrocarbons and aromatics in landfill gas are relevant with regards to emission from landfills into the atmosphere, as well as corrosion problems during gas utilization. In addition metals at low concentrations have been detected in landfill gas (Stegmann, 1989b).

If rainfall, corresponding to the average for a moderate climate (> 500 mm y⁻¹), is guaranteed to enter the landfill, then acidogenic processes are activated within six months. These processes are characterized by high CO₂ contents in the gas (> 75% (v/v)) which has a typical smell of C₄ - C₅ fatty acids. This is followed by the establishment of the methanogenic phase which coincides with an increase in methane content (60 - 64% (v/v)) and a decrease in the CO₂ content (< 40% (v/v)) (Straka, 1989; Young, 1990). The H₂S concentration also decreases (Straka *et al.*, 1993). The constant evolution of gas facilitates internal circulation of water in the landfill (Baccini, Henseler, Figi and Belevi, 1987).

The actual gas production rates of decomposing refuse are difficult to obtain (Hartz and Ham, 1982). In many cases the total volume of gas produced is calculated from measured or estimated parameters. If the composition of refuse is used to calculate the biogas volume, it would be more realistic to consider only the biodegradable components such as fat, protein and cellulose (carbohydrate) (James, Watson-Craik and Senior, 1996). More than 90% of the methane potential of refuse can be attributed to the cellulose/hemicellulose fraction of the waste (Barlaz, Schaeffer and Ham, 1990). The following equation can be used to calculate the total volume of gas if the refuse carbon content is fully converted to biogas (Ehrig, 1991):

$$G_e = 1.868 * C \quad [1.6]$$

where: G_e is the total gas production
(m³ (STD) tonne⁻¹ refuse); and
 C is the carbon content (kg tonne⁻¹ refuse).

The total period of landfill gas production is also very difficult to predict and is usually calculated as up to 10 years after site closure. It is common to estimate gas production with time from the following equation (Stegmann, 1989a):

$$G_t = G_e (1 - e^{-kt}) \quad [1.7]$$

where: G_t is the accumulative gas production with time (t)

($\text{m}^3 \text{ tonne}^{-1}$ SW);

G_e is the total gas production

($\text{m}^3 \text{ tonne}^{-1}$ MSW, dry solids);

t is the time (years);

k is $2/H$; and

H is the half life (years).

According to studies undertaken (Hartz and Ham, 1983), the maximum rate of methane production is in the order of $6.25 - 37.5 \text{ l kg}^{-1} \text{ y}^{-1}$ or $0.006 - 0.038 \text{ m}^3 \text{ kg}^{-1} \text{ y}^{-1}$ for wet refuse during the period of optimum methane production. Young (1990) reported that the rate of change of barometric pressure is much more important than its absolute value on the bulk volume of gas emissions. In a later study, Young (1992) concluded that the rate of gas venting depends linearly on the rate of change of the atmospheric pressure with the stoichiometric variations depending additionally on the physical characteristics and moisture distribution within the site.

1.9.2 Odour and Emission Control

The unpleasant and distinctive odour of landfill gas can be attributed to the presence of trace concentrations of volatile molecules which constitute $< 1\%$ of the total volume. Of the more than 100 different molecules detected few are odorous (Young and Parker, 1984). Alkyl benzenes and limonene are probably responsible for the background smell of landfill sites. Molecules such as esters and organosulphates which are not as widespread also contribute to the unpleasant odour (Senior and Kasali, 1990).

In general, odours of landfill gas represent environmental and public nuisances rather than a toxic hazard (Young and Heasman, 1985).

A range of site management strategies which may be used to achieve a reduction of odour can be implemented. For example, vertical gas migration may be controlled with low pore-size soils, particularly clays, as cover material (Borgardus, 1984). Biofilters packed with peat have proved effective biological deodorizers (Zhang, Kuniyoshi, Hirai and Shoda, 1991) but gas flaring has been considered to be the most cost-effective method of destroying odorous compounds (Knop, 1984). Despite the content of CO₂, biogas burns readily but requires a high ignition temperature (700 °C) whereas for methane the ignition temperature is 645 °C (Large, 1983). In Germany, the possibility that complete incineration of the gas components in flares was feasible was discussed (Stegmann, 1982). If incomplete incineration takes place, theoretically, the production of dioxins and furans cannot be excluded (Stegmann, 1989b).

The need to control gas emissions from landfill sites is becoming an increasingly important facet of site operation and in many areas it is now, or will soon become, subject to legal regulation. It is difficult to measure the total volume of gas escaping from a site. Therefore, it is more usual to monitor the chemical composition of the gas or to use both as a measurement of the internal state of the landfill and the environmental impacts it has (Young, 1992).

1.9.3 Environmental Effects

The environmental effects of landfill gas can be considered in terms of: 1. The global effects of methane and CO₂ as greenhouse gases; 2. The effects of odours; 3. Local effects of vegetation dieback; and 4. The hazardous effects of flammable gases (Parker *et al.*, 1993; Boeckx, Van Cleemput and Villaralvo, 1997; El-Fadel, Findikakis and Leckie, 1997). The first effect has had much media coverage but researchers have now shown that with a good cover of biologically-active soil much of the methane is oxidized (Jones and Nedwell, 1993).

The top soil of a landfill is a dynamic mixing zone for air and landfill gas. Methane emissions through the cover soil are greatly reduced by the relative abundance of methanotrophic bacteria within the aerated soil (Jones and Nedwell, 1993). The encouragement of methane oxidation in the landfill covering soil is, therefore, important to reduce the emission of methane (Boeckx *et al.*, 1996). The second effect is also reduced by a good soil cover. The third effect severely limits re-vegetation of landfill sites by removing oxygen from the root zones of plants. The fourth effect is, potentially, the most serious (Hartz and Ham, 1982; Parker *et al.*, 1993).

1.9.4 Gas Utilization and Optimization of Gas Production

The methane produced in landfills represents a usable but underutilized form of energy. Projects to recover landfill gas are frequently rejected because the onset of methanogenesis is unpredictable and yields are, typically, 1 to 50% of the volumes predicted from refuse biodegradability data (Barlaz *et al.*, 1989b). Two main types of landfill gas utilization have been established in Germany (Stegmann, 1989c):

1. Production of electricity and heat in internal combustion engines with heat recovery. Landfill gas is very corrosive and water saturated. This has to be borne in mind when the materials for gas pipes, valves and seals are chosen. In addition, trace components in the gas may be converted into strong acids which may cause corrosion (Dernbach, 1985); and
2. Direct heat production for industry or for heating. The efficiency of using landfill gas for heat production would increase dramatically if it were possible to use the gas throughout the year (Stegmann, 1989c).

Due to the importance of landfill gas as an energy source, optimization of the biological processes in a landfill is necessary to shorten the time period of gas production (1.7.1). The following key variables were identified by Pohland (1975) and Barlaz *et al.* (1987) to accomplish this: the use of old, anaerobically-degraded refuse as a diluent and a "seed" of methanogenic bacteria; the addition of anaerobically-digested sewage sludge as a "seed" of anaerobic bacteria; the use of sterile cover soil; and leachate recycling.

Enhancement of landfill gas production was tested in landfill simulators (Kinman, Nutini, Walsh, Vogt, Stamm and Rickabaugh, 1987). Specifically, accelerated moisture infiltration, elevated moisture content, leachate recycle and buffer (calcium carbonate)-, nutrient (ammonium phosphate)- and/or sewage sludge additions were examined. The results indicated that sewage sludge additions, buffer additions and nutrient additions were useful enhancement techniques. Moisture infiltration and elevated moisture content also showed beneficial effects. These results verified previous studies (SCS Engineers, 1984).

1.10 Critical Site Conditions for the Optimization of Refuse Catabolism

1.10.1 Optimum Site Conditions for Methanogens

There are various site conditions which are critical for the optimization of refuse catabolism specific to methanogenic activity:

Temperature. A temperature range of between 29 and 37°C. Kasali and Senior (1989) found that with an increase from ambient temperature (18.7°C) to 30°C a 2.6-fold increase in gas production rate was recorded while a 7.8-fold increase was recorded when the temperature was raised from 18.7 to 40°C;

Absence of Air (Oxygen). Methanogenic bacteria are the most sensitive anaerobes to oxygen and require a redox potential ≤ -200 mV (Levett, 1990);

pH. A pH range of 6.8 - 7.2. Initiation and, subsequent, optimization of methanogenesis in the refuse mass may be promoted by acetic acid: alkalinity ratios < 0.8 (Ehrig, 1983) or by increases in the buffering capacity by the addition of exogenous calcareous materials (Buivid, Wise, Blanchet, Remedios, Jenkins, Fojo and Pacy, 1981). Laboratory studies with sodium bicarbonate supplementation showed that in the presence of 2.5% (m/v) sodium bicarbonate, acidogenesis and methanogenesis were both promoted compared with glass-distilled water controls (Kasali, Senior and Watson-Craik, 1989);

Moisture Content. Water/moisture addition stimulates reaction rates. The main effect of increased moisture content is the facilitated exchange of substrates, nutrients and buffers and the dilution of inhibitors (Christensen and Kjeldsen, 1989). Any promotion is via two separate variables: the water content as such; and its movement through the refuse mass (1.8.1). Studies have shown that with a moisture content increase from 55 to 75% (m/m), a 2.4-fold increase in the total volume of methane produced resulted (Kasali, Senior and Watson-Craik, 1990a). The density of the refuse mass also plays an important role in the fermentation. High density refuse absorbs less water than low density refuse. The mass of water absorbed is inversely proportional to the refuse density (Rees and Grainger, 1982);

Absence of Toxins or Inhibitors. Methanogens are considered to be particularly sensitive to inhibitors (1.7.3). The inhibitory effects of oxygen, hydrogen, sulphate, electron donor concentration, carbon dioxide, salt ions, sulphide, heavy metals and specific organic compounds have been investigated (McCarty and McKinney, 1961; Hanson and Molin, 1981; Zehnder, Ingvorsen and Marti, 1982; Heuvel, 1985; Christensen and Kjeldsen, 1989);

Nutrients. The anaerobic ecosystem must contain electron donors plus essential nutrients such as nitrogen and phosphorus. All the necessary micronutrients, e.g. sulphur, calcium, magnesium, potassium, iron, zinc, nickel and copper, are considered to be present in most landfills. In general, the refuse mass is not nitrogen or phosphorus-limited although, due to ineffective mixing of the waste, nutrient limited environments can develop (Christensen and Kjeldsen, 1989). Attention to nutrients in anaerobic processes has been limited largely to a consideration of the need to supplement nitrogen, phosphorus or buffering capacity (Callander and Barford, 1983). Speece and Parkin (1986) showed that trace metal supplementations stimulate the rate of anaerobic digestion. According to these authors the presence of detectable concentrations of trace metals cannot be equated to adequate bioavailability.

1.11 Site Reclamation and Settlement

Among the practical problems of utilizing landfill sites for development, including recreation facilities, settlement may be the most significant (Morris and Woods, 1990). Settlement occurs, essentially, in three known stages: 1. Initial Compression. This is settlement that occurs directly when an external load is applied to a landfill. It is generally associated with the immediate compaction of void space due to superimposed weight (Wall and Zeiss, 1995); 2. Primary Compression. This is compaction due to the dissipation of pore water and gas from the void spaces (Gordon, Lord and Twine, 1986); and 3. Secondary Compression. This is generally due to biological decay. Settlement due to Secondary Compression can account for a major portion of the total landfill settlement and can take place over many years (Wall, 1992).

Site reclamation is essential for the continued acceptance of landfill technology. Reclamation success may be evaluated in many ways particularly by minimized visual intrusion. Revegetation is often a key element since soil structure and fertility may be improved, pollution may be counteracted and aesthetic problems obviated (Senior *et al.*, 1991).

1.12 Co-Disposal Practice

1.12.1 Nature and Aim of Co-Disposal

The debate continues on the future role of landfilling in integrated waste management systems for treatment and disposal of wastes. Included in this debate are the types of waste to be accepted in future landfill sites, the preferred engineering design to provide protection at sites and to what extent other waste treatment options should receive priority over landfill disposal (Campbell, 1994).

Co-disposal is defined as the incorporation of commercial, industrial and domestic wastes into a single disposal site, usually a landfill. In the UK > 78% (v/v) of hazardous wastewaters and sludges are co-disposed with domestic, industrial and commercial refuse in Class I or Class II landfill sites (Senior *et al.*, 1990).

Table 1.3 compares sanitary landfill sites (1.1) and landfill sites where co-disposal is practised.

Table 1.3. Comparison of sanitary landfills and co-disposal sites (Cope *et al.*, 1983)

Sanitary landfill	Co-disposal
Confines waste to smallest practical area	Spreads waste over maximum area to encourage evaporation
Impermeable cover and vent pipes control emissions of inflammable gases	Absence of control permits release of inflammable gases over wide surface area
Aerobic decomposition at first followed by anaerobic processes	Anaerobic decomposition rapidly sets in creating higher quantities of methane and H ₂ S
Minimises the quantity of leachate produced	Maximises the quantity of leachate generated and relies on evaporation and transpiration to control it
Operation geared to maintaining acceptable aesthetic features	Operation is less concerned with aesthetic features

Co-disposal is considered to be an appropriate disposal option in the UK. At present it is the cheapest method of disposal and leachate analysis for several co-disposal sites has demonstrated no significant reduction in leachate quality resulting from this activity when it is correctly operated (Watson-Craik and Sinclair, 1995). Co-disposal has been practised at Pitsea in Essex (UK) since the 1950s and at Himley Wood (UK) since 1982. Leachate quality is similar to that at sites accepting domestic refuse only and there is no evidence of elevated concentrations of potentially inhibitory compounds or trace molecules such as heavy metals or phenols (Watson-Craik, Sinclair and Senior, 1992b).

The motivating factor is undoubtedly cost. Return on investments invariably favours product research and development to the exclusion of pollution control. Therefore, more costly means of disposal will only be employed when cheaper means have proved ineffective or their use is prohibited (Watson-Craik and Senior, 1991).

The enthusiasm in the UK is, however, not shared by some industrialized nations particularly the USA, Canada and Germany where the practice is often discouraged or even outlawed. The suspicious reaction to the technology is often based on previous indiscriminate activities which resulted in severe environmental impacts (Senior *et al.*, 1991).

The landfill provides a solid matrix which is extremely heterogeneous both physically and chemically (Knox and Gronow, 1989; Sulisti, Watson-Craik and Senior, 1996).

Thus, it provides numerous pathways for transformation and transport of co-disposed pollutants. Within the refuse mass a whole range of physico-chemical and microbial processes effect attenuation of the co-disposed molecules (Senior *et al.*, 1991). These attenuation phenomena may be summarized as follows:

1. Physical and chemical-physical phenomena: adsorption, filtration and dispersion;
2. Chemical phenomena: acid-base interaction, oxidation, precipitation and ion-exchange; and
3. Biological phenomena: aerobic and anaerobic microbial degradation

(Cossu and Serra, 1989).

One primary aim of co-disposal research is to accelerate the onset of methanogenesis via the following:

1. The liquid sludge increases the moisture content of the refuse.
This enhances biodegradation (1.8.1)(Ehrig, 1980);
2. Anaerobic sludge provides an inoculum of methanogenic bacteria (Kinman *et al.*, 1987; Craft and Blakey, 1988; Novella, Lord, Stow, Fawcett and Greenhalgh, 1994); and
3. Phosphoric and nitrogenous nutrients in the sludge supplement deficiencies in the refuse (Chapman and Ekama, 1992).

1.12.2 Loading Rates for Co-Disposal Landfill Sites

A practical definition of a loading rate for the landfilling of an industrial waste is the maximum quantity (concentration) that can be disposed with 1 kg of domestic refuse without adversely affecting the quantity (concentration) of the leachate (Campbell, 1994). The environmentally acceptable operation of co-disposal sites is clearly dependent on factors such as the identity and loading rates of the wastes, emplacement methods, microbial degradation and leachate treatment strategies (Watson-Craik and Senior, 1991). Site loading rates utilized at a co-disposal landfill must be specific and must satisfy three criteria: 1. No impairment of leachate quality; 2. No inhibition of microbial catabolic processes; and 3. Immobilization or transformation/mineralization of the co-disposed molecule(s) (Senior *et al.*, 1991). Co-disposal cannot be accepted indiscriminately for all types of toxic residues and the environmental situation of the area where the co-disposal landfill is to be situated should always be carefully considered (Cossu and Serra, 1989).

The loading rate must be carefully determined in relation to the site water balance when the co-disposed waste is either a sludge or liquid. The refuse infiltration capacity must not be exceeded otherwise leachate will be released before the refuse field capacity has been reached (Watson-Craik and Senior, 1989a).

In the presence of low organic loadings, microbial diversity may be reduced by the selective enrichment of catabolic species. It is important, however, that the concentration does not fall below about 1000 mg l^{-1} since it is often accepted as the minimum required to sustain microbial growth (Senior *et al.*, 1991). For all co-disposed molecules, it is important that the biological filter (refuse mass) is not subjected to inhibitory/toxic concentrations (shock loads) of applied molecules). Organic loading optimization must, therefore, be made in conjunction with hydraulic loading rates (Senior *et al.*, 1991).

1.12.3 Environmental Impacts of Sludge Co-Disposal

Volatile Fatty Acids (VFA)

Leachate VFA concentrations vary considerably depending on factors such as the site age, volume of water ingression and refuse/sludge composition. Volatile fatty acid concentrations may actually decrease as a result of sewage sludge co-disposal (Farrel, Dobson, Stamm and Walsh, 1987; Craft and Blakey, 1988) with a noted reduction in COD.

Heavy Metals

The behaviours of heavy metals in landfilled refuse have been examined (Newton, 1977). With a digested industrial waste sludge and a high sludge hydraulic loading rate, an inhibition of waste stabilization processes occurred due to the presence of toxic concentrations of heavy metals. It is unlikely, however, that the presence of domestic sludges would inhibit the stabilization processes as the heavy metal concentrations, even at high sludge hydraulic loading rates, should not adversely effect the processes (Pohland and Gould, 1986).

Nitrogenous Compounds

The presence of nitrates in landfill leachate would not be expected normally. The one exception is leachate percolating from fairly young landfills ([4 years). The presence of ammonium can, however, be expected. Ammonium is usually present in high concentrations in landfill leachate and, if left untreated, could contaminate groundwater resources (Price, 1987).

Activated sewage sludge emplacement in landfill sites adds nitrogenous compounds in several forms, the most common of which are organic nitrogen, $\text{NH}_4^+/\text{NH}_3$ and NO_3^- (Sinclair, 1994).

Pathogens

Sewage sludge contains a variety of pathogenic organisms such as viruses, bacteria and parasites which vary in numbers and diversity. Destruction of pathogenic organisms in sludge/refuse mixtures emplaced in a landfill occurs due to heat, competition and depletion of nutrients (Pereira-Neto, Stentiford and Mara, 1986). It can be expected that the survival of pathogens in landfill leachate should not be prolonged (Ware, 1980).

Gases

See section 1.9.

Realistic guidelines and strategies for co-disposal implementation will only result from an understanding of the fundamental microbiology and biochemistry of co-disposal, derived from environmentally relevant model systems (Watson-Craik and Sinclair, 1995).

1.12.4 Co-Disposing Sludges from Wastewater Treatment Plants

The positive influence of co-disposing sludges (raw, dewatered, digested) from industrial wastewater and sewage treatment plants with domestic refuse has been experimented widely (Farrel *et al.*, 1987; Kinman *et al.*, 1987; Craft and Blakey, 1988; Daneel, 1996, Percival, 1996).

The disposal of wastewater sludges in sanitary landfills is by no means a new concept. In the UK, where about 1.2 million tonnes (dry weight) of sludge are produced annually, approximately 24% is disposed of in landfills (Watson-Craik *et al.*, 1992a). In the USA, where landfilling of sewage sludges is viewed as, primarily, a disposal method, about 25% of the generated sludge is landfilled (USEPA, 1984).

1.12.5 Sewage Sludge

Classification of Sewage Sludge

Sewage sludge is classified as four types A, B, C and D in a decreasing order of its potential to cause odour nuisances and fly-breeding as well as to transmit pathogenic organisms to man and animals (Van der Merwe and Vivier, 1994).

Sewage Sludge Disposal

The traditional methods of sewage sludge disposal have been via three routes: agricultural utilization; ocean dumping; and landfilling (Matthews, 1985). Increases in sludge quantities, combined with few sludge disposal options, means that economical and acceptable disposal options are limited.

In South Africa, historically, sewage sludge has been seen as a nuisance causing substance and a potential health hazard. The control of sludge has, therefore, rested largely with the Department of National Health and Population Development (DNH&PD) which developed guidelines for using various types of sludges for agricultural purposes. The emphasis of these is on human health and protection of soil and little attention is given to protection of water quality (Crawford, Bredenhann and Van der Westhuizen, 1994)

Until recently, the Department of Water Affairs and Forestry's only practical involvement in controlling sewage sludge was the implementation of Section 21(4) of the Water Act, 1956. This section controls the quality of effluent returned to a particular water course and some attention is given to sludge. Sludge must not cause nuisance and must be disposed of in accordance with DNH&PD guidelines.

The DNH&PD guidelines list the safe use of various types of sewage sludge but do not describe how sludge must be disposed of (DNH&PD, 1991).

There is no existing legislation regarding the disposal of sewage sludge in landfill sites in the UK (Brunner and Lichtensteiger, 1989). However, landfills which accept sludge waste must be licenced under the Control of Pollution Act, 1974.

In a survey undertaken by Smith and Vasiloudis (1991) regarding the disposal methods of sludge in South Africa, it appeared that 47% (m/m) of sludge is disposed of on land sacrificed for disposal purposes, 3% (m/m) is disposed of in refuse sites, 20% (m/m) is stockpiled or lagooned and 28% (m/m) is used beneficially. About three-quarters of the beneficially-used sludge is used as soil conditioner and a quarter for brick making (Slim and Wakefield, 1991).

In Japan, the equivalent position is as follows: the majority of all sludges produced (82% (m/m)) is disposed of in landfill sites. The remainder is divided between agriculture and ocean disposal while new research focuses on thermochemical liquefaction and incorporation into construction materials (Garvey, Guarino and Davis, 1993).

According to a survey, the situation of sewage sludge utilization and disposal in the Member States of the European Community is as follows:

1. 37% is recycled to land (agriculture, land reclamation, horticulture, forestry and parkland);
2. 44% is disposed of in landfill sites;
3. 9% is incinerated;
4. 7% is disposed of to the sea; and
5. 3% is disposed of to a number of minor outlets including sacrificial land and sludge farms

(Newman and Bowden, 1988).

Sewage sludge is a product whose quality is not strictly controllable and which entails processing, transport and disposal costs for up to half the cost of operating the sewage works. The disposal of sewage sludge always requires careful management but the ease or difficulty with which disposal is achieved and the costs involved depend on the circumstances. Local and national geographical, agronomic, economic and political factors also have some influence (Bruce and Davis, 1989).

Co-disposal of sludge, produced at sewage treatment plants, with municipal solid waste possibly holds promise for dealing with two problems of waste management: 1. An option for sewage sludge disposal; and 2. The presence of sludge may accelerate the onset of methanogenesis in co-disposal sites as opposed to prolonged periods in sanitary landfilling (Chapman and Ekama, 1992).

The landfill option in Europe usually involves a co-disposal operation with refuse, rather than a monofill with sludge alone as is sometimes practised in the USA. The addition of sludge to refuse in a ratio of about 1:10 (m/m) appears to accelerate chemical and physical stability of the landfill (Smith and Vasiloudis, 1991). The goal is now for more engineering of the sites for full containment with leachate collection and treatment (Garvey *et al.*, 1993).

Various sludge types could be used in co-disposal practices. Primary sludge (of which the chief component is human faeces and, in its raw state, is putrescible and rapidly develops offensive odours), anaerobically digested sludge (considered to be most suitable for co-disposal because it is stabilized), waste activated sludge (in the activated sludge process, bacteria and other microorganisms metabolise influent organic matter and produce additional cell mass) and chemical sludge (which can be obtained from wastewater treatment plants where more and more operations combine chemical and biological treatment) (Novella *et al.*, 1996).

1.13 Phenol

1.13.1 Phenol and Phenolics

Phenols constitute a major group of organic compounds and are of particular interest because the molecule contains an aromatic ring and may, therefore, indicate the potential of a wide range of other organic compounds for co-disposal. Aromatic compounds exist in a variety of biogenic and abiogenic products which are released into the environment (Knox, 1989). Phenolics are among the most utilized organic compounds in the world.

In 1983 the annual production of phenol was 1.2×10^9 kg, placing it among the 50 chemicals produced in the highest quantities in the USA (Young and Rivera, 1985). Phenol and phenolic compounds are toxic pollutants and inhibitors of biodegradation (Fedorak and Hrudey, 1984a; Holladay, Hancher, Scott and Chilcote, 1986) and have been used as model molecules to investigate the effects of similar substrates on microbial metabolism and growth (Rozich, Gaudy Jr. and D'Adamo, 1983; 1985). These compounds are widely used in synthetic chemical processes and are also found as products of pesticide decomposition (Munnecke, 1981). They are produced by chemical, pharmaceutical and gas industries. Phenol is a common constituent of effluents from polymeric resin production plants, oil refineries and paper pulp processing and coal liquefaction industries (Hill and Robinson, 1975). The entrance of phenolic compounds into the environment may be deliberate, as in pest control, or accidental, as in seepage from toxic waste disposal sites.

Phenols are also released into the environment from natural sources including the urine of some animals and the decay of vegetation (Rosfjord, Trattner and Cheremisinoff, 1976). They are a health hazard since they are toxic at high concentrations and have genotoxic properties at low concentrations (Dean, 1978). Phenol bestows an unpleasant taste to drinking water (Lallai and Mura, 1989). At 0.002 mg l^{-1} phenol in potable water is apparent as a medicinal taste and odour particularly in the presence of chlorine (Rosfjord *et al.*, 1976). The permissible limit of phenol in discharged effluent is 1 mg l^{-1} since higher concentrations affect aquatic life and result in ecological imbalance (Satsangee and Ghosh, 1990).

1.13.2 Phenol Catabolism

The degradation of aromatic compounds in nature by aerobic processes has been known for a long time (Wagner, 1914; Stanier, 1950) and high removal rates in aerobic bioreactors have been reported (Bettmann and Rehm, 1985; Ehrhardt and Rehm, 1985). Metabolism of the aromatic nucleus under aerobic conditions relies on the mono- and di - oxygenase enzymes which are responsible for the incorporation of molecular oxygen into the compounds (Young and Rivera, 1985).

Aromatic compounds can also be degraded under anaerobic conditions: by photometabolism (Dutton and Evans, 1967); by nitrate-dependent metabolism (Taylor and Heeb, 1972; Williams and Evans, 1973; 1975); during sulphate reduction (Widdel, 1980); and during methanogenesis (Fina, Bridges, Coblenz and Roberts, 1978; Szewzyk, Szewzyk and Schink, 1985; Tschech and Schink, 1985).

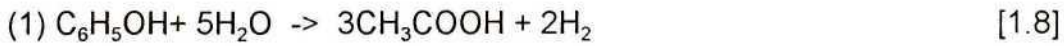
A major reductive pathway under methanogenic conditions was reported by various authors (Balba, Clarke and Evans, 1979; Barik, Brulla and Bryant, 1985; Grbic-Galic and Vogel, 1987). Phenol is first reduced to cyclohexanol and to cyclohexanone and then cleaved by hydrolysis to yield aliphatic acids (Bisaillon, Lépine and Règean, 1991).

Thermodynamically, monosubstituted aromatic compounds such as phenol can only be metabolised at very low hydrogen partial pressure (Thauer, Jungermann and Decker, 1977). Thus, phenol can only be degraded by syntrophic acetogenic microorganisms. A second pathway, under methanogenic conditions, was reported by Neufeld, Mack and Strakey (1980). Here, the molecule was first carboxylated to benzoate before reduction and cleavage of the aromatic ring.

Evans (1977) summarized probable pathways for the anaerobic biodegradation of aromatic compounds. He established that the conversion of aromatic molecules to CH_4 and CO_2 is accomplished, first, by the hydrogenation of the benzene nucleus with formation of some alicyclic compounds as intermediate products. The alicyclic rings are then cleaved to form aliphatic rings and, subsequently, volatile organic acids. Finally, the acids are converted to suitable substrates (acetate, hydrogen, formate) for the methanogens to complete the process (Wang *et al.*, 1989).

Sheridan, Jones, Wolfe and Suidan (1985) and Dwyer, Krumme, Boyde and Tiedje (1986) described an association which consisted of three types of bacteria for the conversion of phenol to CH_4 and CO_2 .

The following steps in the overall conversion of phenol to CH₄ were proposed:



It was concluded that acetate accounted for approximately 86% of the methane produced during phenol fermentation (Sheridan *et al.*, 1985).

A study by Knoll and Winter (1987) investigated the anaerobic degradation of phenol in sewage sludge (Figure 1.5). Acetate first accumulated but was subsequently cleaved to methane and, presumably, CO₂.

Evidence for the metabolism of phenol via benzoate was presented by Sharak, Genter, Townsend and Chapman (1989) and Zhang and Whiegel (1990). The formation of benzoate from phenol and H₂/CO₂ or CO is energetically favourable but it remains to be elucidated whether the initial carboxylation proceeds with CO₂ and H₂ or carbon monoxide.

Bèchard, Bisailon, Beaudet and Sylvestre (1990) concluded that the methanogenic degradation of phenol involved co-metabolism since carboxylation was accomplished by specialized microorganisms which co-existed with the acetogenic and methanogenic bacteria.

The study revealed that sludge from aerobic phenol-bearing wastewater treatment plants may be used directly as the inoculum for anaerobic processes thus eliminating the long acclimation period required when the supernatant of digested sludge of an anaerobic wastewater treatment plant serves as the inoculum. Young and Rivera (1985) used a batch anaerobic bioassay technique to study the methanogenic degradation of four phenolic compounds: phenol, *p*-cresol, hydroxyquinone and phloroglucinol. Digester sludge was used as the inoculum and acclimation to each phenol was examined when the concentration was increased from 200-300 mg l⁻¹ to 400-800 mg l⁻¹. Acclimation was the slowest for *p*-cresol and took 6 months although mineralization was observed after acclimation. The effects of acclimation can be dramatic. Even when xenobiotic compounds are added at concentrations < 100 ppb (100 ng l⁻¹) the degradation rates can be 1000 - fold higher in populations that have been pre-exposed to the compound (Spain and Van Veld, 1983).

A study was undertaken to investigate the role and bioavailability of nutrients in the methanogenic degradation of phenol and *p*-cresol (Fedorak and Hrudey, 1984b). Supplementations with various combinations of nutrients (macro- and trace elements, as well as B vitamins) to duplicate batch cultures which contained a synthetic phenol solution were examined. Domestic anaerobic sewage sludge served as the source of the methanogens. The deletion of any essential cation (Na⁺, NH₄⁺, Ca²⁺, Mg²⁺) stopped the methanogenic fermentation. Similarly, omission of phosphate inhibited methanogenesis.

Omissions of the trace mineral solution and vitamin B solution did not effect a decrease in methane production although a previous study had shown that trace minerals were necessary for optimum methane production rates (Murray and Van den Berg, 1981).

1.13.4 Phenol Co-Disposal

Various studies have been made to determine the treatability of a phenolic wastewater by co-disposal with refuse (Tibbles and Baecker, 1989; Daneel, 1996; Percival, 1996) (1.12). In landfill sites, several factors might be expected to reduce the achievable rates of phenol removal since landfills appear to be less efficient than conventional bioreactors based on carbon turnover. They may also contain a variety of toxicants and there may be nutrient limitations.

In contrast, other factors might lead to an increase in removal rates. For example, the variety and physical separation of micro- environments in the refuse might provide adsorption surfaces (Knox, 1989).

It was reported that the adsorption of phenols from solution by refuse would be insufficient to minimize leachate concentrations from phenol-bearing lime sludges (Knox, Newton and Stiff, 1977). However, it was assumed that the adsorption which occurred could have delayed the passage of phenols long enough to allow a phenol-catabolizing population to establish (Blakey and Knox, 1978).

The direct interaction of three phenols (phenol, 200-2000 mg l^{-1} ; *p*-cresol and 2,6-xyleneol, 100-1000 mg l^{-1}) in aqueous solution with domestic refuse was examined by Knox and Newton (1976) and Knox *et al.* (1977) in equilibration studies.

Knox and Newton (1976) used "fresh" refuse (8-weeks old) and Knox *et al.* (1977) used well-decomposed refuse (4-years old). The results proved that all three phenols were adsorbed to a significant extent. The concentrations then fell further over a 60-day period and this was attributed to biodegradation. The extent of adsorption varied with the age of the refuse. "Fresh" refuse had a higher adsorptive capacity than aged refuse but the pattern between the individual phenols varied.

In an investigation of the fate of phenol (150 - 1 000 mg l^{-1}) in simulated sites it was found that removal by abiotic processes accumulated phenol on the soil particles or in the interstitial fluids of the refuse while that removed by biotic processes was mineralized (Tibbles and Baecker, 1989). These findings supported the contention of Alexander (1981) that abiotic processes rarely effect significant changes in chemical structure and that biotransformations are more important in the removal of toxic xenobiotics.

Godsy, Goerlitz and Grbiè-Baliè (1992) studied the methanogenic degradation of phenolic compounds in batch microcosms. They concluded that the presence of solid surfaces is a major factor affecting microbial growth and catabolism. Surfaces may affect the bioavailability of organic chemicals, change the concentrations of various organic and inorganic nutrients or immobilize microbial enzymes or microorganisms.

Two perfusion strategies were used to examine the effects of a model phenolic wastewater on refuse catabolism and, in particular, methanogenesis (Watson-Craik and Senior, 1989b). Leachate recycle was found to promote the establishment of a phenol-catabolizing microbial population in refuse. With a dilution rate of 0.03 h^{-1} , 100% removal of phenol (188 mg l^{-1}) was achieved with both "fresh" (1-month old) and "active" (4-months old) refuse. With a second perfusion strategy (single elution), and a comparable dilution rate, the removal efficiencies decreased to 41.5% and 47.5% with the "fresh" and "active" refuse, respectively.

A further study by Watson-Craik and Senior (1990) investigated the impacts of phenol organic loads on refuse catabolism in a multi-stage model. Various phenol concentrations ($188, 376, 470, 564$ and 752 mg l^{-1}) were investigated. With loadings of $188, 376$ and 470 mg l^{-1} complete removals of phenol were observed. A lower dilution rate was, however, required for the same removal with 564 mg l^{-1} while 752 mg l^{-1} phenol proved inhibitory.

It is, however, doubtful that degradation rates recorded with laboratory-scale microcosms could be achieved in a landfill. The irrigation rates, for example, would be lower and the larger particle sizes in crude refuse may lead to reduced efficiency. Under achievable optimum conditions, however, landfill sites might be expected to perform favourably (Knox, 1989).

1.14 Heavy Metals

Species of a single metal are cations in solution and whose oxides can form hydroxides with water. Heavy metals are metals with a specific gravity > 5 (Gadd, 1988). The term 'heavy metals' may also be included in an enormous number of individual chemical species whose chemical and environmental behaviours vary widely (Knox, 1989). Many heavy metals are essential for microbial growth and metabolism in low concentrations. Examples of these include copper, zinc and manganese. In contrast, other heavy metals such as gold, silver, lead and cadmium have no known biological functions (Gadd, 1988). Species of a single metal is cationic but can, however, form complexes, of high or low toxicity (depending on the specific metal and concentration), and of high or low solubility (Young, Baldwin and Wilson, 1984; Gadd, 1988).

Thus, the environmental impacts and fates of a particular metal are very dependent on the properties of the particular chemical species (Young *et al.*, 1984).

Metal pollution of water bodies is particularly difficult to control and is potentially more hazardous than organic pollution (Anon, 1990) as metals are non-biodegradable and once they enter the environment their toxicity is controlled by biological and environmental factors (Sterritt and Lester, 1980; Sahoo, Kar and Das, 1992).

Selective extraction of heavy metals from industrial effluents will diminish disposal problems (for example, by co-disposal with refuse), decrease environmental pollution and facilitate the recycling of valuable metals (Gadd, 1988). This needs to be done at source before natural aquatic systems become polluted (Sahoo *et al.*, 1992).

1.14.1 Environmental Factors Affecting Metal Toxicity

Metal toxicity is dependent on the physico-chemical characteristics of the environment (Babich and Stotzky, 1979) as these determine chemical speciation and, therefore, bioavailability (and toxicity) to the indigenous microbiota (Babich and Stotzky, 1979; Hughes and Poole, 1991).

The availability of heavy metals is restricted by their natural abundance and solubility in water (Wood and Wang, 1983). Solubility is influenced by pH, temperature, redox potential, the presence of competing ions and the presence of surface-active molecules, such as particulates and macromolecules, including proteins, humic acids, clays and other organics (Babich and Stotzky, 1979; Wood and Wang, 1983). Kuyucak and Volesky (1985) found that of all the environmental factors, pH has the most significant effect on metal toxicity.

pH

pH affects the adsorption of metal cations to microbial surfaces, the chemical form of a metal species and the extent of complexation of metals with organic and inorganic constituents (Kuyucak and Volesky, 1985; Zhou and Kiff, 1991).

Redox Potential

Redox potential is a measure of the availability of electrons (Babich and Stotzky, 1980). Reducing environments have a negative E_h while oxidizing environments have a positive E_h (Collins and Stotzky, 1989).

Heavy metals deposited in an environment with a negative E_h may combine with sulphide ions to form insoluble sulphide salts which are then unavailable to the environment (Collins and Stotzky, 1989). Redox potential also effects the valence state of a metal. For example, chromium can exist as Cr^{3+} or as the more toxic Cr^{6+} depending on the E_h of the environment (Babich and Stotzky, 1980).

Ion Interactions

The activities of heavy metals can be markedly affected by the presence of other ions either in cation exchange (non-specific adsorption) or precipitation (Newton, 1977; Pohland and Gould, 1980; Babich and Stotzky, 1985; Alloway, 1990; Meyer, 1995).

Cations can reduce metal toxicity, possibly by competing for uptake systems (Collins and Stotzky, 1989), while antagonistic interactions may result from competition between metals for common binding sites on microbial cells and inorganic or organic surfaces (Babich and Stotzky, 1985; Alloway, 1990).

Cation binding depends on valency, the degree of hydration and the ionic radius (Alloway, 1990). The higher the valency of an ion, the greater is its replacing power. Thus Cr^{3+} , for example, has a higher binding capacity for refuse surfaces than Ni^{2+} . The greater the degree of hydration of binding sites, the lower the replacing power of hydrogen ions (Kelly, 1950; Alloway, 1995).

The interactions between cations and soil constituents vary and include reversible cation exchange where different cations compete for a fixed amount of exchange sites. The exchanger (adsorbent) can exhibit low to moderate preference for one cation species or can be highly selective and effect partial reversible adsorption of certain cation species (Bruggenwert and Kamphorst, 1979).

Anions reduce metal toxicity by precipitation. For example, hydroxyl, phosphate, thiosulphate, chloride, carbonate, bicarbonate and sulphide ions form precipitates with metal ions depending on their concentrations and the pH of the environment (Gadd and Griffiths, 1978; Babich and Stotzky, 1983). Mosey and Hughes (1975) and Pohland *et al.* (1982) concluded that sulphide precipitation may be the ultimate control of many heavy metals. With sulphate reduction, insoluble sulphide salts are formed which are sequestered from the environment (Lawrence and McCarty, 1965). Chloride complexes are found in all natural soil and water environments and are the most mobile and persistent of the complexing agents with regard to heavy metals (Hahne and Kroontje, 1973).

Organic Constituents

Organic molecules can effect a decrease in the toxicity of heavy metals. Organic matter reacts with metal ions by either covalent or coordination bonding which results in the formation of compounds which are less toxic than the metal ions themselves (Babich and Stotzky, 1980; Bagy, Elsharou and Elshanaw, 1991).

The formation of chelate complexes between metal ions and organic molecules such as proteins, amino acids and low to high molecular weight acids, prevents metal precipitation (Fletcher and Beckett, 1987; Alloway, 1995). Humic acids which are a complex assemblage of aliphatic and aromatic constituents (Dissanayake, 1983) are especially important in aquatic environments (Gadd and Griffiths, 1978). Chen and Stevenson (1986) reported that humic compounds with suitable reactive groups such as hydroxyl, phenoxyl and carboxyl form complexes with metallic ions.

Temperature

Temperature can affect the toxicity of heavy metals to microorganisms by altering the physiological state of the cells rather than affecting the chemical speciation or availability of the metals (Collins and Stotzky, 1989). Generally, at temperatures optimum for growth, the toxicity of heavy metals increases (Collins and Stotzky, 1989).

1.14.2 Heavy Metals and Co-Disposal

The fates of heavy metals are important aspects of co-disposal (Gregson, Roberts and Roberts, 1988). Heavy metals are used in a variety of industrial processes and, thus, are present in many industrial and household products. As a consequence, they are present in many industrial wastes, liquid, solid and sludge, and are components of household refuse (Knox, 1989). If a co-disposal site is operated as a bioreactor, there is the possibility that immobilized metals would gradually increase in concentration within refuse mass (Blakey, 1988).

Researchers (Berrow and Burrige, 1979; Stevens and Jenkins, 1982; Campbell, 1983; Young *et al.*, 1984; MacNicol and Beckett, 1989) have reported different heavy metal concentrations present in domestic refuse and sewage sludge (Table 1.4).

Table 1.4. Heavy metal concentrations (mg kg⁻¹ dry weight) in refuse and sewage sludge

	Researcher	Zn	Cu	Ni	Cr	Pb	Cd
Refuse	Campbell (1983)	542	244	68	71	152	54
		210	-	10	85	120	3.0
	Young <i>et al.</i> (1984)	1 050	95	79	155	106	1.7
		520	105	135	58	116	1.1
	Stevens and Jenkins (1982)	4 500	1 025	400	175	2 200	10
		740	6 750	238	39	31	6
Sewage Sludge	Berrow and Burrige, 1979	1 130	463	28	81	322	7
	MacNicol and Beckett, 1989	4 700	760	76	-	-	27
		1 300	680	65	-	-	5.5

The distribution and chemical form of bound metals and the nature of potential binding sites is important in both conventional digesters and landfills and may have critical influences on their fates when introduced into landfills (Mosey and Hughes, 1975). The solid matrix in landfills is very different to, and much more heterogeneous than, sewage sludge digesters. If direct binding is important then refuse could behave in a significantly different way than sewage sludge (Mosey, 1976). For indirect interactions it would be expected that the same binding mechanisms would occur in both bioreactor types.

The ability of sludges to bind and retain relatively high concentrations of heavy metals has been reported (Berrow and Burrige, 1979; MacNicol and Beckett, 1989). In contrast, Myers, Francingues, Thompson and Malone (1980) and Jones and Malone (1982) found that electroplating sludge promoted metal leaching by establishing elevated pH values.

1.15 The Principal Objectives of this Study

The principal objectives of this study were:

1. To examine nutrient limitation in activated sewage sludge and activated sewage sludge plus phenol co-disposals with refuse with specific reference to the effects of nutrient supplementation on the solid-state fermentation and the resultant leachate quality; and
2. To investigate the retention / mobility of four heavy metals (Cr^{3+} , Cu^{2+} , Ni^{2+} and Zn^{2+}) by co-disposed sewage sludge with "young" synthetic refuse to determine if nitrate reduction inhibited the onset of sulphate reduction and, hence, heavy metal precipitations as insoluble sulphides which minimize heavy metal mobilization as free cations in leachate and thus danger to groundwater.

CHAPTER 2

Materials and Methods

2.1 Refuse

2.1.1 Landfill Refuse

Refuse (age 6 - 8 weeks) was collected from the New England Road Landfill Site, Pietermaritzburg and hand sorted to remove non-degradable components such as plastic, metal and glass. The refuse was stored at 4°C. Prior to use, the refuse was homogenized in a Haecksel Max 1500 (Steinmax and Company, Model D-8800 Ansbach) garden blender.

The moisture content of the refuse was determined by taking two samples (100g each) and drying at 60°C for 72 h. The samples were weighed before and after drying and the moisture content was determined by difference.

2.1.2 Synthetic Refuse

A synthetic refuse was made by combining equal volumes of shredded paper obtained from a paper recycling plant and vegetable plus garden wastes. The moisture content of the synthetic refuse was determined as described above.

2.2 Sewage Sludge

Activated sewage sludge was collected from the return channel of the Darvill Sewage Works, Pietermaritzburg. The sludge was stored overnight at 4°C to allow settlement of solids. Thereafter, the sludge was centrifuged in a Chrisa Laboratory Centrifuge (Universal Junior III) at 650 r.p.m. x g for 8 minutes and the supernatant discarded.

To determine the dry solids content, two samples of sludge (100g each) were dried at 70°C for 72 h and weighed as before.

2.3 Analyses

2.3.1 Ions

Leachate ammonium and the anions sulphate, nitrate, nitrite and phosphate were quantified with a Spectroquant analysis system (Merck Laboratory Supplies, Germany). Leachate samples were collected with hypodermic needles connected to plastic syringes (20 ml). Different reagents for each of the anions assayed were added to the leachate samples in glass vials and quantization was as per the Spectroquant analysis system.

2.3.2 Chemical Oxygen Demand (COD)

The method used to determine the COD values was the same as the one described by Hoffman (1986).

Reagents

Potassium dichromate ($K_2Cr_2O_7$) solution. Potassium dichromate (12.59 g) was dissolved in glass-distilled water and diluted to 1 l.

Ferrous ammonium sulphate (FAS) solution. Ferrous ammonium sulphate (40 g) was dissolved in 400 ml distilled water in a 1 l volumetric flask. Concentrated sulphuric acid (98 % v/v) (20ml) was added and the resulting solution was cooled and diluted to 1 l with distilled water.

Sulphuric acid - silver sulphate reagent. Silver sulphate (25 g) was slowly dissolved in 2.5 l of concentrated sulphuric acid (98 % v/v).

Method

Mercuric sulphate (0.4 g) was weighed into each digester vessel. The samples (20 ml or a suitable aliquot diluted to 20 ml) plus 10 ml of potassium dichromate reagent were pipetted into the vessels followed by 30 ml of sulphuric acid-silver sulphate reagent. A few boiling stones were added to each and the contents were shaken. The vessels were heated in the digester (Büchi 425 model) for 2 h at 150 °C after which they were allowed to cool to room temperature. The condensers of each vessel were washed with 40 ml/glass-distilled water before disconnection. The contents of each vessel were decanted into 250 ml flasks. Three drops of ferroin indicator were added before titration with FAS solution. For each series of samples, one blank, containing glass-distilled water instead of the sample, was used.

Standardization of FAS Titrant

Potassium dichromate solution (10 ml) was pipetted into a 250 ml flask. Glass-distilled water (50 ml) and 30 ml of concentrated sulphuric acid were added. The solution was cooled and was then titrated against standard FAS solution in the presence of three drops of ferroin indicator.

The normality of the FAS solution was determined as follows:

$$2.5/\text{ml FAS} = \text{molarity of the FAS solution (N)} \quad [2.1]$$

The COD was then calculated from the following equation:

$$\text{COD (mg l}^{-1}\text{)} = \frac{(a-b) \times N \times 8\,000}{\text{m/ undiluted sample}} \quad [2.2]$$

where: a is the titration of the blank (ml); b is the titration of the sample (ml); and N is the molarity of the FAS solution.

2.3.3 Phenol

Phenol concentrations were quantified by gas chromatography. A glass column (length 2m, i.d. 4mm) packed with 5% OV101 on a Chromosorb WHP support (mesh 80-100) was used. Samples (1 μ l) were injected into the column held in a Varian 3600 gas chromatograph equipped with a flame ionization detector. The injector and detector temperatures were maintained at 200 °C and 250 °C, respectively. The column temperature was maintained at 70°C for 0.5 minutes then increased to 150°C at a rate of 50 °C min⁻¹. Phenol standards of 100, 200, 500 and 1 000 mg l⁻¹ were used to calibrate the gas chromatograph and the sample phenol concentrations were determined by comparison of peak areas.

Prior to analysis, the samples were centrifuged in an Eppendorf centrifuge 5410 at 11 000 r.p.m. x g for 15 minutes.

2.3.4 Methane

Gas samples (100 μ l) were injected into a Varian 3600 gas chromatograph equipped with a flame ionization detector. A glass column (length 1.45m, i.d. 3 mm) packed with Propak T (80/100 mesh) was used. The injector, detector and column temperatures were maintained at 110 °C, 200 °C and 35 °C, respectively. Methane standards (10, 25, 50 and 100 % v/v) were prepared from pure methane gas (Fedgas). The concentrations of the samples were calculated by comparison of peak areas with the standards.

2.3.5. Volatile Fatty Acids (VFA)

A glass column (length 2m, internal diameter 4mm) packed with 10% FFAP + 1% phosphoric acid on WAW (mesh 80-100) was used. Acidified samples (1 μ l) were injected into the column held in a Varian 3600 gas chromatograph equipped with a flame ionization detector. The injector and detector temperatures were 200 °C and 220 °C, respectively. The column temperature was initially held at 100°C for 1.5 minutes then programmed to increase to 160 °C at a ramp rate of 8 °C min⁻¹. Solutions (500, 1 000, 2 000, 5 000 mg l⁻¹) of acetic, propionic, butyric acid and *iso*-valeric acid were used as standards. Acidified samples (1 μ l) were injected and the concentrations of volatile fatty acids in the leachate samples were calculated by peak area comparison. The standards and samples (0.9 ml) were acidified by the addition of 0.1 ml formic acid (98% v/v).

Prior to acidification and analysis the samples were centrifuged in an Eppendorf centrifuge 5410 at 11 000 r.p.m. x g for 20 minutes.

2.3.6 pH

A Crison MicropH 2002 meter fitted with a pH electrode (Ingold) was used to determine the pH values of supernatant samples.

2.3.7 Redox Potential

The redox potential of leachate samples was determined with a combined platinum redox electrode (Crison) connected to a Crison MicropH 2002 meter. A standard ferrous(Fe²⁺)/ferric(Fe³⁺) solution was used to standardize the redox electrode before and after analysis. The standard solution contained (g l⁻¹ distilled water): ferrous ammonium sulphate, 39.21; ferric ammonium sulphate, 48.22; and concentrated sulphuric acid, 56.2 ml. The redox reading of the standard solution averaged +468 mV.

2.3.8 H₂S

Gas samples (10 ml) were injected into a MiniH₂S Series Gas Indicator (MSA Instruments). Prior to each set of analyses the instrument was calibrated with pure H₂S diluted to 10 ppm (MSA Instruments).

2.3.9 Heavy Metals

Supernatant Samples

A Varian Spectra AA-200 atomic absorption spectrophotometer with a nitrous oxide-acetylene flame, to minimize chemical interferences, was used.

The conditions used for each metal analysis were as follows:

Chromium (Cr): Wavelength, 357.9 nm; Spectral Band Pass, 0.2 nm; Lamp Current, 7 mA;

Copper (Cu): Wavelength, 324.7 nm; Spectral Band Pass, 0.5 nm; Lamp Current, 4 mA;

Nickel (Ni): Wavelength, 232.9 nm; Spectral Band Pass, 0.2 nm; Lamp Current, 4 mA; and

Zinc (Zn): Wavelength, 213.9 nm; Spectral Band Pass, 0.1 nm; Lamp Current, 5 mA.

Prior to analysis, each supernatant sample was filtered through a 0.45 μ m cellulose acetate membrane filter.

Refuse and Sewage Sludge Samples

To determine the concentrations of Cr, Cu, Ni and Zn in and adsorbed to the surfaces of refuse/sewage sludge, samples were taken from three depths (13 cm, 25 cm and 40 cm) from the microcosms (4.2.3) at the end of the study period after first draining excess leachate. The samples were centrifuged in a Beckman J2 HS Centrifuge at 10 000 r.p.m. x g for 25 minutes whereafter the supernatants were kept for heavy metal analysis by atomic absorption spectrophotometry (AAS).

The centrifuged samples were then oven dried at 60 °C for 72 h. Approximately 1.0 g, to the nearest mg, of each of the oven-dried refuse/sludge samples was transferred into a wide-form porcelain crucible. After ashing in a pre-heated furnace at 500 °C for 2 h and cooling, the samples were moistened with glass-distilled water and 10 ml of a 4M HCl (32% v/v) / HNO₃ (70.5% v/v) acid mixture were added. Digestion on a sand bath (at 163 ±5°C) followed for 20 minutes. The preparations were transferred quantitatively to 100 ml volumetric flasks with a glass rod to prevent losses and were diluted to volume with distilled water. The initial metal concentrations in the refuse and sewage sludge (supernatant and solids) were also determined by the same procedures.

Filtration through 3.0 μm cellulose acetate membrane filters followed. The crucibles and the precipitates on the filter papers were washed with dH₂O. The digested sample supernatants were then analysed by AAS.

2.3.10 Protein Content

The protein content of the refuse (2.1.1) and sewage sludge was determined by the Department of Animal Science and Poultry Science, University of Natal.

CHAPTER 3

An Assessment of the Effects of Nutrient Supplementation of Co-Disposal, of Activated Sewage Sludge, and Dual Co-Disposal, of Activated Sewage Sludge plus Phenol, with Refuse on the Anaerobic Fermentation and Leachate Quality

3.1 Introduction

With the rise in the world's population and the rapid development of industry, together with the accompanying increase in the volume and complexity of waste material, landfill sites and, specifically, co-disposal sites have become, and continue to be, the ultimate disposal option (Sinclair, 1994). Although co-disposal has been proved to be a successful disposal option, there is an on-going debate on the future role of landfilling in integrated waste management systems for the treatment and disposal of wastes (Campbell, 1994).

The effects of co-disposing sewage sludges (Beker and Van den Berg, 1991; Blakley, 1991; Watson-Craik *et al.*, 1992a; Sinclair, 1994; Percival and Senior, 1998) and phenolic wastewaters (Fedorak and Hruday, 1984a; Watson-Craik and Senior, 1990; Daneel and Senior, 1998a; 1998b) with refuse have been discussed. In particular, a study to address the development of a Code of Practice for co-disposal (anaerobically digested sludge / phenol) to obviate inimical environmental impacts of generated leachates and gases was reported (Daneel, 1996). Protracted periods of adaption to phenol (1 000 mg l^{-1} and 2 000 mg l^{-1}) were recorded while subsequent catabolism, irrespective of the phenol or sludge loadings, was promoted by mineral salts supplementation despite the fact that refuse masses are not usually characterized by nutrient limitations (Senior and Balba, 1991).

This study was, therefore, initiated to determine if activated sewage sludge/phenol co-disposals with refuse were similarly promoted by nutrient supplementation.

3.2 Experimental

3.2.1 Construction and Operation of Microcosms

Twelve glass columns (microcosms) were used in this study (Figure 3).

The columns were packed with refuse and/or waste activated sewage sludge. The different packing configurations and eluent solutions used are detailed in Table 3.1.

The columns were operated under closed culture conditions.

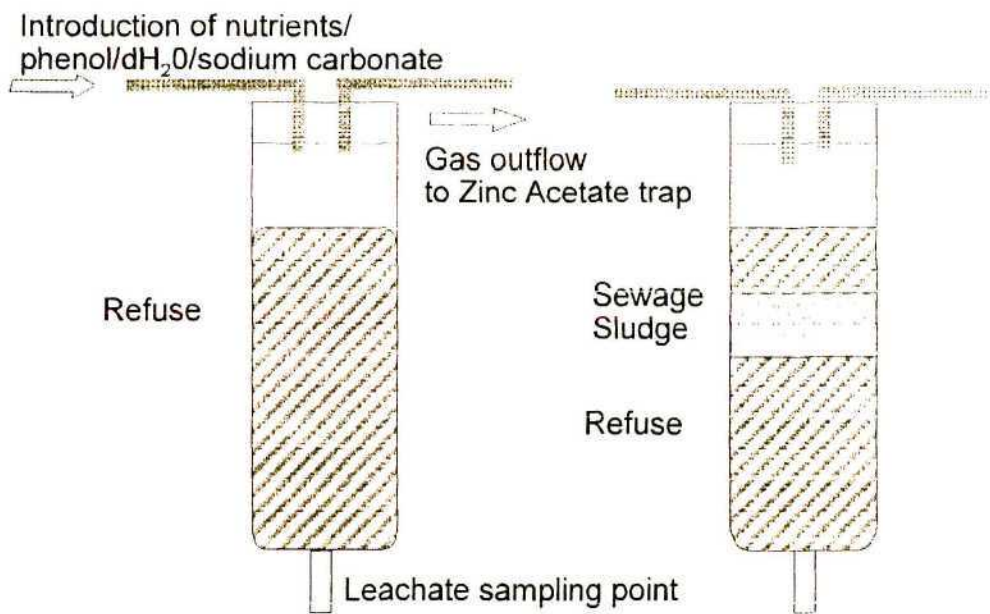


Figure 3.1 Microcosm configuration used to examine the effects of nutrient supplementations on the co-disposal of activated sewage sludge with refuse in the presence and absence of phenol.

The 12 columns (length 50 cm, i.d. 5.5 cm) (Percival, 1996) were set up in groups of four (Group A, B, C and D). The packing ratio (m/m) of refuse to de-watered sewage sludge was 4.1:1 as it has been reported to be the lowest practical ratio (Craft and Blakey, 1988).

The empty bed working volume was 1.1l and the packing density was 750 kg cm^{-3} .

Glass wool was placed at the base of each column to contain the refuse/sludge. The columns were incubated in the dark at 30°C in a temperature controlled box fitted with heating elements. The columns were connected to zinc acetate (0.1% m/v) gas traps to collect hydrogen sulphide as insoluble zinc sulphide.

Table 3.1. Packaging configurations and eluents used in the 12 microcosms

COLUMN No.	PACKING CONFIGURATION	ELUENT
A 1.	Refuse control	Macronutrients
2	Refuse + sludge	Macronutrients
3	Refuse + sludge	Macronutrients + Phenol ($1\,500 \text{ mg l}^{-1}$)
B 4.	Refuse control	Trace nutrients
5	Refuse + sludge	Trace nutrients
6	Refuse + sludge	Trace nutrients + Phenol ($1\,500 \text{ mg l}^{-1}$)
C 7.	Refuse control	Macro- + Trace nutrients
8	Refuse + sludge	Macro- + Trace nutrients
9	Refuse + sludge	Macro- + Trace nutrients + Phenol ($1\,500 \text{ mg l}^{-1}$)
D10.	Refuse control	Distilled water (dH_2O)
11	Refuse + sludge	dH_2O
12	Refuse + sludge	dH_2O + Phenol ($1\,500 \text{ mg l}^{-1}$)

The eluents (nutrients, phenol and distilled water) were introduced by a peristaltic pump (Ismatec peristaltic pump Type IPN 24B) at an empty bed dilution rate of 0.027 h^{-1} . After 22 h, the perfusions were stopped and the columns sealed.

Plastic syringes were connected to the columns to measure, at discrete time intervals, the volumes of gas produced. Prior to the connection of the syringes, the headspace of each column was overgassed with oxygen-free nitrogen (OFN) to displace any gas present.

After 12 weeks and again after 24 weeks, 100 ml of glass-distilled water were added to each column to ensure that the water content did not become limiting. Leachate recycling was practised in microcosms B6, C7 and C9 after 35 weeks of operation by collecting 40 ml from the base of each column with a hypodermic needle connected to a plastic syringe (20 ml) and reintroducing it to the top of the column.

3.2.2 Eluents

Macronutrients

The macronutrient solution was an adapted version of the basic mineral salts medium described by Coutts, Senior and Balba (1987) and contained the following (g l^{-1} glass-distilled water):

K_2HPO_4 , 1.5; NaH_2PO_4 , 0.85; NH_4Cl , 0.9; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2; NaHCO_3 , 0.5; Na_2CO_3 , 0.2; Na_2SO_4 , 0.198; KNO_3 , 0.07.

Trace Elements (Micronutrients)

The trace nutrient solution contained the following (mg l^{-1} glass-distilled water):

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 1500; NaCl , 9000; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 197; CaCl_2 , 90; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 238; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 17; ZnSO_4 , 287; AlCl_3 , 50; H_3BO_3 , 62; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 24.

For the combined nutrient solution, 3 ml of the trace nutrient solution were added to 997 ml of the macronutrient solution.

Sterilization of both solutions was by autoclaving at 121°C for 15 minutes. Each solution was then stored at 4°C until use.

Phenol

The phenol solution (1 500 mg l⁻¹) was prepared by dissolving phenol in glass-distilled water and diluting to 1 l.

Sodium Carbonate Solution

After 42 weeks of operation, two microcosms (B6 and C7) were perfused with sodium carbonate (2.5% m/v, pH 11.6) according to Kasali *et al.* (1989).

Leachate samples were collected with hypodermic needles connected to plastic syringes (20 ml) for quantification of COD, volatile fatty acids, phenol, ammonium, nitrate, nitrite, sulphate and phosphate concentrations together with pH, redox potential and microcosm headspace gas composition (H₂S and methane).

3.3 Results and Discussion

The reason for collection of the activated sludge from the return channel of the sewage works was that a higher solid content was present compared to the aeration tank sludge.

The moisture content of the refuse used in the microcosms was 60.1 % (m/m). The activated sewage sludge was dewatered in accordance with Sinclair (1994) and had a dry solids content of 11.96% (m/m).

3.3.1 An Assessment of the Effects of the Co-Disposal of Activated Sewage Sludge and the Dual Co-Disposal of Activated Sewage Sludge plus Phenol with Refuse on the Refuse Anaerobic Fermentation

Volatile Fatty Acids (VFA)

Individual concentrations of VFA, in the range of 990 mg l⁻¹ to 4 645 mg l⁻¹, were detected in the leachates of columns D10-D12 (Figures 3.2a-c). In particular, elevated concentrations of propionic acid were recorded between weeks 5 and 21. These results contrasted those of Sinclair (1994) who recorded comparable leachate concentrations of propionic acid to other VFA analysed in microcosms packed with refuse and de-watered activated sewage sludge in a ratio of 4.1:1.

For acetic and butyric acid the concentrations were lower although the refuse control recorded a peak in acetic acid (2 356 mg l⁻¹) during week 15. According to Percival (1996), the co-disposal of activated sewage sludge with refuse facilitated the establishment of a highly active acidogenic population but this was not apparent in this study.

The branched-chain fatty acid, *iso*-valeric acid was detected in the refuse (Figure 3.2a) and dual co-disposal (Figure 3.2 c) microcosms but only in low concentrations (≤ 280 mg l⁻¹). This indicated that some protein deamination had taken place (Rees, 1980) with the low concentrations attributed to the low protein content of the refuse (1.5.1) and sewage sludge. The protein content of the refuse was 9.46 % (m/m) while no protein was detected in the activated sewage sludge, explicating the *iso*-valeric acid concentrations detected.

pH and Chemical Oxygen Demand (COD)

Initially, as anaerobic digestion/solid-state fermentation proceeded increases in the VFA concentrations effected decreases in the leachate pH values to between 4.8 and 5.5 (Figure 3.3).

Subsequently, increased leachate pH values were recorded for all three microcosms and coincided with decreased COD values (Figure 3.4). The initial marked increase in the leachate COD of the control (D10) was attributed to the elevated acetic acid concentration (Figure 3.2a).

The higher pH values recorded for the co-disposal and dual co-disposal microcosms compared to the refuse control were attributed to the addition of ammoniacal-N and nitrate to the refuse by sewage sludge co-disposal (Watson-Craik *et al.*, 1992a) since denitrification should have facilitated ammonium production.

Redox Potential

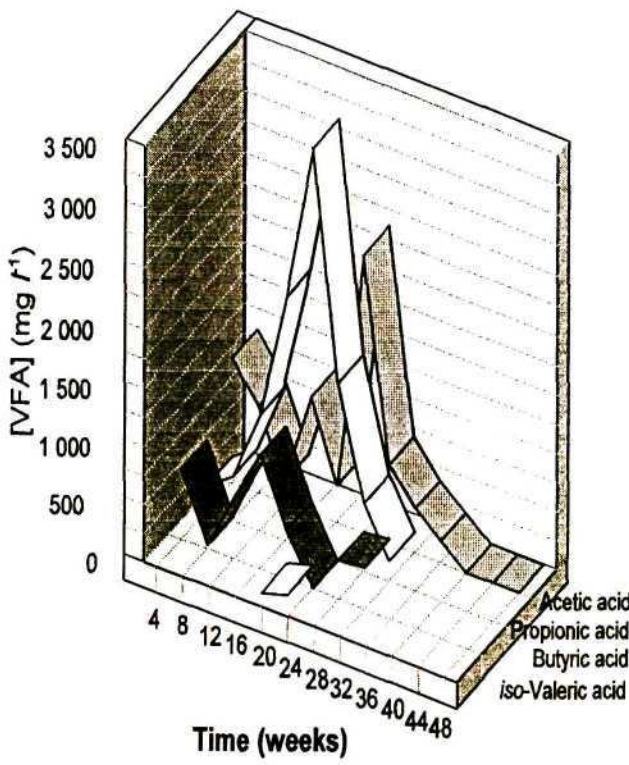
The redox potential changes of the three microcosms were comparable although the co-disposals both promoted earlier changes (Figure 3.5). For each of the self-generating redox gradients stable values were not recorded until > 10 weeks of operation. Values < -200 mV were never recorded although this is a threshold for methanogenesis (Levett, 1990).

Nitrate, Nitrite and Ammonium

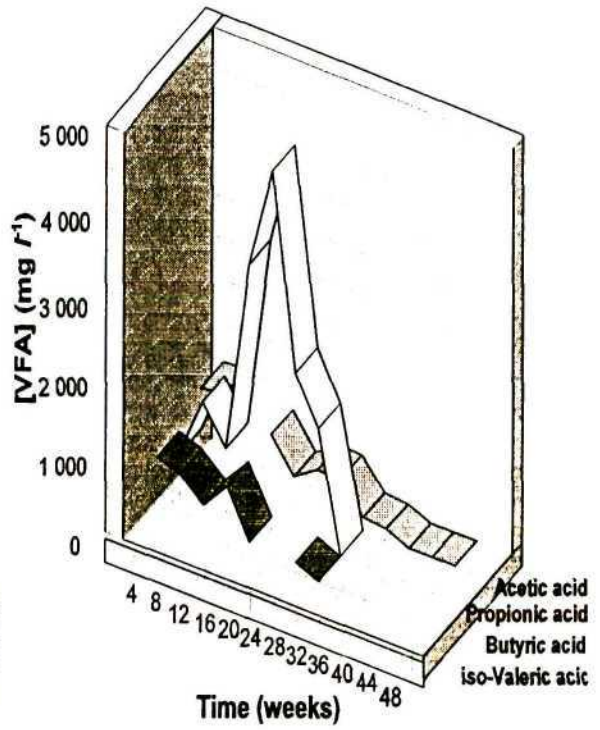
Nitrogenous compounds are added to the refuse mass by sewage sludge co-disposal. The most common molecules are organic nitrogen, ammoniacal-N and nitrate (Watson-Craik *et al.*, 1992a).

Sinclair (1994), however, concluded from co-disposal experiments with activated sewage sludge that the refuse was the main contributing factor to the leachate nitrate concentrations. In the present study it was, perhaps, surprising that, initially, the highest leachate nitrate concentrations was recorded for the refuse control (Figure 3.6) since it was anticipated that the presence of activated sludge would effect high concentrations by displacement and/or nitrification. From the results, it appeared that nitrification was depressed by the presence of phenol (Hockenbury and Grady, 1977) since the lowest nitrate concentrations were recorded in the presence of this molecule. After 12 weeks a low peak of nitrate (6.1 mg l^{-1}) was recorded for the control.

FIG 3.2 a.



b.



c.

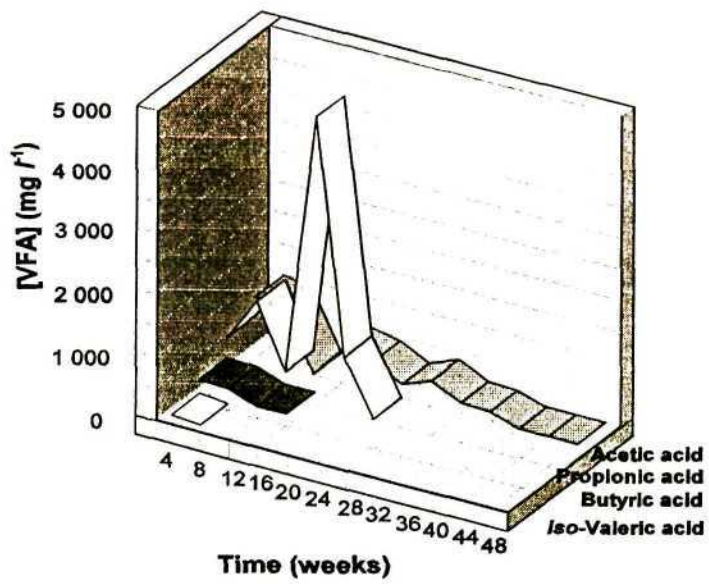


FIG 3.3

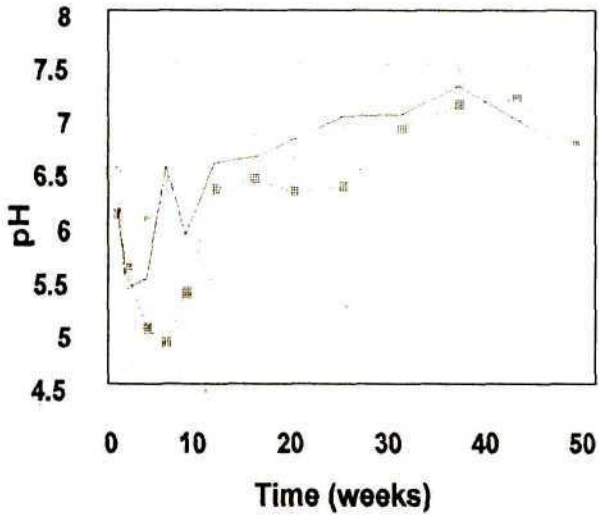


FIG 3.4

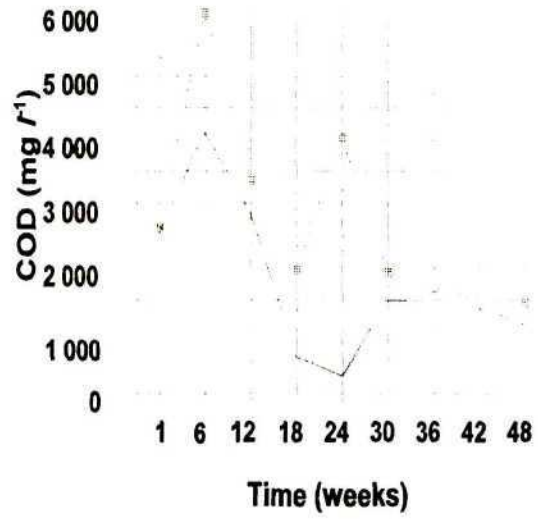


FIG 3.5

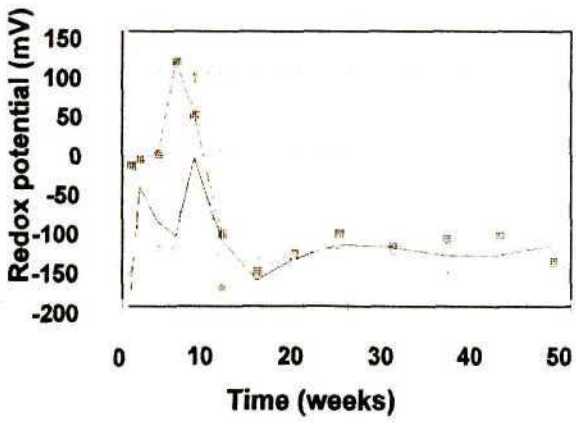
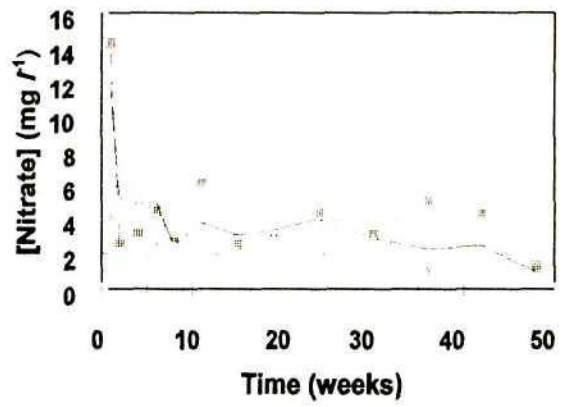


FIG 3.6



This was surprising as the microcosm was operated with no air ingress. A possible explanation was the presence of heterotrophic nitrifying bacteria which are active in both low oxygen (Van Niel, Arts, Wesselink, Robertson and Kuenen, 1993) and low pH (Focht and Chang, 1975) environments.

The nitrite "peak" of the control after 4 weeks (Figure 3.7) could have been due to nitrate reduction. Throughout, the dual co-disposal microcosm was characterized by depressed nitrite concentrations compared with the other microcosms and this was attributed to phenol inhibition of the nitrate-reducing bacteria.

The initial increase in the ammonium concentration of the control microcosm leachate (Figure 3.8) could have been due to dissimilatory nitrate reduction, or ammonification (1.7.2), facilitated by an appropriate redox potential (Figure 3.5), or assimilative nitrate reduction to ammonia by various fungal and bacterial species (Brock and Madigan, 1991).

Sulphate

The elevated leachate sulphate concentrations ($> 300 \text{ mg l}^{-1}$) during the first 15 weeks of operation (Figure 3.9) were attributed to inhibition of sulphate-reducing bacteria by pH values < 6 (Widdel, 1988) in conjunction with slightly unfavourable E_h values (Postgate, 1984). After week 15 the sulphate concentrations decreased probably due to the onset of sulphate reduction (1.7.2) as a more favourable E_h environment was established for the activity of sulphate-reducing bacteria which was identified by Atlas (1984) to be -180 to -220 mV . This was substantiated by the precipitation of zinc sulphide in the gas traps.

The use of available electron acceptors is dictated by energy yield maximization in relation to an available substrate with the principal determinants of metabolic regulation and competition between populations (Nedwell, 1984). Thus, in competition for a substrate between nitrate-reducing and sulphate-reducing bacteria the energy yield would be higher for the former and the latter would be outcompeted (Atlas and Bartha, 1993).

The sulphate-reducing bacteria, in turn, when competing for a common substrate (for example H_2) with methanogens have a higher utilization efficiency and have a lower threshold (Lovley, 1985). As a consequence, the methanogens cannot effectively compete with the sulphate reducers until all or most of the sulphate has been depleted.

Methane

The presence of methanogens in microniches could have accounted for the appearance of methane in the early stages of operation. A concentration of 25% (v/v) was detected by headspace gas analysis for the control microcosm. This production was not maintained, however, probably due to VFA concentration (Figure 3.2a) increases and loss of buffering capacity in the microcosms (Percival, 1996) with the subsequent low pH values (Figure 3.3).

Phosphate

The co-disposal of activated sewage sludge has been regarded as advantageous to the refuse fermentation as it introduces phosphate, a supposed growth-limiting nutrient (Pfeffer, 1978). After the initial high concentrations recorded for the co-disposal microcosm leachate, the phosphate concentration decreased and stabilized (Figure 3.10) possibly due to precipitation or microbial uptake.

FIG 3.7

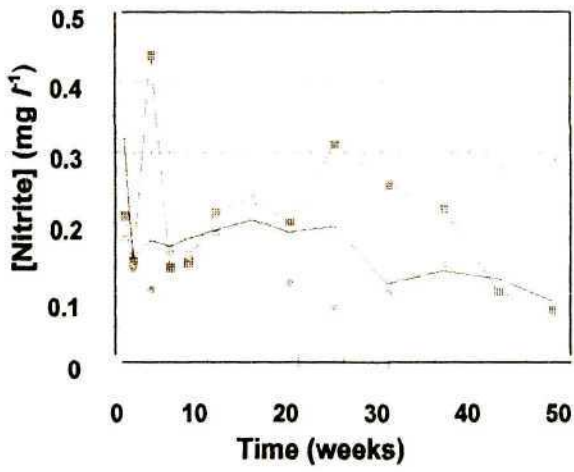


FIG 3.8

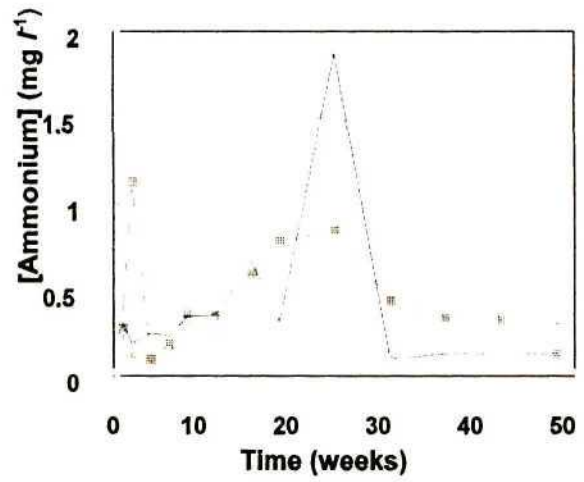


FIG 3.9

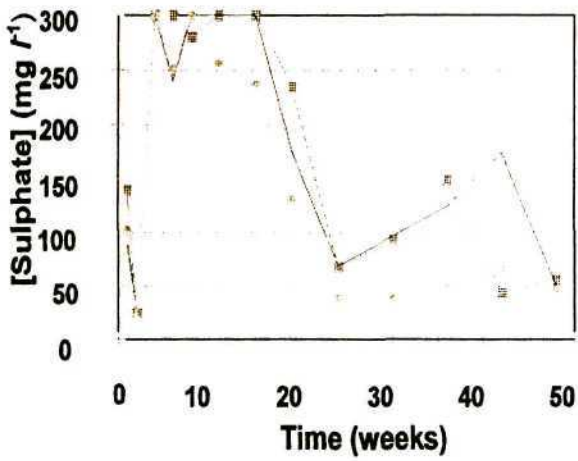
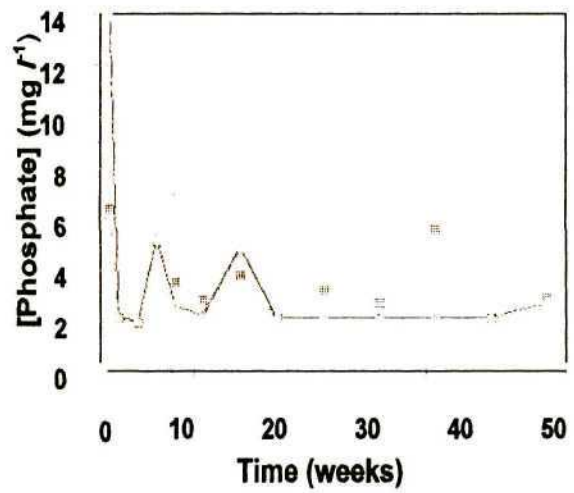


FIG 3.10



3.3.2 An Assessment of the Promotion of the Co-Disposal of Activated Sewage Sludge and the Dual Co-Disposal of Activated Sewage Sludge plus Phenol with Refuse on the Refuse Anaerobic Fermentation by Macronutrient Supplementation

VFA

As with the unsupplemented microcosms, the leachate VFA concentrations of the co-disposal (A2) and dual co-disposal (A3) columns dramatically increased. High concentrations of propionic acid ($\geq 6\,500\text{ mg l}^{-1}$), acetic acid ($> 4\,900\text{ mg l}^{-1}$) and butyric acid ($> 3\,400\text{ mg l}^{-1}$) were recorded (Figures 3.11b and c) and were maintained throughout the study period. It thus appeared that the addition of macronutrients accelerated the establishment of an acidogenic population. The high VFA concentrations and concomitant low pH values (Figure 3.12) were indicative of a rate of acidogenesis $>$ acidotrophy.

The high VFA concentrations and low pH values were similar to the results of Percival (1996) who recorded "souring" in the presence of co-disposed phenol.

The refuse control recorded the highest initial VFA concentrations (Figure 3.11a) indicative of the presence of an active acidogenic population.

The dynamics of the fermentation were exemplified by the discreet propionic acid concentrations which markedly increased at week 5 but then decreased to below the detection limit at week 15. As with the unsupplemented microcosms, the *iso*-valeric acid concentrations were low.

pH and COD

An examination of the pH data (Figure 3.12) shows that low pH values were consistently recorded for the co-disposal microcosms and these coincided with elevated VFA concentrations (Figures 3.11b and c).

High COD values (maximum 28 000 mg l⁻¹) were also recorded for the dual co-disposal microcosm (Figure 3.13). For the control microcosm, despite the addition of macronutrients, the fermentation followed the established pattern (3.3.1).

Redox Potential

A deviation was, however, seen in the redox data (Figure 3.14) since an initial low redox (-204 mV) was recorded for the control followed by a slight increase and stabilization at -135 ± 5 mV. In contrast, the E_h trends of the co-disposal microcosms increased and peaked at +65 mV (co-disposal) and +97 mV (dual co-disposal). The pH (Figure 3.12) and VFA concentration (Figures 3.11b and c) data appeared to confirm a limitation of acidotrophy.

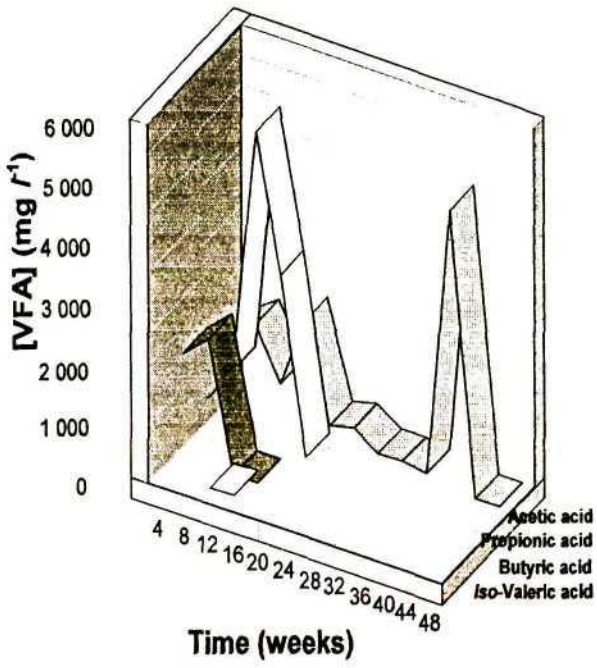
It, thus, appeared that macronutrient supplementation was detrimental to the refuse fermentation.

Nitrate, Nitrite and Ammonium

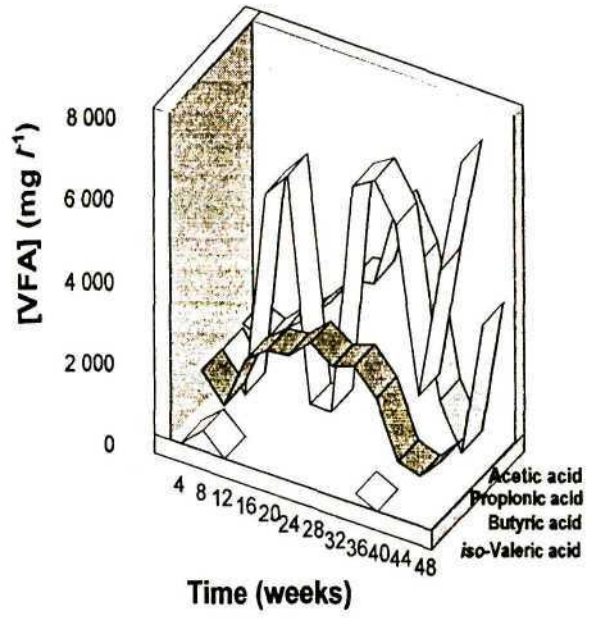
The initial leachate sampled after five days of incubation recorded high a nitrate concentration (88 mg l⁻¹) for the refuse control (Figure 3.15) and this was probably indicative of oxygenation of the refuse during processing and subsequent low ammonium concentrations (Figure 3.16). In comparison to the control, low nitrate concentrations (< 10 mg l⁻¹) were recorded in the co-disposal and dual co-disposal leachates (Figure 3.15). This was probably due to the presence of an active denitrifying population in the activated sludge which lead to the metabolism of nitrate.

The ammonium concentration increases and nitrate concentration decreases in the following weeks in the co-disposal microcosms are difficult to reconcile since dissimilatory nitrate reduction or ammonification should have been limited by the comparatively high E_h values (Figure 3.14) as dissimilatory nitrate reduction is operational at E_h values of approximately -200 mV (Atlas, 1984).

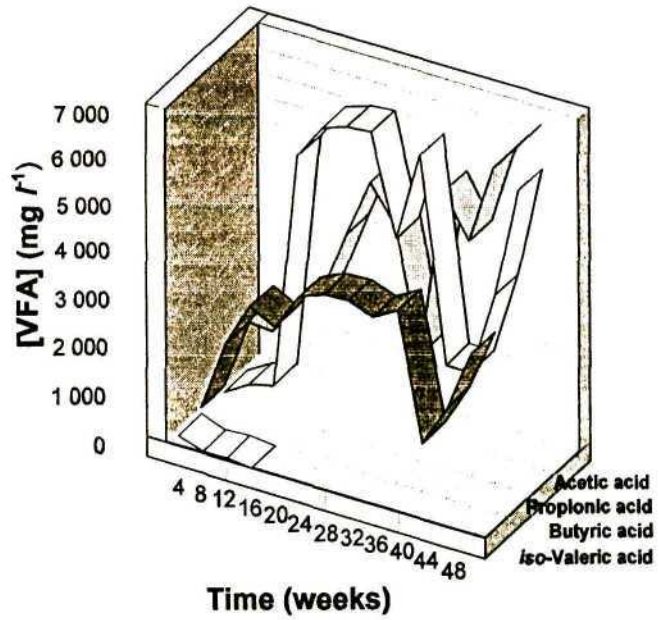
FIG 3.11 a.



b.



c.



Progressive decreases for the nitrite concentrations (Figure 3.16) were generally recorded for all three microcosms from week 16 and, in the co-disposal microcosms, were accompanied by ammonium concentration increases. The presence of phenol appeared to have only a limited inhibitory effect.

Sulphate

The initial high sulphate concentrations recorded for the control and co-disposal microcosms (Figure 3.18) but not the dual co-disposal microcosm could not be accounted for by the macronutrient supplementation. As discussed above, sulphate-reducing bacteria are inhibited by pH values < 6 (Widdel, 1980) and have been shown to be susceptible to elevated organic loadings, e.g. acetic acid ($\geq 6\ 000\ \text{mg}\ l^{-1}$) and propionic acid ($\geq 7\ 300\ \text{mg}\ l^{-1}$) (Watson-Craik, James, Terry and Senior, 1993). With time, the leachate sulphate concentration of the control decreased while the co-disposal columns were both characterized by high values.

The variations recorded between weeks 4 and 11 for the co-disposal microcosms possibly reflected the development of populations of sulphate-reducing bacteria in microniches where the conditions were buffered and the pH values were higher (Widdel, 1980; Percival, 1996). In contrast, the pH (Figure 3.12) and redox potential (Eh of < -180 mV during the initial ten weeks of operation) (Figure 3.14) values of the control were conducive for the development of an active sulphate-reducing bacteria population.

Low H_2S concentrations ($\leq 4\ \text{ppm}$) were measured in week 6 for all three microcosms thus confirming the presence and activity of sulphate-reducing bacteria.

FIG 3.12

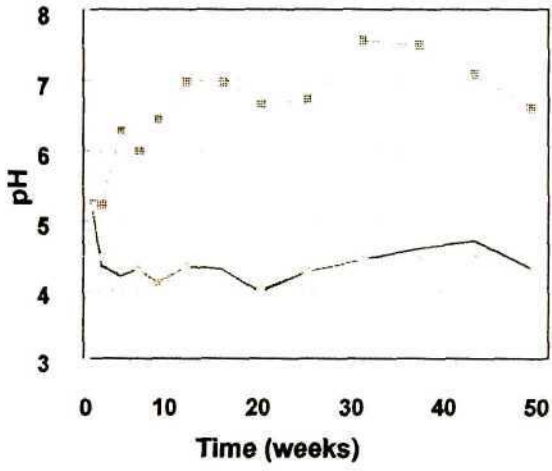


FIG 3.13

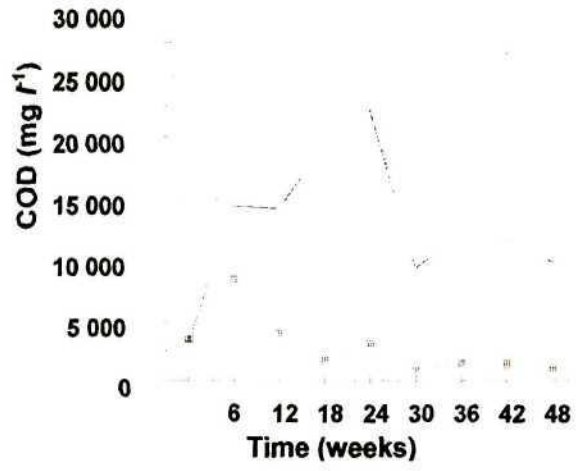


FIG 3.14

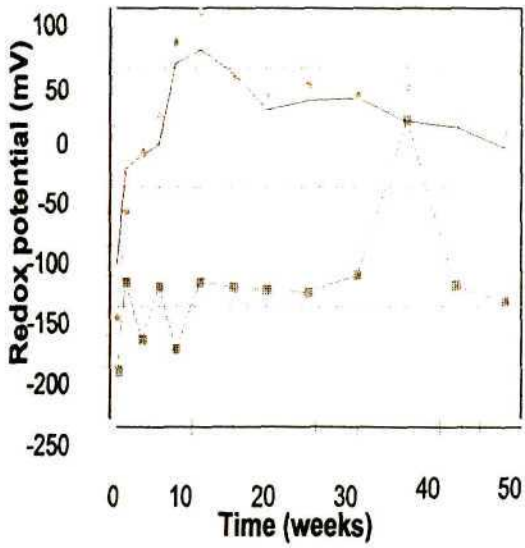


FIG 3.15

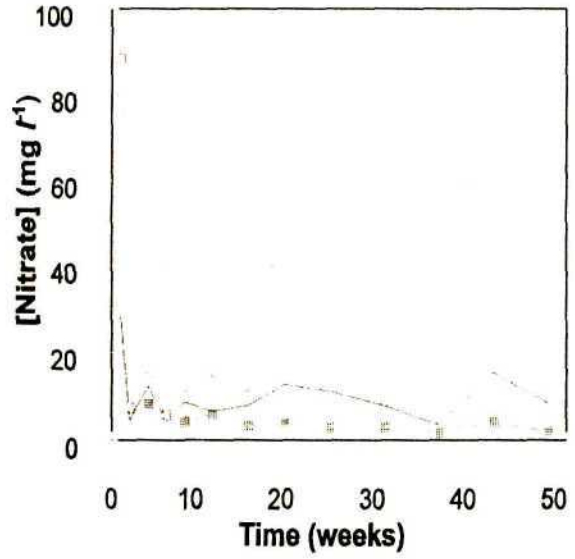


FIG 3.16

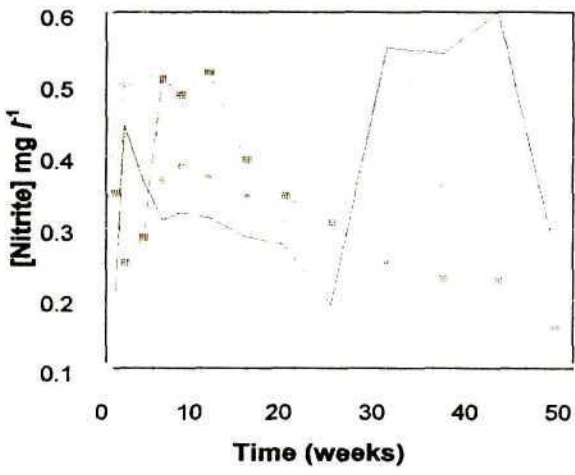


FIG 3.17

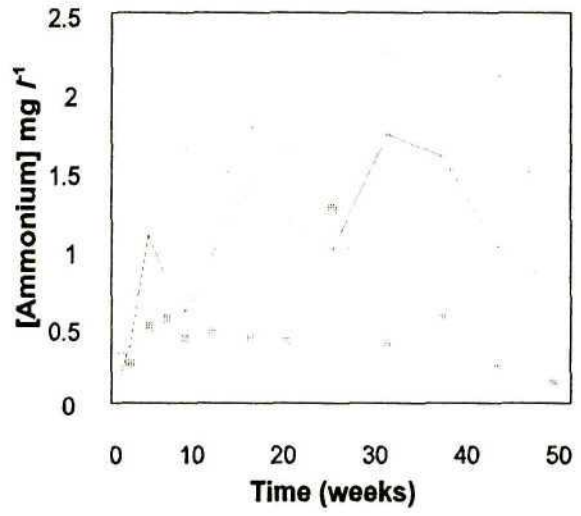


FIG 3.18

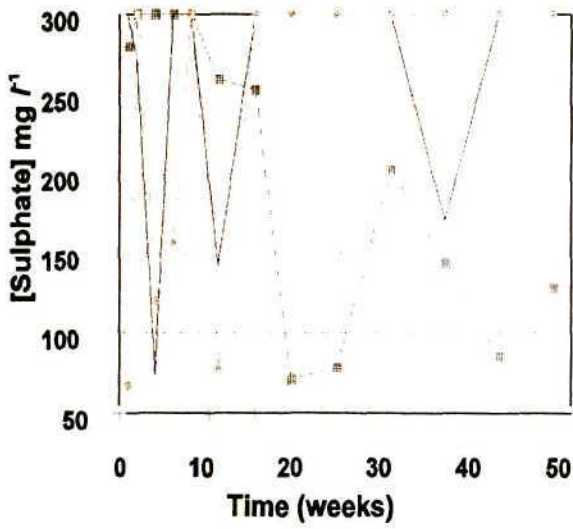
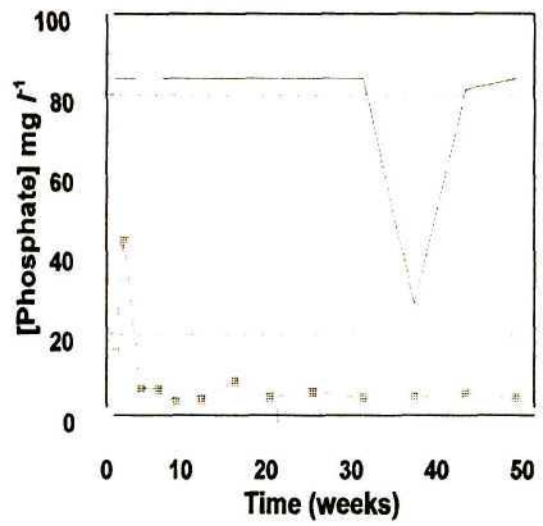


FIG 3.19



Methane

Methane was detected in the headspace of the refuse control on week 2 when the recorded concentration was 11.8% (v/v) while by week 12 the concentration had increased to 88% (v/v). No methane was detected after this despite the favourable conditions for methanogenesis.

Phosphate

Higher phosphate concentrations were measured (Figure 3.19) compared to the unsupplemented microcosms and these were attributed to macronutrient supplementation (K_2HPO_4 , 1.5 g l^{-1} ; NaH_2PO_4 , 0.85 g l^{-1}). The increase in phosphate recorded for the dual co-disposal microcosm was attributed to the fall in pH (Figure 3.12) and thus promotion of cell autolysis (Bull, Evans, Wechsler and Cleland, 1983). The subsequent decrease in phosphate concentration at week 8 was possibly due to microbial utilization and/or chemical precipitation.

The low phosphate concentration in the refuse control leachate could have been indicative of element limitation.

3.3.3 An Assessment of the Promotion of the Co-Disposal of Activated Sewage Sludge and the Dual Co-Disposal of Activated Sewage Sludge plus Phenol with Refuse on the Refuse Anaerobic Fermentation by Trace Element Supplementation

VFA

Concentrations of VFA, in the range of 581 mg l^{-1} to 5964 mg l^{-1} , were recorded in the leachates of the three columns (B4-B6) in the first 11 weeks of operation (Figures 3.20 a-c). In particular, elevated concentrations of propionic acid were recorded between weeks 2 and 11. The dynamics of the fermentations in the refuse and co-disposal columns were demonstrated by the propionic acid concentrations which increased between weeks 2 and 5 but then decreased ($\leq 900 \text{ mg l}^{-1}$) at week 25 for the refuse microcosm (Figure 3.20a) and week 11 for the co-disposal microcosm (Figure 3.20b).

High concentrations of propionic acid ($\geq 4\,700\text{ mg l}^{-1}$) and acetic acid ($\geq 2\,000\text{ mg l}^{-1}$) were recorded and were maintained throughout the study period in the dual co-disposal microcosm (Figure 3.20c). The high VFA concentrations and concomitant low pH values (Figure 3.21) were indicative of a rate of acidogenesis $>$ acidotrophy.

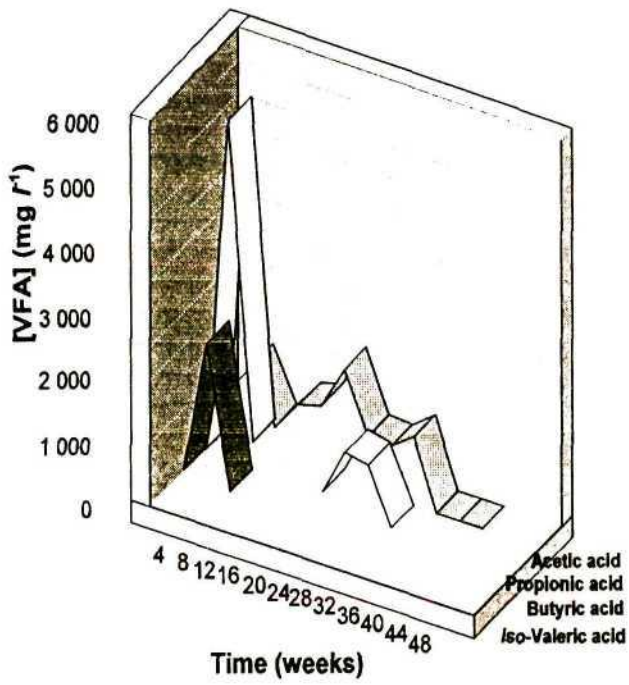
Leachate recycling (after week 35) in Microcosm B6 had no definite effect on the VFA concentrations although a decrease in the acetic acid concentration was measured. Sodium carbonate (2.5%, m/v) was added at week 43 and a beneficial effect resulted as the VFA concentrations decreased to below detectable concentrations. This was also demonstrated in the pH trend (Figure 3.21).

pH and COD

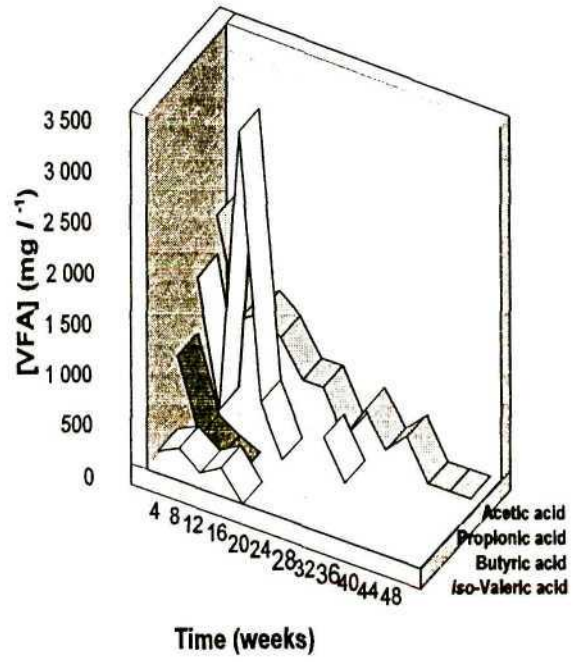
As the solid-state fermentations proceeded increases in the VFA concentrations effected low leachate pH values in the dual co-disposal microcosm (Figure 3.21). Subsequently, increased leachate pH values were recorded with concomitant decreased COD values (Figure 3.22). High COD values (maximum $17\,650\text{ mg l}^{-1}$) were also recorded for this microcosm (Figure 3.22). For the control and co-disposal microcosms (Figure 3.22) the fermentation followed the established pattern. The "souring" of the dual co-disposal microcosm was surprising as the co-disposal microcosm did not record low pH values so the activated sewage sludge was not the causal factor.

In an attempt to resuscitate the fermentation in the dual co-disposal microcosm, a leachate recycling strategy was initiated after week 35 of operation. This seemed to be unsuccessful as no change in the pH was recorded. At week 43 the microcosm was subjected to sodium carbonate addition. This effected an increase in the pH to 5.9 with a continued recycling of the leachate for 4 weeks. Measurement of the leachate COD of the same microcosm indicated a reduction to $< 5\,000\text{ mg l}^{-1}$ by week 48 of operation.

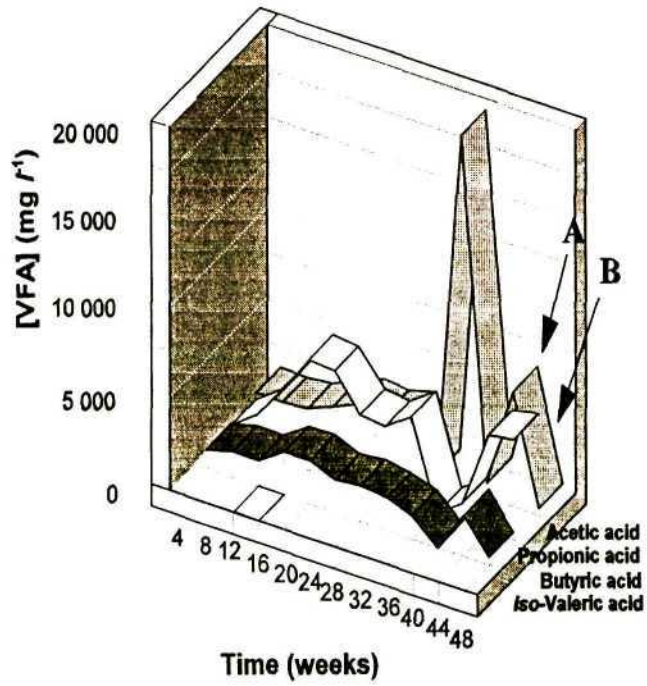
FIG 3.20 a.



b.



c.



Redox Potential

The redox potential changes in the control and co-disposal microcosms were comparable although the latter recorded lower E_h values between weeks 4 and 11 (Figure 3.23). Stabilization occurred at -110 mV after week 24. In contrast, the redox potential trends of the dual co-disposal microcosm increased and peaked at +197 mV.

The pH values (Figure 3.21) and VFA concentrations (Figure 3.20c) appeared to confirm a limitation of acidotrophy in the dual co-disposal microcosm.

Leachate recycling in this microcosm did not affect the E_h measured, whereas the addition of the sodium carbonate caused a decrease to -114 mV in week 48.

Nitrate, Nitrite and Ammonium

The initial high nitrate concentration recorded for the refuse control (Figure 3.24) was probably indicative of oxygenation of the refuse during processing and resulted in subsequent low ammonium concentrations (Figure 3.26) but as explained in the previous section (3.3.2) the presence of an active denitrifying bacterial population in the activated sewage sludge probably facilitated the removal of nitrate in the co-disposal microcosms during the five days before leachate sampling and analysis. It appeared that nitrification was depressed by the presence of phenol since low nitrate concentrations were recorded. The ammonium concentration increases in the following weeks in the dual co-disposal microcosm are difficult to explain since dissimilatory nitrate reduction or ammonification should have been limited by the high E_h values (Figure 3.23). As previously stated, it is possible that assimilatory nitrate reduction could have played a role in the production of ammonium as this pathway is operative under oxic conditions although it does not result in the accumulation of high extracellular ammonium concentrations since NH_4^+ is incorporated rapidly into organic nitrogen (Atlas and Bartha, 1993).

Figure 3.21 Changes in leachate pH of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following trace element supplementation (A = leachate recycle; B = sodium carbonate addition).

Figure 3.22 Changes in leachate COD of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following trace element supplementation (A = leachate recycle; B = sodium carbonate addition).

Figure 3.23 Changes in leachate redox potential of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following trace element supplementation (A = leachate recycle; B = sodium carbonate addition).

Figure 3.24 Changes in leachate nitrate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following trace element supplementation (A = leachate recycle; B = sodium carbonate addition).

FIG 3.21

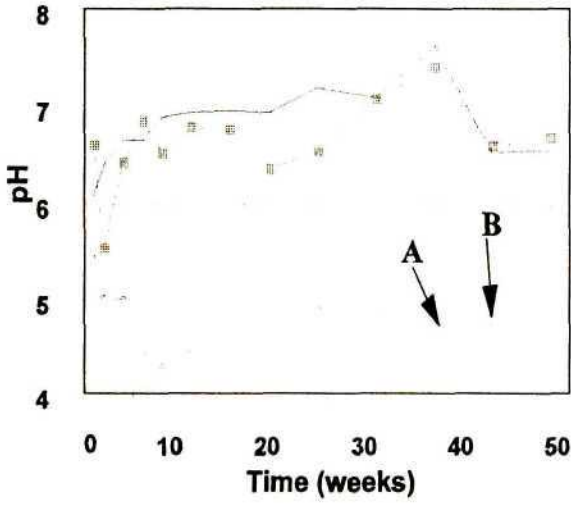


FIG 3.22

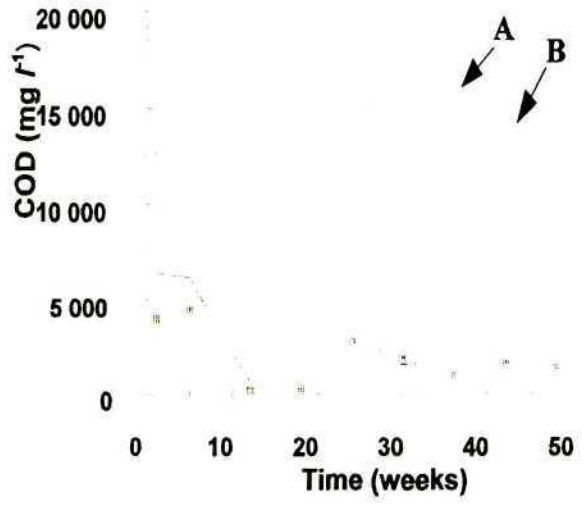


FIG 3.23

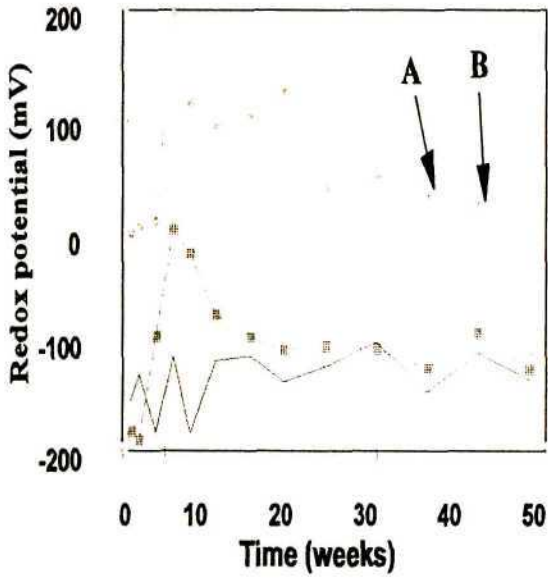
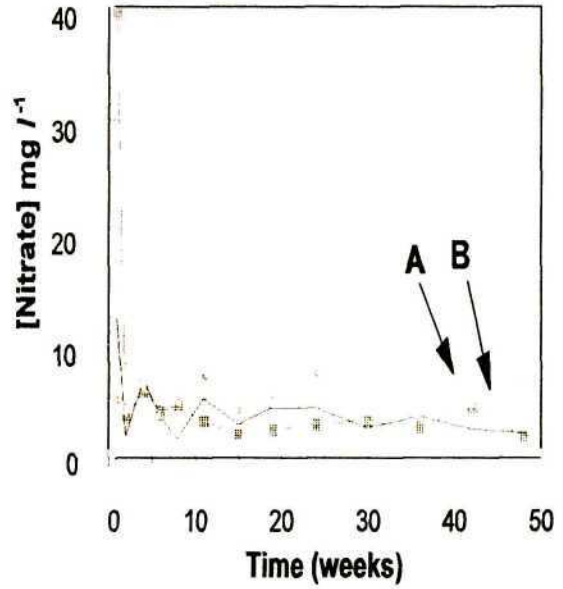


FIG 3.24



With leachate recycling in the dual co-disposal microcosm an increase in the ammonium concentration to 2.44 mg l^{-1} was recorded in week 42. A rational explanation for this is assimilatory nitrate reduction through re-oxygenation of the refuse mass by leachate recycle.

The nitrite peak of the refuse control after week 6 could have been due to nitrate reduction (Figure 3.25). Progressive decreases were generally recorded for all the microcosms. The presence of phenol appeared to have only a limited inhibitory effect although an increase in the nitrite concentration was recorded from week 25.

Sulphate

As discussed above (3.3.2), the initial high sulphate concentrations recorded for the control and co-disposal microcosms but not the dual co-disposal microcosm could not be accounted for (Figure 3.27). The elevated leachate sulphate concentrations ($\geq 290 \text{ mg l}^{-1}$) during the first 6 weeks of operation were attributed to the inhibition of the sulphate-reducing bacteria by low pH values (Figure 3.21). The variations recorded in weeks 2 and 4 for these microcosms and in weeks 24, 30 and 42 for the dual co-disposal microcosm possibly reflected the development of sulphate-reducing bacteria in microniches where the conditions were buffered. After 6 weeks the sulphate concentrations decreased in the control and co-disposal microcosms, probably due to the onset of sulphate reduction. The dual co-disposal microcosm was characterized by high values ($\geq 300 \text{ mg l}^{-1}$). The pH (Figure 3.21) and redox potential (Figure 3.23) values were not conducive for the development of an active sulphate-reducing bacteria population.

With the addition of the sodium carbonate to the dual co-disposal microcosm, an increase in pH (Figure 3.21) and decrease in E_h (Figure 3.23) were effected, while a high sulphate concentration ($> 300 \text{ mg l}^{-1}$) was recorded. Thus, it appeared that an active sulphate-reducing population had not established even though the conditions were more favourable.

Figure 3.25 Changes in leachate nitrite concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following trace element supplementation (A = leachate recycle; B = sodium carbonate addition).

Figure 3.26 Changes in leachate ammonium concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following trace element supplementation (A = leachate recycle; B = sodium carbonate addition).

Figure 3.27 Changes in leachate sulphate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following trace element supplementation (A = leachate recycle; B = sodium carbonate addition).

Figure 3.28 Changes in leachate phosphate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following trace element supplementation (A= leachate recycle; B = sodium carbonate addition).

FIG 3.25

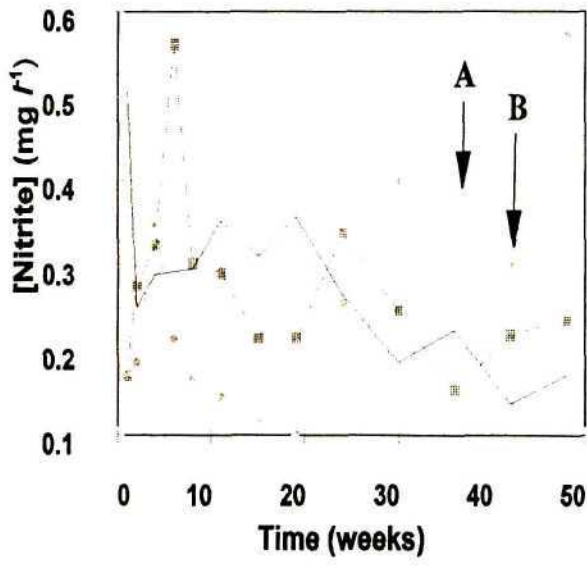


FIG 3.26

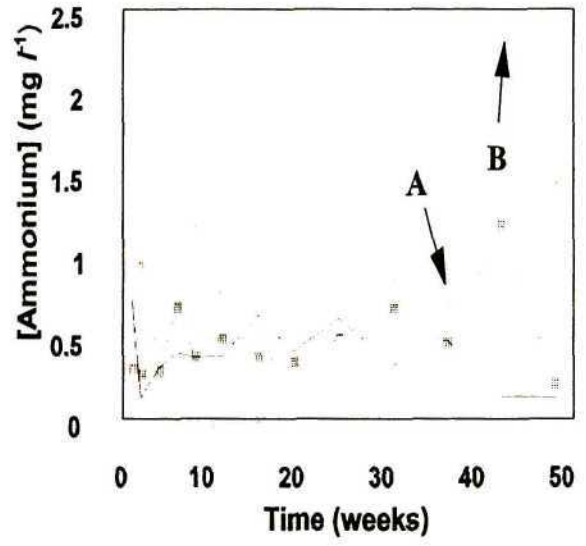


FIG 3.27

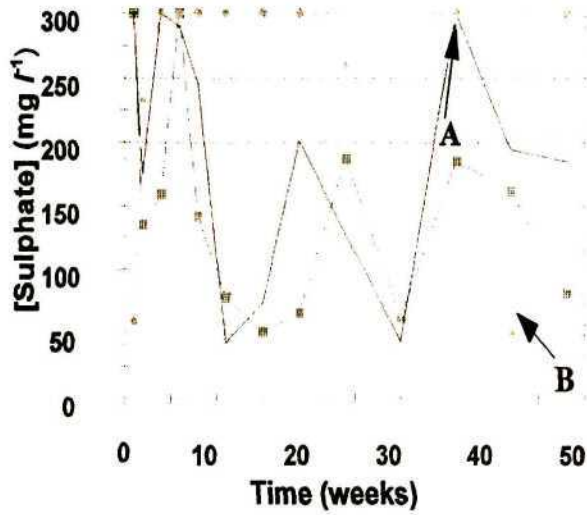
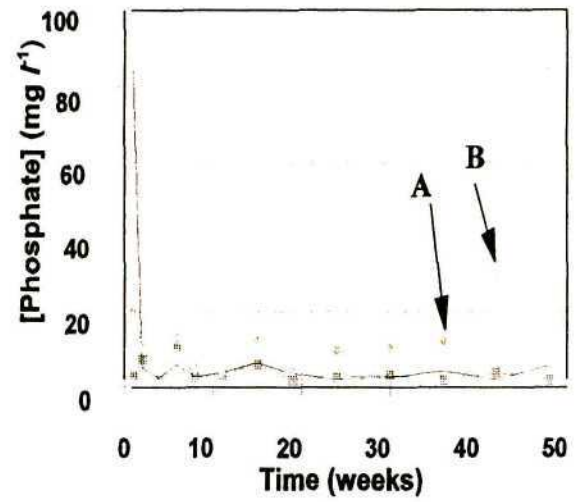


FIG 3.28



Methane

A methane concentration of 29% (v/v) was recorded in the co-disposal microcosm during week 12.

Phosphate

The initial phosphate concentration peak in the co-disposal microcosm (Figure 3.28) was surprising since no macronutrient supplementation was administered.

The phosphate concentrations fluctuated during the study period possibly due to microbial uptake/autolysis and/or chemical precipitation. The low pH values (Figure 3.21) in the dual co-disposal microcosm did not seem to influence phosphate utilization although with leachate recycling (week 36) and sodium carbonate addition (week 43), the phosphate concentration increased to $> 84 \text{ mg l}^{-1}$ in week 48. This was a surprise as an increase in pH was measured which should have minimized cell autolysis and favoured microbial utilization and/or precipitation.

3.3.4 An Assessment of the Promotion of the Co-Disposal of Activated Sewage Sludge and the Dual Co-Disposal of Activated Sewage Sludge plus Phenol with Refuse on the Refuse Anaerobic Fermentation by Macronutrient plus Trace Element Supplementation

VFA

The leachate VFA concentrations of the three microcosms (C7-C9) dramatically increased with high propionic acid concentrations ($>5\,000 \text{ mg l}^{-1}$), acetic acid concentrations ($>3\,500 \text{ mg l}^{-1}$) and butyric acid concentrations ($>2\,700 \text{ mg l}^{-1}$) recorded and maintained throughout the study (Figures 3.29a - c). As discussed above (3.3.2), it appeared that the addition of macronutrients accelerated the establishment of acidogenic populations. With trace element plus macronutrient supplementation, acidogenesis was enhanced compared with macronutrient supplementation alone (3.3.2).

Leachate recycling promoted decreases in the VFA concentrations which were also demonstrated by the elevated pH values recorded (Figure 3.30). Sodium carbonate effected an increase in the pH of the control in week 43 but this was not paralleled by the VFA concentrations detected. Recycling in the dual co-disposal microcosm had a beneficial effect with a decrease in the volatile fatty acid concentrations recorded after week 35 (Figure 3.29c).

pH and COD

The low pH values which were consistently recorded in the microcosms (Figure 3.30) coincided with elevated VFA concentrations (Figures 3.29a-c). These were indicative of acidogenesis > acidotrophy. Elevated COD concentrations were also recorded, which peaked at $\geq 24\ 800\ \text{mg l}^{-1}$ in the dual co-disposal microcosm and $\geq 25\ 000\ \text{mg l}^{-1}$ in the co-disposal microcosm (Figure 3.31).

Leachate recycle promoted an increase in pH to 6.76 in the dual co-disposal microcosm but affected the pH of the refuse control to a lesser extent. In contrast, sodium carbonate addition to the control effected an increase in pH but, surprisingly, an increase in pH was also recorded for the co-disposal microcosm although no attempt was made to ameliorate the unbalanced fermentation in this column.

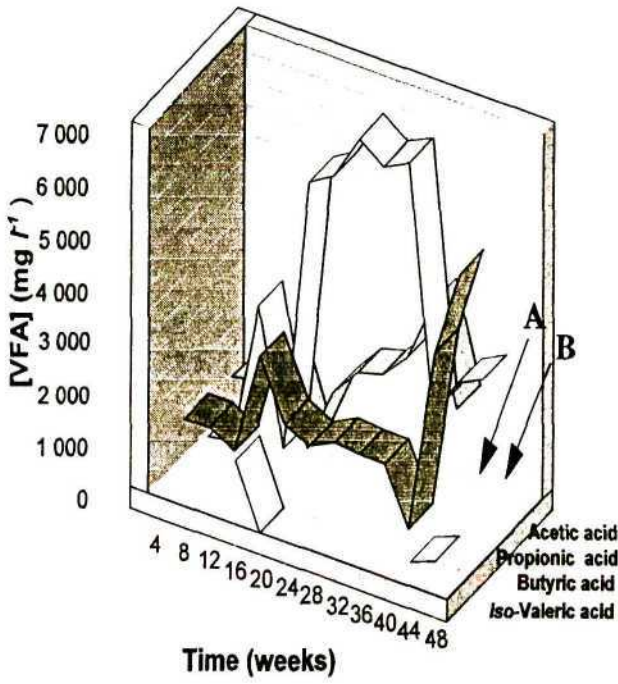
A decrease in the leachate COD to $\leq 1\ 600\ \text{mg l}^{-1}$ was recorded in the co-disposal microcosm between weeks 42 and 48 whereas a similar decrease in the refuse control was only achieved after the addition of sodium carbonate.

Redox Potential

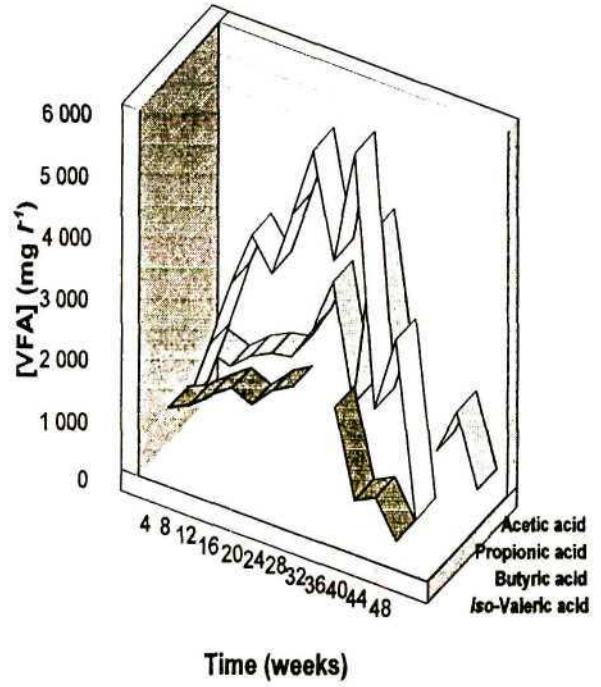
Initial low redox values were recorded for the three columns followed by increases which peaked at +150 mV for the dual co-disposal microcosm (Figure 3.32). These increases were followed by decreases after recycling operation was initiated in the dual co-disposal microcosm.

Figure 3.29 Changes in the concentrations of acetic, propionic, butyric and *iso*-valeric acid in the leachates of microcosms subjected to packing regimes of refuse (control) (C7) (a), refuse plus activated sewage sludge (C8) (b) and refuse plus activated sewage sludge plus phenol (C9) (c) and operated under closed culture conditions following macronutrient plus trace element supplementation (A = leachate recycle; B = sodium carbonate addition).

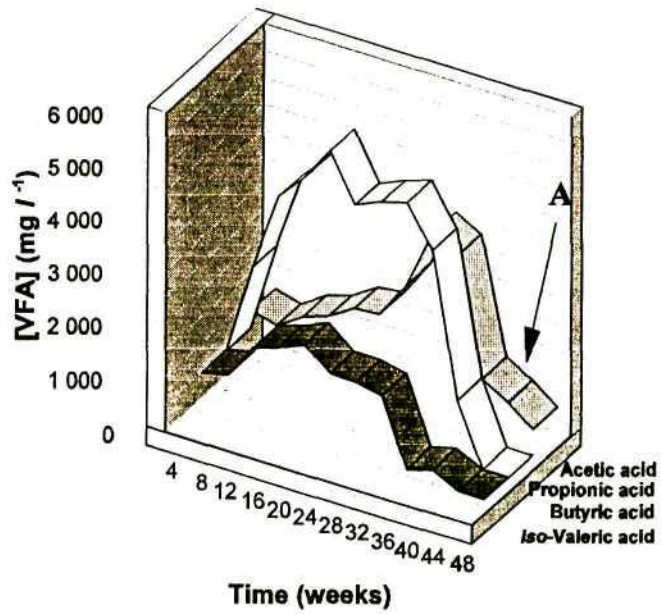
FIG 3.29 a.



b.



c.



Slight decreases were also recorded in the other two microcosms in week 42, whereafter larger decreases were recorded, especially in the co-disposal microcosm which was not subjected to recycling or sodium carbonate addition.

Nitrate, Nitrite and Ammonium

The changes in the leachate nitrate concentrations in the three microcosms were surprising (Figure 3.33) as the microcosms were operated with no air ingression.

A possible explanation, as discussed earlier (3.3.1), was the presence of heterotrophic nitrifying bacteria which are active in low pH environments. The nitrite "peaks" recorded in the control and co-disposal microcosms (Figure 3.34) could have been due to dissimilatory nitrate reduction facilitated by the initial E_h .

Throughout, the dual co-disposal microcosm was characterized by the lowest nitrite concentrations and these were attributed to phenol inhibition of the nitrate-reducing bacteria.

The ammonium concentration increases recorded in the refuse control and co-disposal microcosms from week 11 (Figure 3.35) are difficult to explain as dissimilatory nitrate reduction or ammonification should have been limited by the high E_h values (> 0 mV) (Figure 3.32) as dissimilatory nitrate reduction occurs at approximately -200 mV (Atlas, 1984). Assimilatory nitrate reduction, though operational under oxic conditions, seems unlikely to have contributed to the ammonium increases because it does not result in the accumulation of high concentrations of extracellular NH_4^+ (Atlas and Bartha, 1993). Also, nitrate removal was not recorded. The ammonium concentrations decreased after week 36 in the three columns. The reduced E_h values measured should have facilitated dissimilatory nitrate reduction thus leading to increases in the ammonium concentrations.

Figure 3.30 Changes in leachate pH of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient plus trace element supplementation (A = leachate recycle; B =sodium carbonate addition).

Figure 3.31 Changes in leachate COD of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient plus trace element supplementation (A = leachate recycle; B =sodium carbonate addition).

Figure 3.32 Changes in leachate redox potential of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient plus trace element supplementation (A = leachate recycle; B =sodium carbonate addition).

Figure 3.33 Changes in leachate nitrate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient plus trace element supplementation (A = leachate recycle; B = sodium carbonate addition).

FIG 3.30

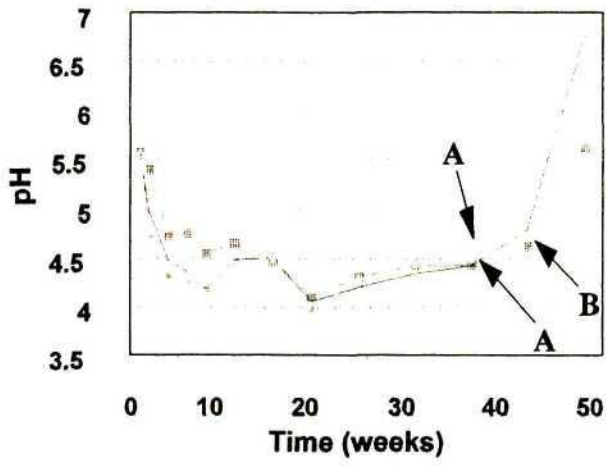


FIG 3.31

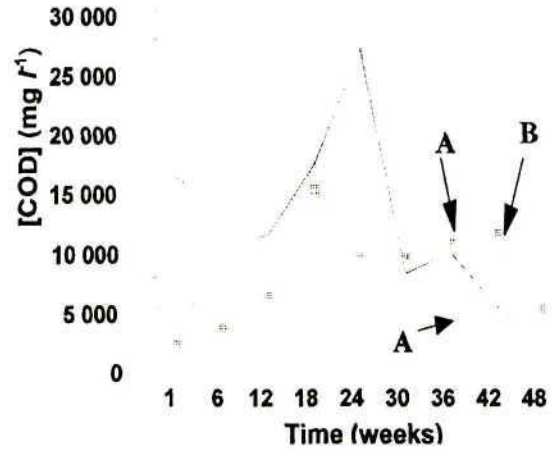


FIG 3.32

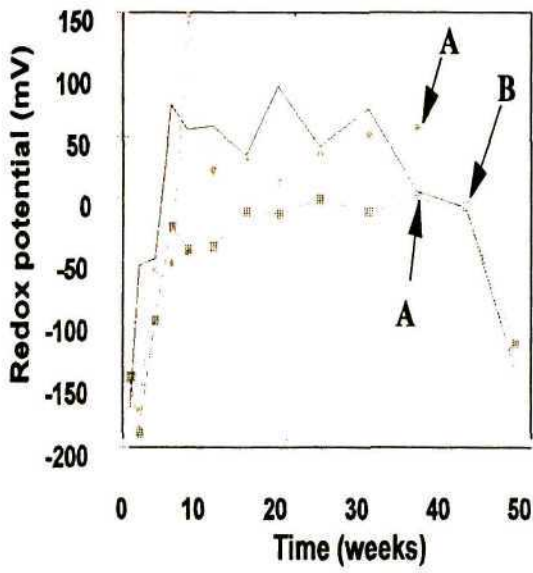
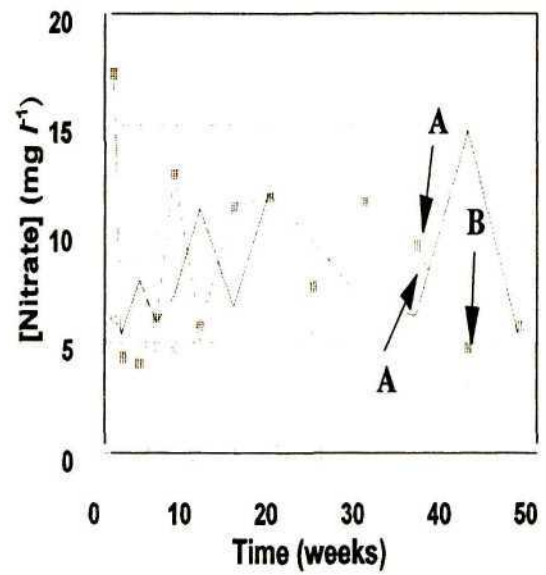


FIG 3.33



Sulphate

The three microcosms were characterized by high leachate sulphate concentrations ($\geq 300 \text{ mg l}^{-1}$) (Figure 3.36) which were maintained probably due to the elevated pH values (Figure 3.30) and redox potentials (Figure 3.32) which were not conducive to the reduction of sulphate. The reduced sulphate concentration at week 24 in the dual co-disposal microcosm possibly reflected sulphate-reducing bacteria development in microniches where the conditions were favourable.

The decreases in the redox values (after week 35) did not facilitate active sulphate reduction in the refuse control although sulphate-reducing bacteria appeared to establish in the co-disposal microcosms as precipitation of zinc sulphide was observed in the gas traps.

A low H_2S concentration (9ppm) was recorded in week 6 in the refuse control gas headspace.

Methane

No methane was detected by headspace gas analysis.

Phosphate

High phosphate concentrations were measured (Figure 3.37) and these were attributed to macronutrient supplementation (K_2HPO_4 , 1.5 g l^{-1} ; NaH_2PO_4 , 0.85 g l^{-1}). Throughout, high phosphate concentrations were recorded in the three microcosms which suggested minimal microbial uptake or chemical precipitation. The low pH values (Figure 3.30) and the promotion of cell autolysis (3.3.2) may also have contributed to the maintenance of these phosphate concentrations.

Figure 3.34 Changes in leachate nitrite concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient plus trace element supplementation (A = leachate recycle; B =sodium carbonate addition).

Figure 3.35 Changes in leachate ammonium concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient plus trace element supplementation (A = leachate recycle; B =sodium carbonate addition).

Figure 3.36 Changes in leachate sulphate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient plus trace element supplementation (A= leachate recycle; B = sodium carbonate addition).

Figure 3.37 Changes in leachate phosphate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient plus trace element supplementation (A= leachate recycle; B =sodium carbonate addition).

FIG 3.34

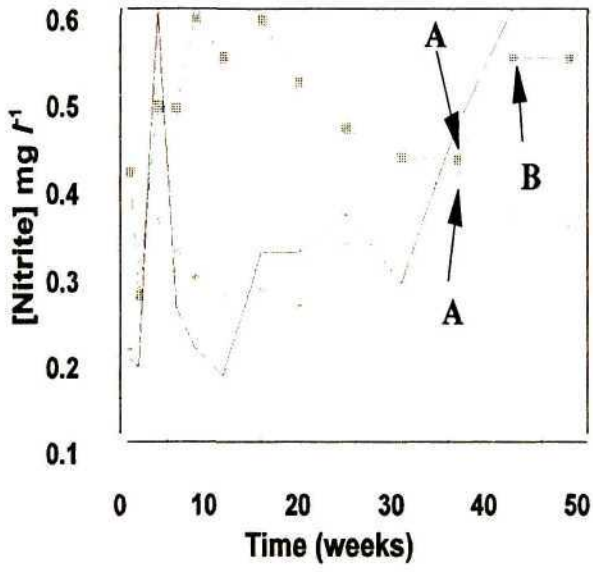


FIG 3.35

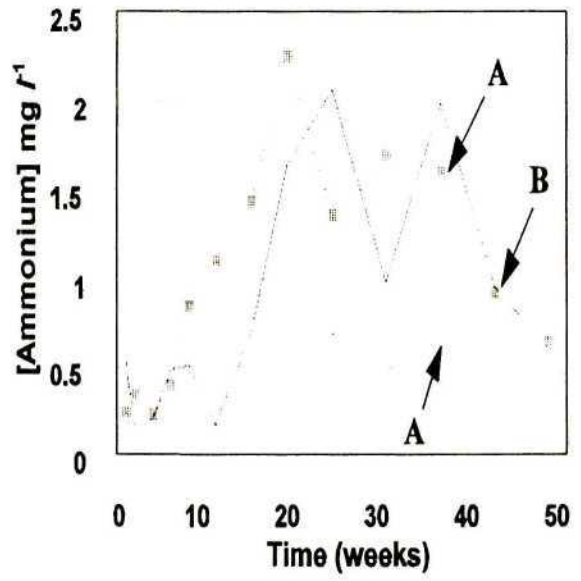


FIG 3.36

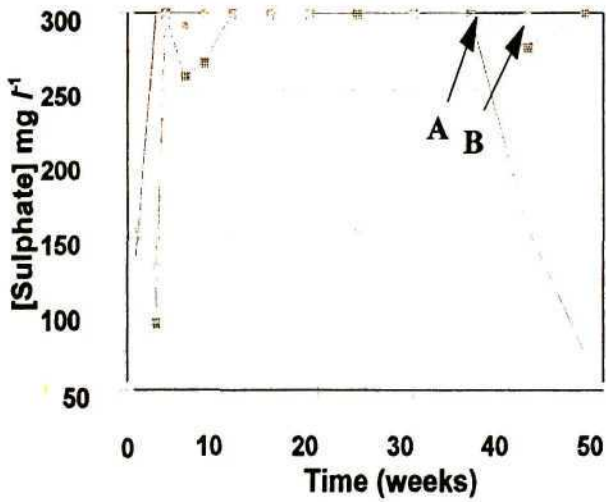
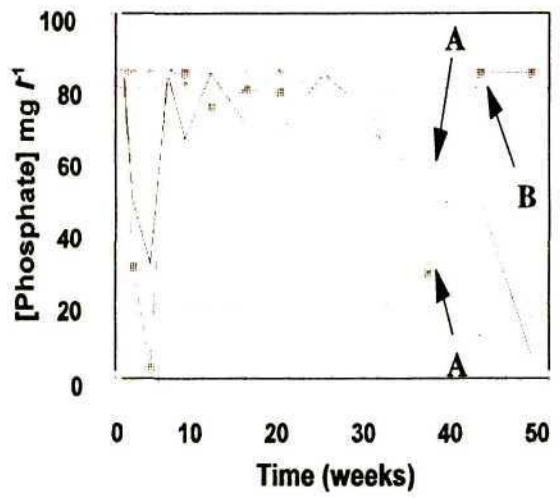


FIG 3.37



For all three microcosms, the trends resulting after week 24 were possibly due to chemical precipitation and microbial uptake as the pH changes recorded (Figure 3.30) were conducive for the establishment of a phosphate-utilising population.

3.3.5 Phenol Catabolism

The initial low residual phenol concentrations (Figure 3.38) could possibly be attributed to adsorption on the refuse / activated sewage sludge matrix or the presence of anaerobic or facultative anaerobic phenol degraders although it is unlikely that such microbial populations could have developed in such a short time. Also, limited liquid movement through these microcosms would mean a limited chance of desorption occurring.

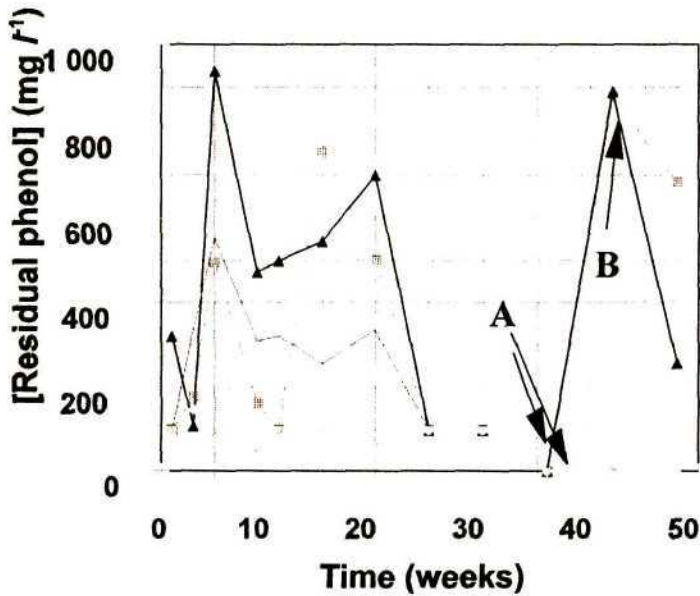


Figure 3.38 Leachate phenol concentrations of dual co-disposal microcosms supplemented with macronutrients (■), trace elements (▲), macronutrients plus trace elements (+) and distilled water (Control) (●) (A = leachate recycle; B = sodium carbonate addition).

The subsequent low pH values recorded in the macronutrient (3.3.2), trace element (3.3.3) and macronutrient plus trace element supplemented microcosms (3.3.4) should have influenced the rapid desorption of the phenol from the refuse / sewage sludge matrix thereby leading to an increase in residual phenol concentrations in the leachates (Figure 3.38).

The low pH values should also have increased the bactericidal/bacteriostatic effects of the phenol (Percival ,1996).

Since phenol degraders require a very low hydrogen partial pressure for metabolism the molecule must be catabolized by species in syntrophy with hydrogen- and acetate-consuming microorganisms (Thauer *et al.*, 1977).

Thus, with elevated VFA concentrations recorded in the macronutrient-supplemented microcosm (A3), a high hydrogen partial pressure probably persisted thus inhibiting the phenol-catabolizing population.

However, despite the fact that unfavourable physiological conditions for phenol catabolism were present complete removal was recorded by week 36 for all four microcosms. Perhaps surprisingly, for the macronutrient-supplemented and trace element-supplemented microcosms dramatic residual phenol concentration increases were recorded in week 42. At this point, leachate recycle was practised with the latter and could have accounted for phenol desorption. This explanation does, however, seem unlikely since the macronutrient-supplemented microcosm without leachate recycle also recorded elevated residual phenol concentrations.

The control microcosm was characterized throughout by a phenol concentration of $< 100 \text{ mg l}^{-1}$.

3.4 Conclusions

As co-disposal (in this study with activated sewage sludge) and dual co-disposal (with activated sewage sludge and phenol) are superimpositions on the refuse fermentation, the effects of these on the solid-state fermentation were investigated.

A batch culture strategy was chosen, although it is not representative of all landfill co-disposal operations where fed-batch is often employed, to investigate the effects of macronutrient/trace element supplementations.

From the results it was concluded that nutrient limitation is not necessarily rate-limiting for refuse catabolism either alone or following co-disposal with phenol and/or waste activated sewage sludge. Anaerobic catabolism of phenol quickly established in the presence/absence of macronutrient/trace element supplementation.

Perhaps surprisingly, nutrient supplementation of the co-disposal microcosms had, in most cases, a detrimental effect on the fermentation. In the presence of macronutrients and macronutrients plus trace elements, low pH values with elevated VFA and COD concentrations resulted. The redox potentials also appeared to militate against anaerobic catabolism. In contrast, the refuse control microcosm retained a balanced fermentation in the presence of the macronutrient supplementation.

The addition of trace elements to the macronutrients probably exacerbated the problem in the co-disposal columns. The results of the leachate sulphate and phosphate analyses supported this contention as limited uptake and utilization or chemical precipitation were recorded.

The phenol co-disposal microcosm in the presence of, for example, trace elements "soured" whereas the dual co-disposal microcosm progressed favourably. Phenol co-disposal had no obvious effect on the overall fermentation.

Leachate recycling and the addition of an alkali (sodium carbonate) to the microcosms were the strategies employed in attempts to reinstate the unbalanced ("soured") fermentations in the dual co-disposal microcosm (trace element-supplemented group) and in the refuse control and dual co-disposal microcosms (macronutrient plus trace element-supplemented group). Leachate recycling effected an increase in the pH and a reduction in the E_h in the dual co-disposal microcosm supplemented with macronutrients plus trace elements whereas it had no effect on the solid-state fermentations in the other two microcosms. The addition of the sodium carbonate seemed to have a limited positive influence on leachate quality.

Surprisingly, the refuse fermentation in the macronutrient plus trace element-supplemented co-disposal microcosm progressed favourably as indicated by leachate pH increases and COD decreases and the onset of sulphate reduction after 42 weeks.

Refuse in sanitary landfill sites has been considered to be nutrient deficient (Cossu, Blakey and Trapani, 1987; Pacey, 1989). Rees (1980) and Senior and Balba (1991), however, concluded that refuse masses are not characterized by nutrient limitations since phosphorus and nitrogenous compounds appear in landfill leachate and the refuse *per se* contains concentrations of nitrogen and phosphorus in excess of those required for forming bacterial biomass. It has been reported in the literature (Speece and Parkin, 1986) that trace elements have a beneficial effect on anaerobic digestion and Daneel (1996) observed favourable results with mineral salts supplementations to co-disposal (anaerobically digested sewage sludge / phenol with refuse) microcosms. These results were not repeated in the present study.

It is, however, important to note that refuse is not homogeneous and degradation occurs at different rates throughout the landfill since nutrients are unevenly distributed and used at different rates (Rees, 1980; Röhrs, Fourie and Blight, 1998).

If refuse is considered nutrient deficient then co-disposal with sewage sludge, which contains relatively high concentrations of nitrogen and phosphorus (median concentrations for South African sludge approximate to 2.89% and 1.35 % (m/m dry weight), respectively (Smith and Vasiloudis, 1989; Ratsak, Maarsen and Kooijman Salm, 1996)) may be complementary to refuse catabolism.

Any attempts to promote the co-disposal of phenol in the presence of sewage sludge by macronutrient/trace element supplementation must be exercised with extreme care and must only be applied to anaerobically digested sludge (Daneel, 1996; Röhrs *et al.*, 1998) since the same addition(s) to waste activated sludge may result in compromised leachate quality.

CHAPTER 4

Investigation of the Retention / Mobility of Four Heavy Metals in Co-Disposal Microcosms of “Young” Synthetic Refuse plus Activated Sewage Sludge

4.1 Introduction

Heavy metals are present in a range of industrial wastes, as they are used in a huge variety of industrial processes, and industrial and household products and are, therefore, components of household refuse (Roberts, 1983; Knox, 1989). Since the chemical and environmental behaviours of heavy metals vary widely and they are non-biodegradable (Knox, 1989), the fates of heavy metals are important aspects of co-disposal.

Three major potential effects of heavy metals in landfill bioreactors can be identified (Knox, 1989):

1. The concentrations may reach high enough levels to influence refuse degradation;
2. The capacity of the landfill to immobilize and retain heavy metals may be exceeded leading to appearances at elevated concentrations in leachates; and
3. They could be re-released at some time in the future as a results of changes in environmental conditions within the landfills.

The toxicity of heavy metals in anaerobic digestion depends on the various chemical forms which may result at specific temperature, pH and E_h (1.14.1) values (Ahring and Westermann, 1983). The mechanisms involved in maximizing or minimizing their inhibitory effects include the metal binding capacity of a particular sludge (1.14.2), the ion and organic constituent interactions (1.14.1) and the specific dissolved metal species present and their concentrations (Mueller and Steiner, 1992).

For this investigation of immobilization / mobilization of heavy metals during co-disposal operation, four species were chosen on the basis of their variable mobilities and presence in refuse and sewage sludge.

Nickel, copper, chromium and zinc have show different retention patterns in refuse with the general order of $Cr > Cu > Ni = Zn$ (Jones and Malone, 1982). Researchers have reported the following concentration ranges ($mg\ kg^{-1}$ dry weight) in refuse and sewage sludge, respectively: 210 - 4 575 (Zn), 65 - 6 750 (Cu), 10 - 400 (Ni), 11 - 256 (Cr) (Stevens and Jenkins, 1982; Campbell, 1983; Young *et al.*, 1984); and 1 300 - 4 700 (Zn), 463 - 760 (Cu), 28 - 76 (Ni), 81 (Cr) (Berrow and Burrige, 1979; MacNicol and Beckett, 1989).

The present study was made with the principal objective of investigating the mobility of four metal species (Zn^{2+} , Cu^{2+} , Cr^{3+} and Ni^{2+}) in co-disposal (refuse plus activated sewage sludge) microcosms.

4.2 Experimental

4.2.1 Refuse

See section 2.1.2.

4.2.2 Sewage Sludge

For this study, the waste activated sewage sludge was not centrifuged. To determine the moisture content, two samples (100g each) were dried at $70^{\circ}C$ for 72 h and weighed as before.

4.2.3 Construction and Operation of Microcosms

Six glass columns (length 50 cm, i.d. 5.3 cm) (Percival, 1996) were used. The microcosms were packed with synthetic refuse and/or sewage sludge (Table 4.1). Two refuse : sewage sludge packing ratios were used: 4.1:1 and 4.1:2.

The operation strategy (empty bed working volume, initial dilution rate, collection of H_2S) was the same as described above (3.2.1). The refuse packing density was $830\ kg\ m^{-3}$. Leachate was recycled daily by removing 40 ml from the base of each microcosm with a hypodermic needle connected to a plastic syringe (20 ml) and reintroducing it to the top of the column.

Table 4.1. Packing materials and heavy metal loadings

MICROCOSM No.	PACKING MATERIALS	HEAVY METAL LOADING
1.	Refuse + sludge (4.1:1)	Heavy metal "spiked" sludge (100 mg l ⁻¹)
2.	Refuse + sludge (4.1:1)	Sludge not "spiked"
3.	Refuse + sludge (4.1:2)	Heavy metal "spiked" sludge (200 mg l ⁻¹)
4.	Refuse + sludge (4.1:2)	Sludge not "spiked"
5.	Refuse	dH ₂ O plus heavy metal (200 mg l ⁻¹)
6.	Refuse control	dH ₂ O

Heavy Metals

The activated sewage sludge was "spiked" with heavy metal salts prior to introduction into the microcosms. One hundred mg l⁻¹ (refuse : sludge ratio 4.1:1) and 200 mg l⁻¹ (refuse : sludge ratio 4.1:2) each of nickel sulphate (Ni²⁺), zinc sulphate (Zn²⁺), cupric chloride (Cu²⁺) and chromium chloride (Cr³⁺) were dissolved in the sludge supernatant.

Refuse Control Microcosms

For Microcosm 5, 200 mg l⁻¹ of each of the chosen heavy metal salts were dissolved in distilled water prior to addition while distilled water alone was added to Column 6.

Increases in Heavy Metal Dosages

The heavy metal dosages of Microcosms 1,3 and 5 were increased from week 11 by dissolving the salts in distilled water and applying the resulting solution (4.1:1, 30 ml; 4.1:2, 60 ml) at each dosage point by means of plastic syringes (20 ml) at an irrigation rate of 10 ml h⁻¹.

The concentrations added to each of the microcosms for each metal were as follows: 150 mg l^{-1} , Microcosm 1 and 300 mg l^{-1} , Microcosms 3 and 5, week 11; 200 mg l^{-1} , Microcosm 1 and 400 mg l^{-1} , Microcosms 3 and 5, week 13; 400 mg l^{-1} , Microcosm 1 and 800 mg l^{-1} , Microcosms 3 and 5, week 14; and 800 mg l^{-1} , Microcosm 1 and 1 600 mg l^{-1} , Microcosms 3 and 5, week 15. The unspiked microcosms received equivalent volumes of distilled water at each dosage point.

4.3 Results and Discussion

Leachate from each microcosm was analysed for pH, redox potential and heavy metal concentrations. The moisture content of the refuse and sewage sludge was 45.5 % (m/m) and 89 % (m/m), respectively.

4.3.1 pH

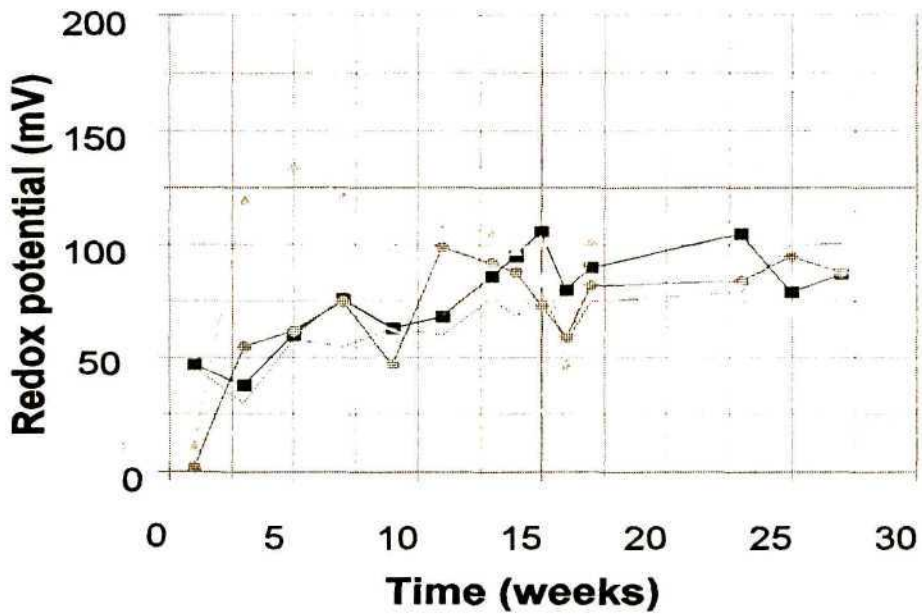
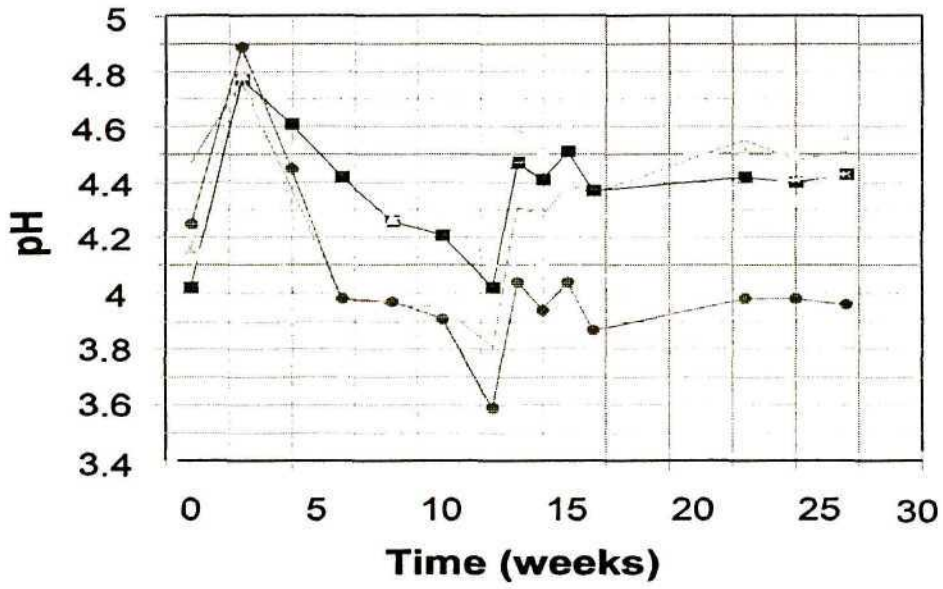
Low pH values (≤ 4.8) (Figure 4.1) were recorded during the 27-week study period. The “young” synthetic refuse used, which contained freshly sampled vegetable and garden waste material, probably facilitated the production of volatile fatty acids (VFA) during the solid-state fermentation process (1.7.1) which, in turn, effected the pH. The presence of heavy metals did not facilitate the low pH values due to heavy metal toxicity and, specifically, the inactivation of hydrogen sinks such as the methanogens as the un-supplemented microcosms (Microcosms 5 and 6) exhibited comparable trends.

4.3.2 Redox Potential

The redox potentials recorded did not approach the optimum for the solid-state refuse methanogenic fermentation and were in the range of +2 to +170 mV (Figure 4.2). The metal-supplemented and non-supplemented microcosms recorded comparable leachate redox potentials.

Figure 4.1 Changes in leachate pH of Microcosms 1 (+), 2 (▼), 3(■), 4 (✕), 5 (▲) and 6 (●) packed as detailed in Table 4.1.

Figure 4.2 Changes in leachate redox potentials of Microcosms 1 (+), 2 (▼), 3(■), 4 (✕), 5 (▲) and 6 (●) packed as detailed in Table 4.1.



With the use of fresh organic waste material in the microcosms and as nitrification by heterotrophic nitrifying bacteria is active in both low pH (Focht and Chang, 1975) and low oxygen (Van Niel *et al.*, 1993) environments, with nitrate stable under oxidising conditions at pH values > 3 (Bohn, McNeal and O'Conner, 1979), the influences of nitrates on the redox potential are important. These effects have been documented (Bohn *et al.*, 1979; Bartlett, 1981). In particular, the presence of nitrates is indicative of high positive E_h values which, in turn, favour the existence of oxidised species. Thus, the NO_3^- concentration may limit reduction. In this study, the conditions in the microcosms did not favour nitrate reduction as self-generating redox gradient did not establish. Nitrate reduction is usually active at $\pm + 420$ mV (Atlas, 1984).

4.3.3 Heavy Metal Mobility and Immobilisation

The chromium, copper, nickel and zinc mass of the solid and liquid fractions of refuse and sewage sludge after centrifugation (2.3.9) and the total mass loading applied to each microcosm are presented in Table 4.2. The table also details the metals released and percentages not immobilized.

Refuse Control Microcosms

Comparing the heavy metal concentrations leached from Microcosms 5 and 6, elevated Ni concentrations were detected with the former (total mass leached 2.7 mg, compared to 0.43 mg from Microcosm 6) (Figures 4.3c and 4.4c). A dramatic increase was particularly evident after the metal dosages had been increased to the highest concentration. The concentration measured in the supernatant at the 40 cm sampling depth (54.46 mg l^{-1}) was also higher than Microcosm 6 (5.87 mg l^{-1}) (Table 4.3). Although Microcosm 5 received an applied Ni dosage, > 99 % immobilized compared to ~ 98.04 % immobilisation in Microcosm 6. The Ni holding capacity of the refuse was not exceeded by the dosage increases thus facilitating low leachate concentrations. Comparatively similar Cr and Cu concentrations were detected in the leachates of the two microcosms (Figure 4.3a,b and 4.4a,b) although higher Cu concentrations were initially measured in Microcosm 5.

Table 4.2. Chromium, copper, nickel and zinc mass (mg) of the solid and liquid fractions of refuse and sewage sludge, total heavy metal loadings applied (mg), metals released (mg) and percentages not immobilized for each microcosm

	Chromium	Copper	Nickel	Zinc
Initial Mass				
Synthetic Refuse:				
Supernatant	0	2.45	4.95	12.23
Solid	24.85	3.49	17.0	52.75
Total:	24.85	5.94	21.95	64.98
Sewage Sludge:				
Supernatant	0.003	0.02	0.013	0.01
Solid	26.63	20.06	18.31	373.65
Total:	26.63	20.08	18.32	373.66
Total (Refuse plus Sludge):	51.48	26.02	40.27	438.64
Heavy Metal Loadings:				
Microcosm 1 (4.1:1)	65.7	65.7	65.7	65.7
Microcosms 3,5 (4.1:2)	250	250	250	250
Microcosm 1 (4.1:1)				
Total Initial Mass	51.48	26.02	40.27	438.64
Heavy Metal Loading	65.7	65.7	65.7	65.7
Mass Leached	0.2	0.13	1.88	7.85
% Not Immobilised	~0.17	~0.14	~1.77	~1.56
Microcosm 2 (4.1:1)				
Total Initial Mass	51.48	26.02	40.27	438.64
Mass Leached	0.08	0.06	0.21	1.5
% Not Immobilised	~0.16	~0.23	~0.52	~0.34
Microcosm 3 (4.1:2)				
Total Initial Mass	51.48	26.02	40.27	438.64
Heavy Metal Loading	250	250	250	250
Mass Leached	0.81	0.17	2.01	5.41
% Not Immobilised	~0.27	~0.06	~0.69	~0.79

Table 4.2. Continued

	Chromium	Copper	Nickel	Zinc
Microcosm 4 (4.1:2)				
Total Initial Mass	51.48	26.02	40.27	438.64
Mass leached	0.07	0.08	0.19	1.46
% Not Immobilised	~0.14	~0.31	~0.47	~0.33
Microcosm 5 (4.1:2) Control				
Total Initial Mass (Refuse)	24.85	5.93	21.95	64.98
Heavy Metal Loading	250	250	250	250
Mass Leached	0.15	0.15	2.71	6.23
% Not Immobilised	~0.05	~0.06	~0.99	~1.98
Microcosm 6 (4.1:2) Control				
Total Initial Mass (Refuse)	24.85	5.93	21.95	64.98
Mass Leached	0.17	0.06	0.43	17.55
% Not Immobilised	~0.68	~1.01	~1.96	~27

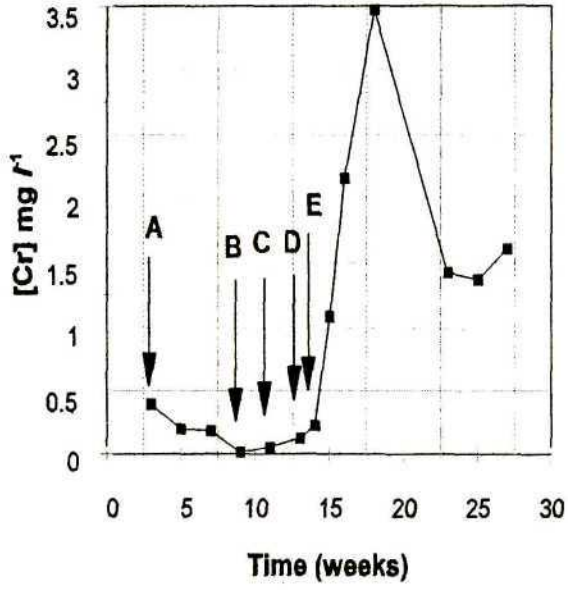
Following each dosage steady decreases resulted. Thus, the applied concentrations were probably adsorbed thus facilitating low leachate concentrations. For each metal comparable concentrations were displaced although the total mass of chromium (274.85 mg) was higher than the equivalent (255.93 mg) for copper.

The total zinc concentration leached in the 27 weeks of operation of Microcosm 6 was 17.55 mg while the initial mass in the refuse was 64.98 mg (Table 4.2). In contrast, for Microcosm 5, 6.23 mg were leached from a total (refuse plus loading) mass of 314.98 mg. This phenomenon where the mass of the metal leached from the microcosm with an applied dosage was lower than the control microcosm was also marginally apparent for chromium (Table 4.2).

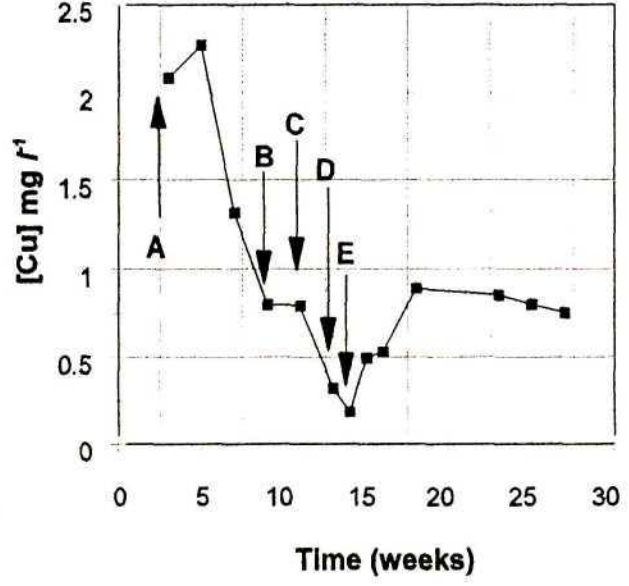
These results contrast but also support previous investigations. Young *et al.* (1984), for example, found that leachate chromium concentrations from metal-dosed (100 mg l^{-1}) microcosms of fresh pulverized refuse packed to a similar density as in the present investigation and operated for 6 months were no different from control microcosms while Zn concentrations fluctuated in both the dosed (100 mg l^{-1}) and control microcosms.

Figure 4.3 Changes in leachate Cr (a), Cu (b), Ni (c) and Zn (d) concentrations of Microcosm 5, packed with refuse alone, following metal supplementations of 200 mg l^{-1} (A), 300 mg l^{-1} (B), 400 mg l^{-1} (C), 800 mg l^{-1} (D) and 1 600 mg l^{-1} (E).

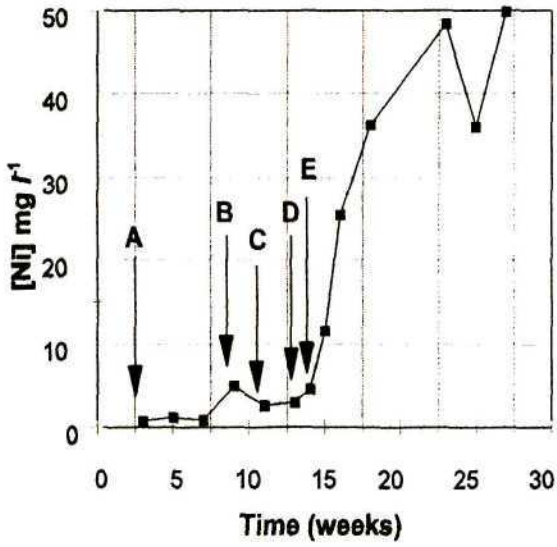
FIG 4.3a.



b.



c.



d.

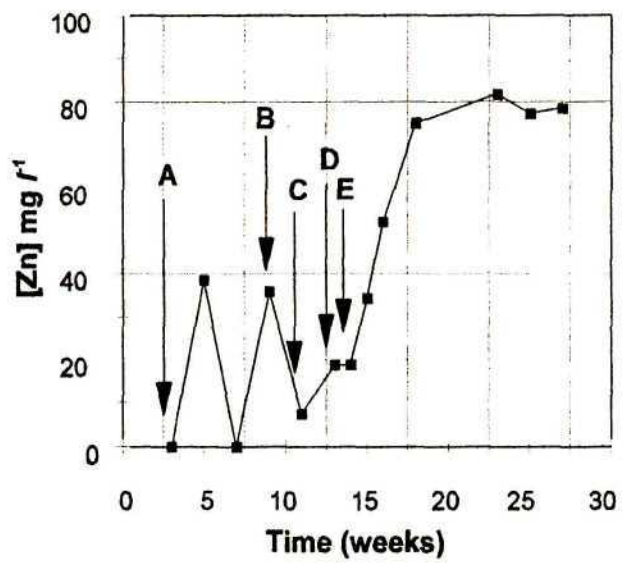
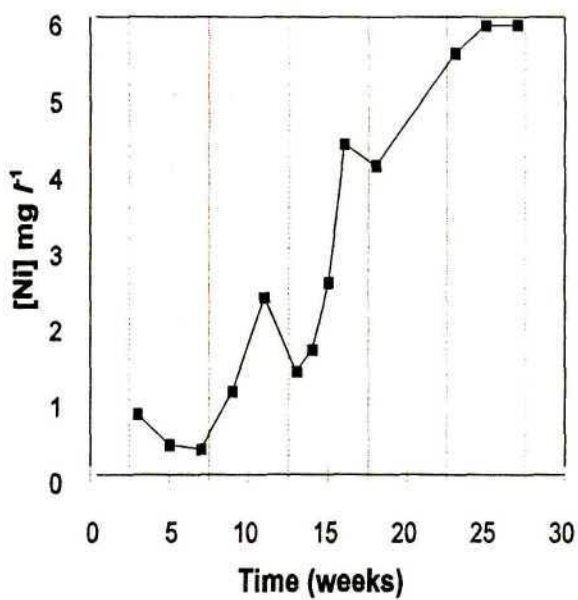
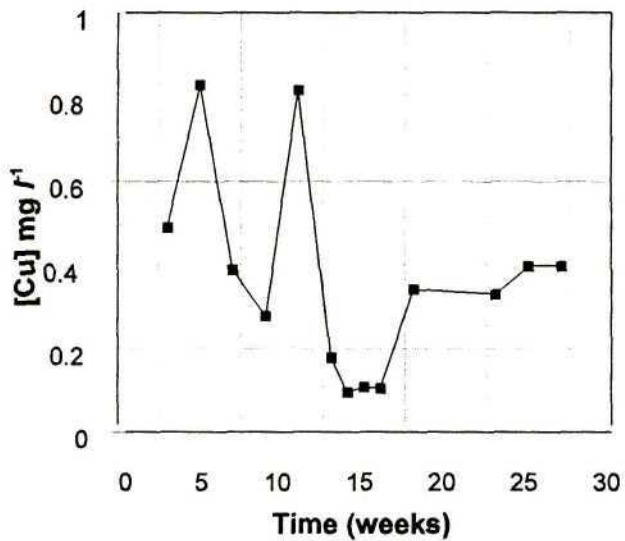
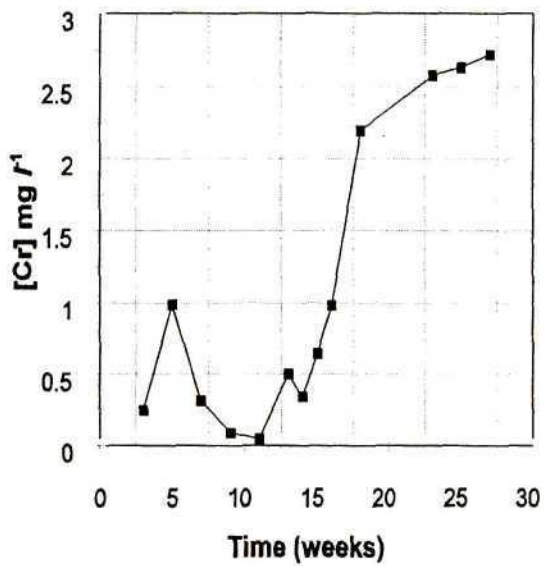


Figure 4.4 Changes in leachate Cr (a), Cu (b), Ni (c) and Zn (d) concentrations of Microcosm 6, packed with refuse alone.

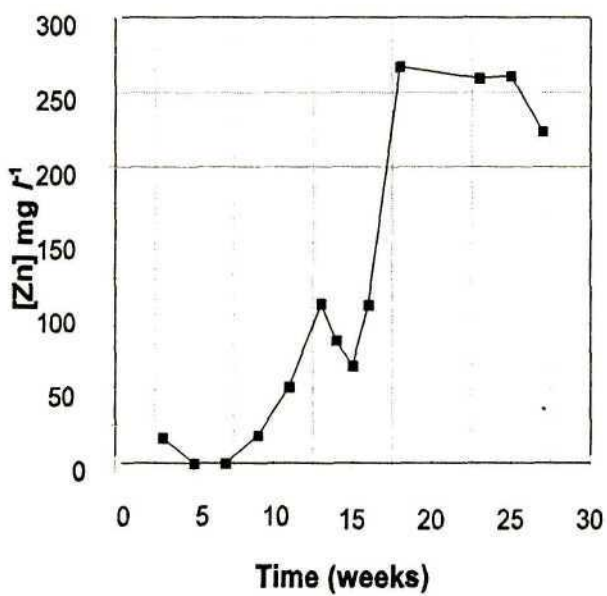
FIG 4.4a.

b.



c.

d.



Nickel exhibited distinct elevations in the leachate of metal-dosed columns while persisting concentrations in the interstitial leachates were also detected. According to their mass balances, ~ 10.2 % of the applied Ni remained as soluble fractions in the columns or leached out .

Dent, Baldwin and Pugh (1988) did not record elevated Cu and Zn concentrations in leachates of microcosms packed with "old" pulverized refuse loaded with Cu and Zn concentrations of 200 mg l^{-1} and 110 mg l^{-1} , respectively. Barber, Maris and Johnson (1980), Campbell, Emberton, Fletcher and Peck (1986) and Aldous, Blakey, Clark, Craft, Fleet and McNally (1988) recorded comparable Cu concentrations with control and experimental microcosms with a high proportion of the applied copper (578 mg kg^{-1} wet weight, Barber *et al.*, 1980; 452 mg kg^{-1} dry weight, Campbell *et al.*, 1986) removed from solution by the refuse (~ 99% adsorbed / immobilized). For chromium (applied dosage 578 mg kg^{-1} wet weight, concentration 5 700 mg l^{-1}), ~ 94 % immobilization resulted in 360 m³ lysimeters during an operation period of 177 weeks. For nickel, however, less removal was recorded (~ 70 % adsorbed) while < 0.5% of an applied Ni loading (98 mg kg^{-1} wet weight, concentration 2 500 mg l^{-1}) was detected in leachates with pH values of ≤ 3 (Dent *et al.*, 1988). In comparison, in this study ~ 0.99 % of the applied Ni (271.95 mg kg^{-1} wet weight) leached out with comparable pH values. It could thus be assumed that the Ni holding capacity of the refuse was exceeded with increased applied dosages.

Refuse Control vs Co-Disposal Microcosms

Comparing the heavy metal concentrations of the leachate of Microcosms 5 and 6 (Figures 4.3 and 4.4) and the co-disposal microcosms (Microcosms 1 - 4) (Figures 4.5 - 4.8), no distinct differences were detected in the metal-dosed columns for Cr and Cu (Figures 4.3a,b; 4.5a,b and 4.7a,b). For each an initial Cu "peak" was detected followed by a progressive decrease to low concentrations concurrent with the highest applied dosage after week 15.

When the percentages of Cu leached from the microcosms are taken in account (~ 0.14 %, Microcosm 1; ~ 0.06 % Microcosm 3; ~ 0.06 % Microcosm 5) (Table 4.2) it is apparent that the refuse/sludge Cu binding capacity were not exceeded. Nickel exhibited higher mobility than Cu and Cr (~ 1.77 %, Microcosm 1; ~ 0.69 %, Microcosm 3; ~ 0.99 %, Microcosm 5).

The refuse control microcosm (Microcosm 6) and unspiked co-disposal microcosms (Microcosms 2 and 4) showed variable Cr, Cu and Ni displaced masses (Table 4.2) and these variabilities were even more pronounced for Zn. It should be noted, however, that although the masses of zinc displaced were high, the immobilized masses were still high.

As sewage sludge was excluded from the controls, the cation exchange capacity (1.14.1) was possibly reduced. The metal binding characteristics of sludges have been discussed (1.14.2). In this study the presence of sludge appeared to have a minimal effect on heavy metal retention compared with the refuse microcosms. Thus, similar masses of Cr, Cu, Ni and Zn were displaced from Microcosms 2 and 4 (Table 4.2).

Co-Disposal Microcosms

Elevated Cr, Ni and Zn concentrations were measured in the leachates of metal-dosed microcosms (Microcosms 1 and 3) (Figures 4.5a,c,d and 4.7a,c,d) after week 15. Increases were also detected in the unspiked microcosms (Microcosms 2 and 4) (Figures 4.6a,c,d and 4.8a,c,d). Nickel and Zn showed distinct increases, with recorded leachate Zn concentrations $\geq 218 \text{ mg l}^{-1}$ (weeks 25 - 27) and $> 60 \text{ mg l}^{-1}$ (weeks 23 - 27) for Microcosm 1 and 3, respectively (Figures 4.5d and 4.7d). Although higher Ni and Zn concentrations were detected in the leachates of the metal-dosed microcosms compared with the unspiked columns, no specific trends in the totals leached compared with the initial loadings were recorded (Table 4.2). In contrast, the total Cu displaced never exceeded 0.17 mg thus it appeared that the Cu holding capacity had not been exceeded by either loading.

With the exception of chromium (Microcosm 3), the higher moisture contents of Microcosms 3 and 4 did not effect elevated metal mobilization although the intention was to maximize solubility.

The possibility existed that the prolonged acidic conditions that prevailed favoured free cations since it has been established that an acid pH and high E_h facilitate increased metal solubility (Wood and Wang, 1983). Metal adsorption (1.14.1) is usually enhanced at neutral pH (Ferris, Schultze, Witten, Fyfe and Beveridge, 1989) and as low pH trends (Figure 4.1) were recorded in all the microcosms, immobilization of the metals was not favoured. Despite this, the masses of Cr, Cu, Ni and Zn displaced were low compared with the original loadings (0.81, 301.48; 0.17, 276.02; 2.01, 290.27; and 5.41, 688.64 mg).

Adsorbed / Immobilized Heavy Metal Concentrations

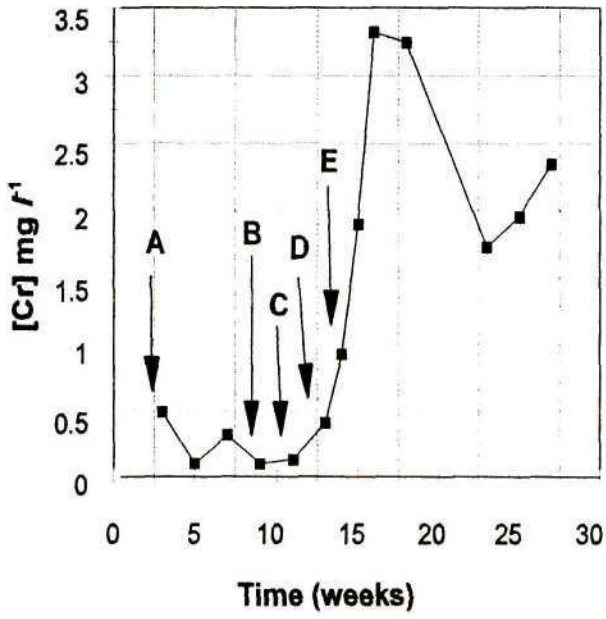
Figures 4.9-4.11 show the immobilized / adsorbed heavy metal concentrations measured at three sampling depths (15, 25 and 40 cm) in Microcosms 1, 3 and 5 after 28 weeks while Table 4.3 gives the concentrations of the solid and liquid fractions at the same sampling depths in Microcosms 1-6.

Microcosms 1,3 and 5 were characterized by chromium retention at a depth of 15 cm. In contrast, the nickel concentrations were comparable at the three different sampling depths while for copper and zinc no distinct patterns emerged.

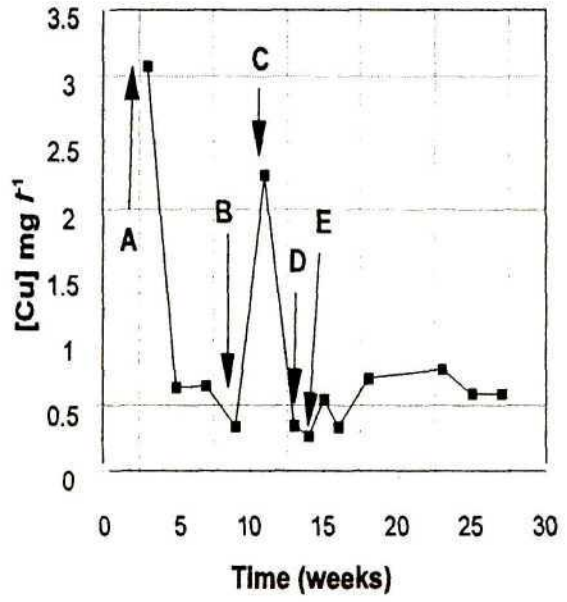
These results were comparable with previous investigations (Jones and Malone, 1982; Young *et al.*, 1984) where cation exchange and ionic radius (1.14.1) were found to play significant roles. With refuse microcosms (length 50 cm, i.d. 10 cm), Young *et al.* (1984) showed that with eight metal species, each applied at a concentration of 1 000 mg l⁻¹, metal immobilization tended to be consolidated near the surface of each column, with maximum retention in the top 20 cm of the refuse. Also, the interstitial fluids from the upper horizon of the dosed columns had high pH values and lower VFA concentrations than control microcosms. Acetogenesis appeared to be inhibited in the top 20 cm of the columns.

Figure 4.5 Changes in leachate Cr (a), Cu (b), Ni (c) and Zn (d) concentrations of Microcosm 1, packed with refuse plus activated sewage sludge (4.1:1), following metal supplementations of 100 mg l⁻¹(A), 150 mg l⁻¹(B), 200 mg l⁻¹ (C), 400 mg l⁻¹ (D) and 800 mg l⁻¹ (E).

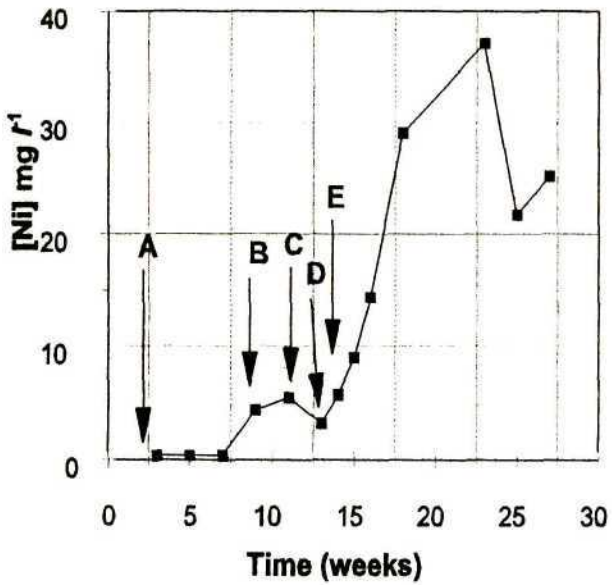
FIG 4.5a.



b.



c.



d.

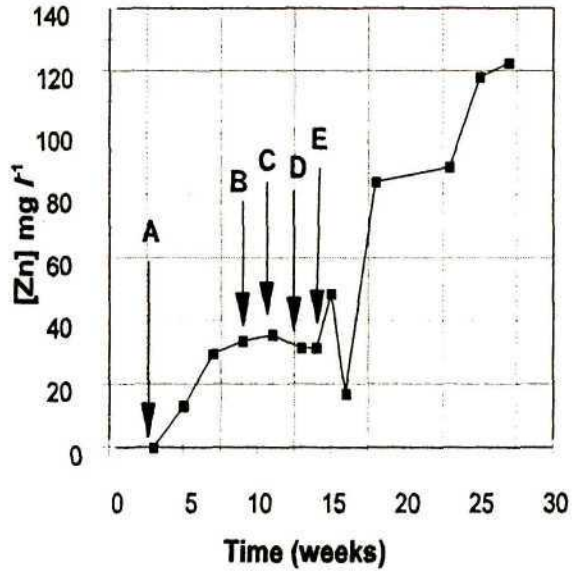
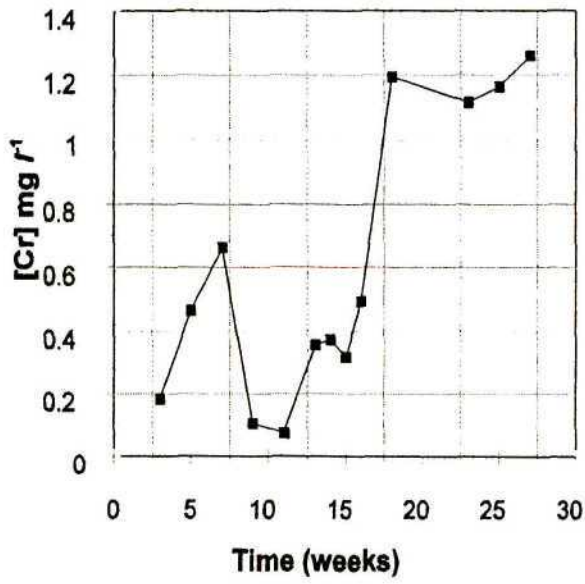
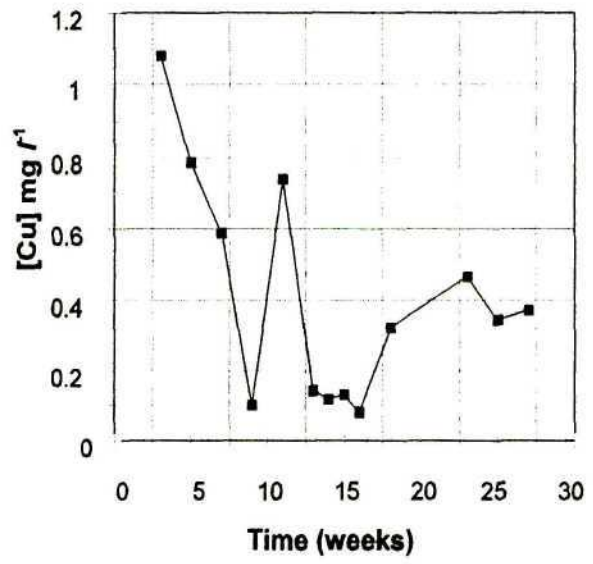


Figure 4.6 Changes in leachate Cr (a), Cu (b), Ni (c) and Zn (d) concentrations of Microcosm 2, packed with refuse plus activated sewage sludge (4.1:1).

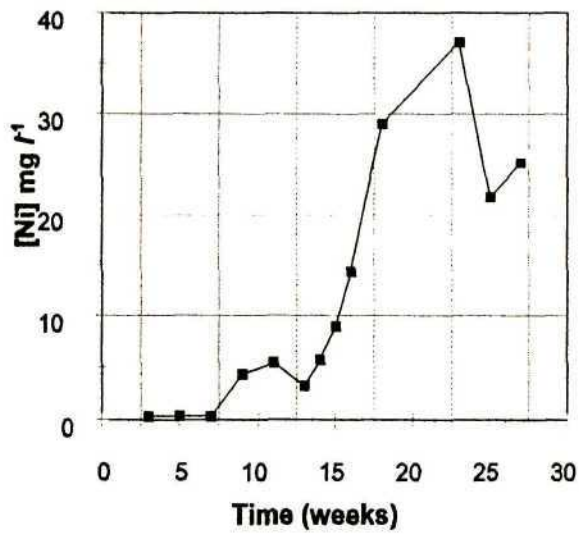
FIG 4.6a.



b.



c.



d.

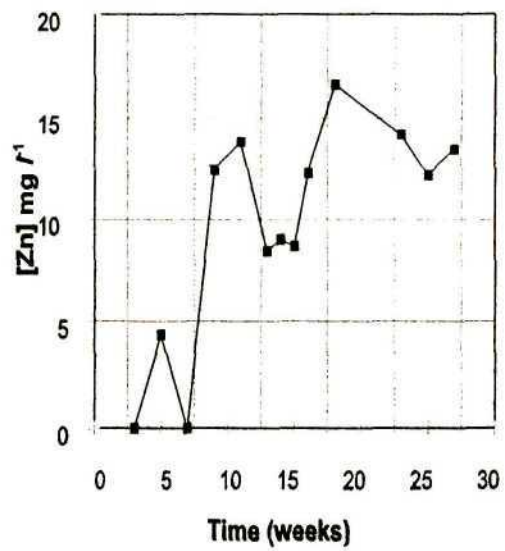
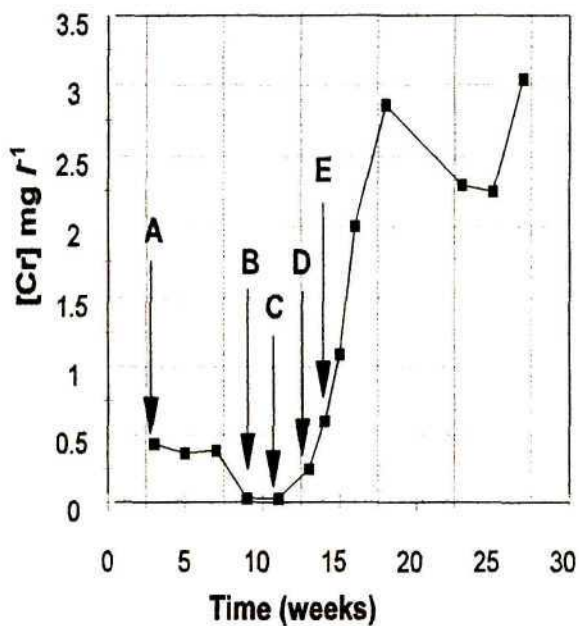
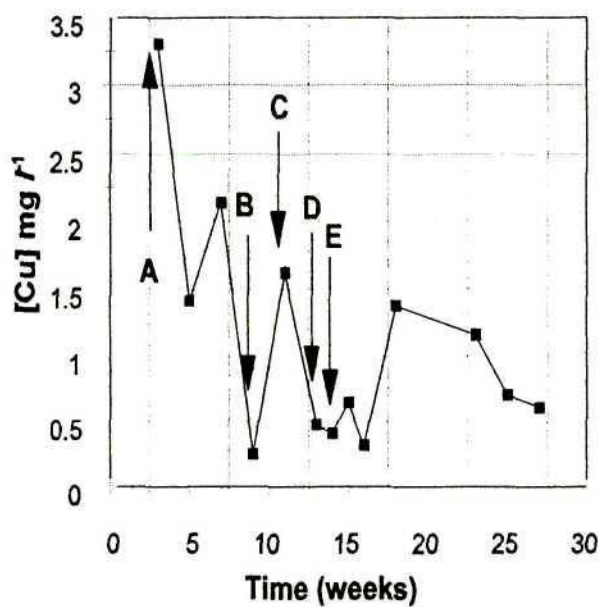


Figure 4.7 Changes in leachate Cr (a), Cu (b), Ni (c) and Zn (d) concentrations of Microcosm 3, packed with refuse plus activated sewage sludge (4:1:2), following metal supplementations of 200 mg l^{-1} (A), 300 mg l^{-1} (B), 400 mg l^{-1} (C), 800 mg l^{-1} (D) and 1600 mg l^{-1} (E).

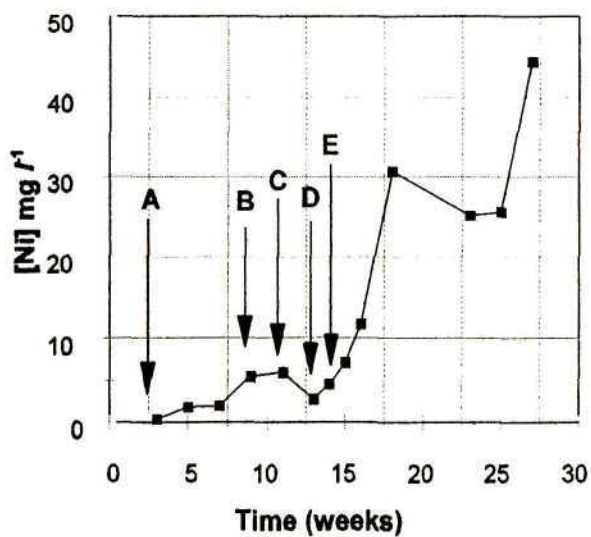
FIG 4.7a.



b.



c.



d.

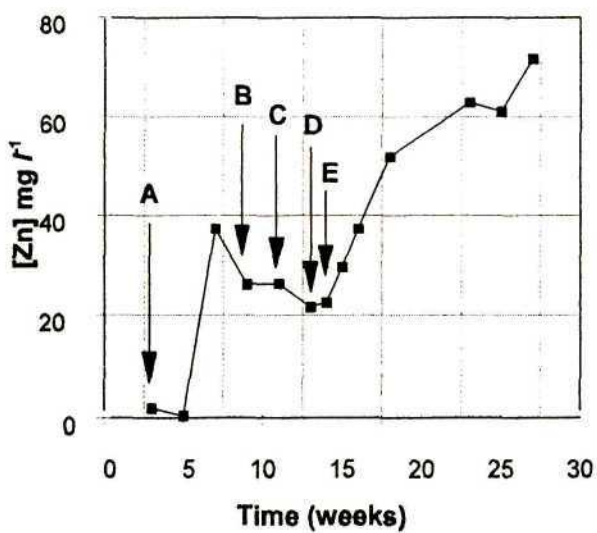
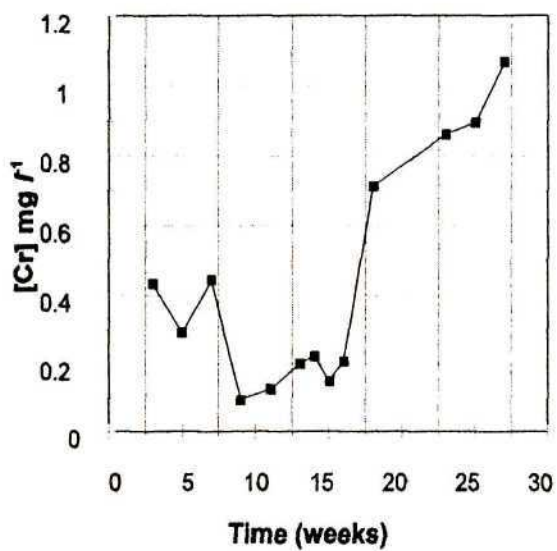
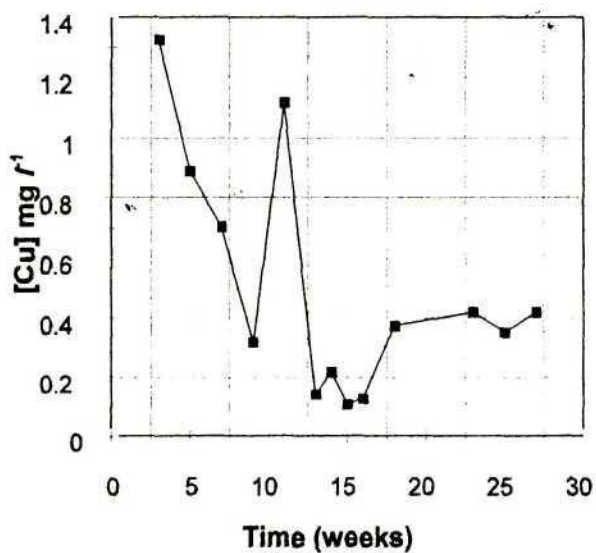


Figure 4.8 Changes in leachate Cr (a), Cu (b), Ni (c) and Zn (d) concentrations of Microcosm 4, packed with refuse plus activated sewage sludge (4.1:2).

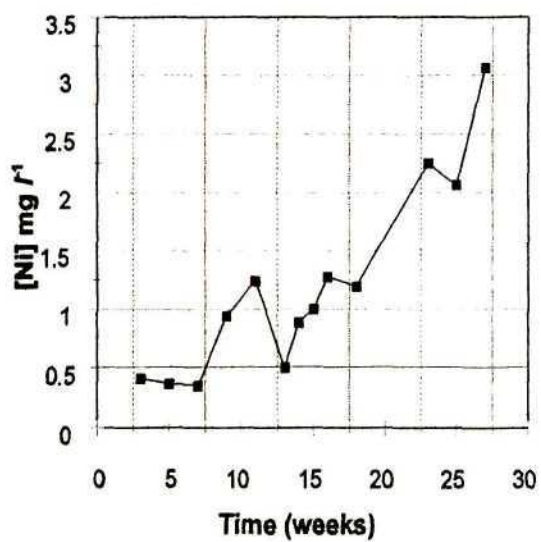
FIG 4.8a .



b.



c.



d.

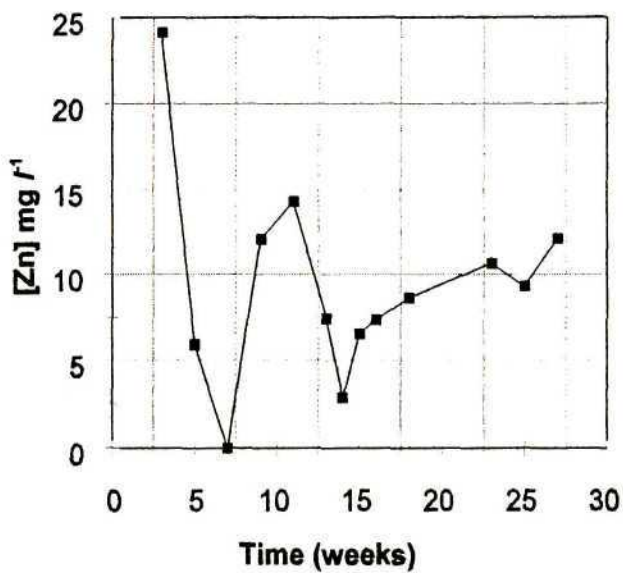


Table 4.3. Chromium, copper, nickel and zinc concentrations of the solid (mg kg^{-1} dry weight) and liquid (mg l^{-1}) fractions at three sampling depths (15, 25 and 40 cm) after 28 weeks of microcosm operation

		[Chromium]	[Copper]	[Nickel]	[Zinc]
Microcosm 1 Sample 1	Supernatant	N/A	N/A	N/A	N/A
	Solid	170.59	504.13	205.46	1 591.4
Microcosm 1 Sample 2	Supernatant	N/A	N/A	N/A	N/A
	Solid	85.57	220.73	238.17	1 705.85
Microcosm 1 Sample 3	Supernatant	N/A	N/A	N/A	N/A
	Solid	74.67	178.76	206.01	1 286.2
Microcosm 2 Sample 1	Supernatant	N/A	N/A	N/A	N/A
	Solid	21.26	68.67	98.64	223.45
Microcosm 2 Sample 2	Supernatant	1.17	1.24	2.62	11.96
	Solid	18.53	24.53	82.3	125.35
Microcosm 2 Sample 3	Supernatant	4.09	0.85	2.61	8.7
	Solid	17.98	56.13	47.96	76.3
Microcosm 3 Sample 1	Supernatant	4.59	52.20	54.88	128.16
	Solid	1 329.8	1209.9	442.54	1 520.55
Microcosm 3 Sample 2	Supernatant	N/A	N/A	N/A	N/A
	Solid	142.79	1 024.6	340.63	1 030.05
Microcosm 3 Sample 3	Supernatant	N/A	N/A	N/A	N/A
	Solid	87.2	456.17	337.9	1 242.6

N/A = Not Available : no supernatant produced by centrifuging of the refuse/sludge samples.
 Samples 1, 2, 3 refer to the depth of refuse/sludge sampled. Sample 1 = 15 cm; Sample 2 = 25 cm;
 Sample 3 = 40 cm.

Table 4.3. Continued

		[Chromium]	[Copper]	[Nickel]	[Zinc]
Microcosm 4 Sample 1	Supernatant	2.2	1.46	4.14	12.15
	Solid	21.8	65.4	76.3	223.45
Microcosm 4 Sample 2	Supernatant	27.4	11.53	47.04	83.3
	Solid	26.71	21.8	38.15	98.1
Microcosm 4 Sample 3	Supernatant	32.4	1.33	38.58	12.56
	Solid	21.8	16.38	32.7	87.2
Microcosm 5 Sample 1	Supernatant	N/A	N/A	N/A	N/A
	Solid	376.05	817.5	463.25	1 144.5
Microcosm 5 Sample 2	Supernatant	N/A	N/A	N/A	N/A
	Solid	130.8	1 372.31	463.25	1 302.55
Microcosm 5 Sample 3	Supernatant	8.39	36.94	54.46	118.58
	Solid	114.45	1 204.45	452.35	1 291.65
Microcosm 6 Sample 1	Supernatant	N/A	N/A	N/A	N/A
	Solid	27.25	43.6	43.6	2 692.3
Microcosm 6 Sample 2	Supernatant	N/A	N/A	N/A	N/A
	Solid	27.25	21.8	27.25	436
Microcosm 6 Sample 3	Supernatant	3.4	2.84	5.87	265.51
	Solid	49.05	79.05	70.85	1 635

N/A = Not Available : no supernatant produced by centrifuging of the refuse/sludge samples.
 Samples 1, 2, 3 refer to the depth of refuse/sludge sampled. Sample 1 = 15 cm; Sample 2 = 25 cm;
 and Sample 3 = 40 cm.

Figure 4.9 Concentrations of adsorbed Cr (●), Cu (+), Ni (▲) and Zn (■) measured at three sampling depths (15, 25 and 40 cm) of Microcosm 1.

Figure 4.10 Concentrations of adsorbed Cr (●), Cu (+), Ni (▲) and Zn (■) measured at three sampling depths (15, 25 and 40 cm) of Microcosm 3.

FIG 4.9

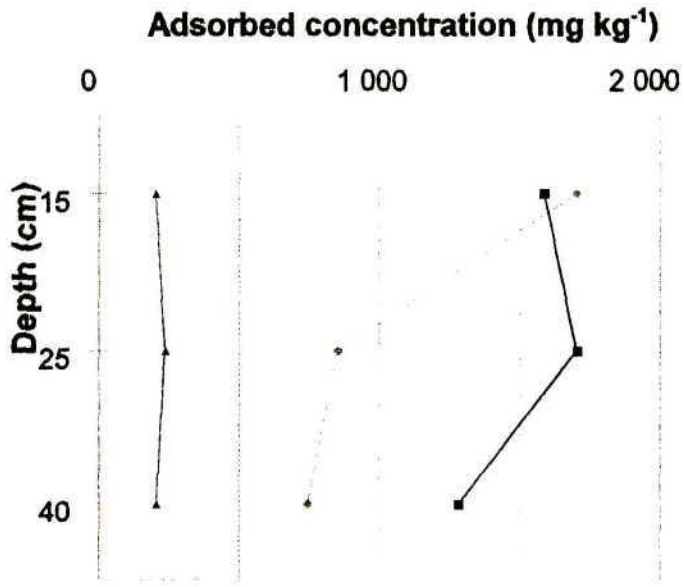
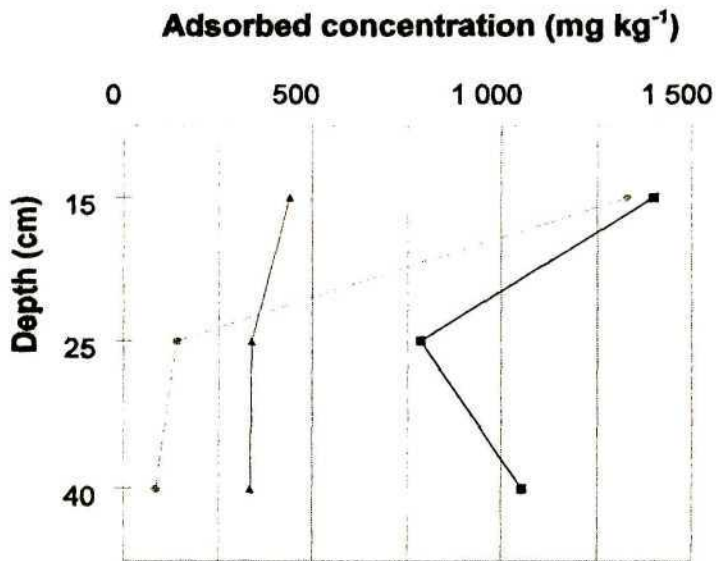


FIG 4.10



The leachate pH values in the columns were between 5.5 and 6 and were accompanied by high VFA concentrations as was recorded in the present study (pH values). The operation strategy was, however, different with single applications and single elution strategies practised.

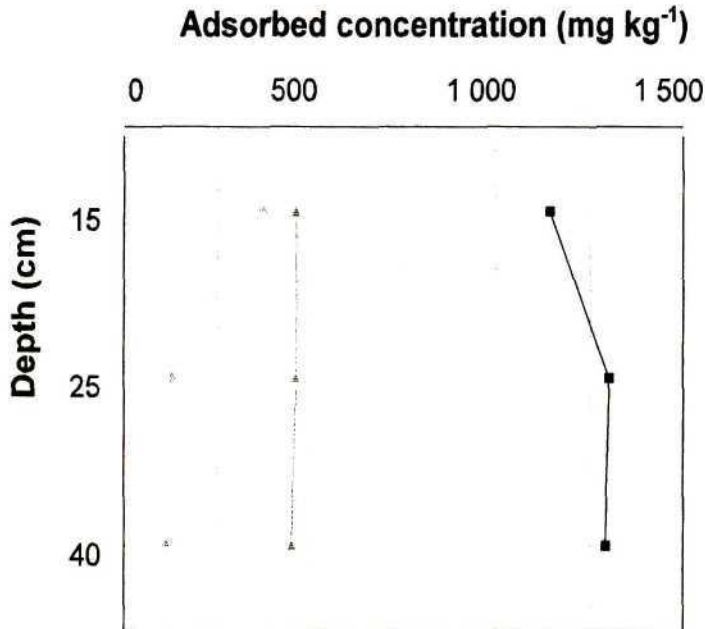


Figure 4.11 Concentrations of adsorbed Cr (●), Cu (+), Ni (▲) and Zn (■) measured at three sampling depths (15, 25 and 40 cm) for Microcosm 5.

From Table 4.3 it can be seen that elevated solubilized Cr, Cu, Ni and Zn concentrations were recorded for Microcosms 3 and 5 when compared to Microcosms 4 and 6. These could be attributed to the applied dosages which, in turn, affected the soluble fractions. These concentrations could be compared in relation to depths but not in relation to the concentration of metals added. The holding capacity of the refuse and sludge for each metal together with local desorption affected the solubilized concentrations detected. It must be noted, however, that after reducing the moisture content to the maximum moisture holding capacity, thus eliminating ponding, and centrifuging the samples, no supernatant resulted for analysis.

Heavy Metal Precipitation

The precipitation of metal species (1.14.1) relies upon the aqueous biodegradation of refuse. Newton (1977), Pohland and Gould (1980) and Pohland *et al.* (1982) concluded that sulphide precipitation may be the ultimate control for many heavy metals in refuse. Mosey (1976) stated that Zn and Cu sulphide precipitates were their main chemical forms while for Ni it was unclear whether a higher proportion was held by organic ligands or as sulphide precipitate. For Cr it has been reported that a stable sulphide does not exist in an aqueous solution and that hydroxide may be the major control (Newton, 1977).

In the present study sulphate precipitation probably did not contribute to metal immobilization as the high E_h values recorded (Figure 4.2) excluded sulphate reduction which is operative at E_h values of ± -220 mV (Atlas, 1984). Also, the low pH values (Figure 4.1) obviated other precipitations since an alkaline pH is required to facilitate hydroxide, oxide and carbonate precipitation (Gadd and Griffiths, 1978; Gadd, 1986).

4.4 Conclusions

Elucidation of the activities (retention and mobilization) of heavy metals in refuse is complex since various factors and mechanisms play fundamental roles. Key mechanisms include cation exchange, formation of chelate complexes with solid-state fermentation intermediates and precipitation.

Factors such as the leachate pH and redox potential, waste type and age, waste surface properties and the effects of changing surface properties during fermentation are responsible for heavy metal displacement and immobilization. In this investigation, unbalanced fermentations developed with acidogenesis > acidotrophy. It was very difficult, therefore, to identify any bactericidal / bacteriostatic effects of the added metals. Interpretation of the results was also complicated by the occurrence of wall effects and short-circuiting within the refuse.

Refuse is a very heterogeneous substrate and localized metal concentrations detected within the microcosms cannot be assumed to be representative of the site situation, therefore the results should be interpreted with a degree of caution. Nevertheless, the leachates contained elevated concentrations of metals which were not attributed to short-circuiting or wall effects.

With the metals added in solution, extensive retention occurred, even at low pH values. Nickel and Zn leachate concentrations were often elevated, even with extensive retention and even when the pH values of the leachates of the metal-dosed microcosms were similar to those of the control microcosms.

The extent of displacement in leachates showed fairly consistent patterns between metals and could be attributed to the metal holding capacity of the refuse and/or sewage sludge for a specific metal, i.e. the cation exchange preference for one metal species compared with another. As the behaviour of any one metal may be changed significantly by its chemical and biological environment, a strict ranking would be unjustified on the basis of the data available but the general order of total retention appeared to be: Cr>Cu>Ni≈Zn.

Co-disposal of sewage sludge plus heavy metal-containing wastewaters with refuse could be advantageous since experiments with sludges generally have showed little enhancement of leachate metal concentrations (Knox, 1989). Also, sludges have the ability to bind and retain relatively high concentrations of metals (Berrow and Burrige, 1979; MacNicol and Beckett, 1989). Sewage sludge co-disposal can definitely be advantageous if the heavy metal adsorption capacity of the refuse is exceeded either initially or with time. It could, however, also be disadvantageous if elevated retained concentrations are displaced by acidogenesis.

Thus, one important aspect of heavy metal co-disposal that needs further investigation is the status of the solid-state fermentation and the effect that it has on metal retention and mobilization. With activated sewage sludge co-disposal with refuse, the effect of nitrates on the progress of the fermentation and the progression of a self-generating redox gradient should be assessed.

The onset and progress of the fermentation should affect metal mobilization as waste surface characteristics and the changes of surface properties should contribute to metal displacement.

With the use of other types of sludges in co-disposal sites, it would be important to investigate and monitor their effects on heavy metal mobilization and retention. If, for example, anaerobically digested sewage sludge is co-disposed with refuse, the impact of the competition between NH_4^+ and metal ions for binding sites, thus affecting the cation exchange and adsorption of the metals, must be assessed.

Thus, aspects which warrant further investigations include:

1. The effects of the type and age of the refuse;
2. The effects of speciation;
3. The type of sludge used in co-disposal technology;
4. The effects of complexation with refuse fermentation intermediates;
5. The progress of the refuse fermentation (acidogenesis vs acidotrophy) and the effects on mobilization and displacement of heavy metals; and
6. Effects of metals on refuse degradation processes.

Summary

Although co-disposal and various aspects of the technology has been extensively studied, there is still uncertainties and ambiguities relating to an actual practice code for implementation and effective operation.

Elucidation of the complex interactions (microbe-microbe, microbe-refuse/sludge, microbe-organic and inorganic pollutants, refuse/sludge-pollutants, etc.) that are present in the co-disposal landfill ecosystem by microcosm-, lysimeter- and pilot-scale-studies have contributed to understanding co-disposal technology but also warrants it as a component of integrated waste management strategies.

The aspects that were investigated in the present study facilitated new information of and broadened insight on, specifically, the activities of the microorganisms which are active in refuse solid-state fermentations under specific circumstances.

Further investigations are necessary to fully comprehend the key factors underpinning anaerobic catabolism in a co-disposal landfill site but also to elucidate key interactions in the landfill ecosystem to implement effective operation codes.

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Figure 3.2 Changes in the concentrations of acetic, propionic, butyric and *iso*-valeric acid in the leachates of microcosms subjected to packing regimes of refuse (control) (D10) (a), refuse plus activated sewage sludge (D11) (b) and refuse plus activated sewage sludge plus phenol (D12) (c) and operated under closed culture conditions.

Figure 3.3 Changes in leachate pH of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions.

Figure 3.4 Changes in leachate COD of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions.

Figure 3.5 Changes in leachate redox potential of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions.

Figure 3.6 Changes in leachate nitrate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions.

Figure 3.7 Changes in leachate nitrite concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions.

Figure 3.8 Changes in leachate ammonium concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions.

Figure 3.9 Changes in leachate sulphate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions.

Figure 3.10 Changes in leachate phosphate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions.

Figure 3.11 Changes in the concentrations of acetic, propionic, butyric and *iso*-valeric acid in the leachates of microcosms subjected to packing regimes of refuse (control) (A1) (a), refuse plus activated sewage sludge (A2) (b) and refuse plus activated sewage sludge plus phenol (A3) (c) and operated under closed culture conditions following macronutrient supplementation.

Figure 3.12 Changes in leachate pH of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient supplementation.

Figure 3.13 Changes in leachate COD of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient supplementation.

Figure 3.14 Changes in leachate redox potential of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient supplementation.

Figure 3.15 Changes in leachate nitrate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient supplementation.

Figure 3.16 Changes in leachate nitrite concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient supplementation.

Figure 3.17 Changes in leachate ammonium concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient supplementation.

Figure 3.18 Changes in leachate sulphate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient supplementation.

Figure 3.19 Changes in leachate phosphate concentrations of microcosms subjected to packing regimes of refuse (control) (■), refuse plus activated sewage sludge (+) and refuse plus activated sewage sludge plus phenol (●) and operated under closed culture conditions following macronutrient supplementation.

Figure 3.20 Changes in the concentrations of acetic, propionic, butyric and *iso*-valeric acid in the leachates of microcosms subjected to packing regimes of refuse (control) (B4) (a), refuse plus activated sewage sludge (B5) (b) and refuse plus activated sewage sludge plus phenol (B6) (c) and operated under closed culture conditions following trace supplementation (A = leachate recycle; B = sodium carbonate addition).