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REFERENCE ONLY

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ERRATA

Page	Location	Correction
40	Line 14	compounds
81	Line 15	0.1 m mol.
84	Line 2	add "not"
103	Figure 3.10	omit "cation"
122	Line 27	surface tension
149	Figure 4.6	a = w/c 0.35; b = w/c 0.6
218	Figure 6.6	y-axis 10^6 Nm^{-2}
270	Line 4	add "than"

ORGANOPHILIC CLAYS IN STABILISATION AND SOLIDIFICATION OF HAZARDOUS WASTES

A thesis submitted to the University of London
in partial fulfilment of the requirements for the degree
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by

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ABSTRACT

The major deficiencies in cement-based stabilisation /solidification (S/S) processes are their inability to treat inorganic wastes contaminated with organic material or organic wastes. In general, organic compounds are poorly retained in cement matrices and frequently have detrimental, poorly understood effects upon cement hydration. This study has shown how the cement-based S/S processes can be modified to allow the treatment of organic wastes by the use of organophilic clays as pre-solidification adsorbents.

Organophilic clays, prepared by the treatment of Wyoming bentonite with a range of quaternary ammonium salts (QAS), were screened and the longer chain QAS-exchanged clays found to act as the best adsorbents for commonly occurring organic compounds. The exchanged clays solidified with cement performed well in physical tests giving high strength and low permeabilities. Leaching tests on the S/S mixes showed good retention of the phenolic compounds compared with the unstabilised cement/phenol mixes. Microstructural analysis showed that phenols inhibit the cement hydration reactions and form phenolates within the cement matrix. The presence of the clay in the cement mix reduced the detrimental effects of the organic compounds on cement hydration, although the clay itself altered the cement hydration reactions.

Three industrial wastes containing metals and organic contaminants were treated with the exchanged clay S/S mix. The samples produced were monolithic solids with good physical properties and good retention of the organic and metal compounds during leach testing. The stabilisation of contaminated soils by the exchanged clay showed large reductions in the release of phenols and polyaromatic hydrocarbons from laboratory dosed soils and soil contaminated with coal tar.

I would like to dedicate this thesis to my parents
in an attempt to express my gratitude for their support
and encouragement throughout my whole university career.

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Notation

DoE = United Kingdom Department of the Environment
WDA = Waste Disposal Authority
HMIP = Her Majesty's Inspectorate of Pollution
HWI = Hazardous Waste Inspectorate
EPA = United States Environmental Protection Agency

S/S = Stabilisation/Solidification
WB = Wyoming Bentonite
QAS = Quaternary Ammonium Salts
OPC = Ordinary Portand Cement
w/c = Water to Cement Ratio
UCS = Unconfined Compressive Strength
TOC = Total Organic Carbon

C_3S = Tricalcium Silicate
CSH = Calcium Silicate Hydrate
CH = Calcium Hydroxide

UV = Ultraviolet Spectrophotometry
A.A. = Atomic Adsorption Spectroscopy
FTIR = Fourier Transform Infrared Spectroscopy
TGA = Thermogravimetric Analysis
XRD = X-ray Diffraction Analysis
SEM = Scanning Electron Microscopy
EDS = Energy Dispersive Spectroscopy
HPLC = High Performance Liquid Chromatography

Units

m = metres
kg = kilograms
mol. = moles
M = molar
l = litres
Nm^{-2} = Newtons per square metre

Prefixes

10^{-9} = nano (n)
10^{-6} = micro (μ)
10^{-3} = milli (m)
10^{-2} = centi (c)
10^{-3} = kilo (k)

1. INTRODUCTION

Waste, an ill-defined and frequently abused word, has historically been classified at the point of production, irrespective of its value for recycling and re-use. The Oxford Dictionary's (1989) definition of waste is:-

> *"Refuse matter, unserviceable material remaining over from any process of manufacture; The useless by-products of any industrial process."*

The disposal of the 500 million tonnes of waste produced annually in the UK (DoE, 1989) is of major public and governmental concern. Waste must be disposed of safely so it does not pollute the environment (Hawkins, 1989). Pollution can take many forms but is best thought of as the introduction, by man, into the environment of substances or energy liable to cause (National Research Council, 1978):-

- Harm to human health
- Harm to living resources and ecological systems
- Damage to structures or amenities
- Interference with the legitimate uses of the environment.

The disposal of waste in the UK is a thriving business, however industrial waste treatment frequently takes a low priority, in both financial and management terms (Royse, 1988). Research into waste disposal is urgently required to ensure a better scientific understanding of the processes occurring and development of new disposal methods for waste (House of Commons, 1989).

This section provides an overview of the legislation relating to waste disposal in the UK and how it is applied in practice. The legal definitions of wastes are stated, and the current disposal methods for the wastes in the UK reviewed. Pretreatment methods for hazardous wastes are reviewed and the role of cement-based stabilisation and solidification in waste disposal is outlined. Finally, the behaviour of cement with wastes is reviewed and the properties of clay minerals, as potential adsorbents outlined.

1.1 LEGISLATION

Legislation to specifically control the disposal and management of waste was first introduced in the UK with the Deposit of Poisonous Waste Act 1972. Prior to that Act the control of wastes had rested in the hands of the local authorities who were given powers under the Public Health Acts of 1936, 1961 and 1969. The Deposit of Poisonous Waste Act (1972) was introduced following several alarming incidents involving the discovery of illegally deposited industrial waste, particularly one case in the Midlands where cyanide-containing wastes were discovered on open waste land (Royal Commission, 1972). The Act's two main features were to establish an "environmental hazard" offence and to introduce a notification procedure for the removal and deposition of wastes. The Deposit of Poisonous Waste Act was superceded in 1981 by implementation of wide ranging regulations, the Control of Pollution (Special Waste) Regulations 1980, derived from the Control of Pollution Act 1974 (CoPA), which deals comprehensively with domestic and industrial waste disposal.

1.1.1 Waste Terminology

One of the major problems in discussing waste management and with waste legislation in general are the basic definitions of waste. Historically waste has been defined at the point of production, but with the increasing interest in reclamation and recycling of materials, one producer's wastes may have become another's assets (Hawkins, 1985). There are a number of terms which attempt to classify waste, and a good summary of these is given by the UK Department of the Environment in evidence given to the House of Commons Toxic Waste Committee (1989).

Controlled Waste

Controlled wastes are the wastes which are the subject of CoPA 1974 (excluding explosive, agricultural, mining and quarry wastes). Controlled wastes are sub-divided into categories relating to their origin eg. "household", "commercial" and "industrial"; for purpose of defining the duties of the local authorities for collection and disposal of each category of waste.

Special Waste

These are a subset of controlled wastes which are, or may be, dangerous or *difficult* to dispose of. Special wastes are defined in terms of their physical and chemical characteristics and not in relation to their source. These wastes include prescription medicines and substances listed in Part 1, Schedule 1 of the Control of Pollution (Special Waste) Regulations 1980, if they are in such a form or concentration to be dangerous to life (Table 1.1).

Hazardous Waste

The House of Lords Select Committee on Science and Technology (1985), adopted the definition of hazardous waste used by the World Health Organisation.

Hazardous wastes are "wastes which present either:-

(i) short term hazards such as acute toxicity by ingestion, inhalation or skin adsorption, corrosivity, or other skin or eye contact hazards, or the risk of fire or explosion

(ii) long term environmental hazards including chronic toxicity upon repeated exposure, carcinogenicity, resistance to detoxification processes such as bio-degredation, the potential to pollute underground or surface waters or objectionable properties such as offensive smells"

An alternative definition of hazardous wastes is given by Her Majesty's Inspectorate of Pollution (HMIP) who consider those wastes defined as *difficult wastes* in the Department of the Environment's Waste Management Paper Number 26 (Appendix 7c) to be hazardous wastes for the purposes of disposal licencing.

Table 1.1: Extract from the Control of Pollution (Special Waste) Regulations 1980

MEANING OF SPECIAL WASTE

SCHEDULE I

PART 1

Listed Substances:-

Acids and Alkalis
Antimony and antimony compounds
Arsenic compounds
Asbestos (all chemical forms)
Barium compounds
Beryllium and beryllium compounds
Biocides and phytochemical substances
Boron compounds
Cadmium compounds
Copper compounds
Heterocyclic organic compounds containing oxygen, nitrogen or sulphur
Hexavalent chromium compounds
Hydrocarbons and their oxygen, nitrogen and sulphur compounds
Inorganic cyanides
Inorganic halogen-containing compounds
Inorganic sulphur-containing compounds
Laboratory chemicals
Lead compounds
Mercury compounds
Nickel and nickel compounds
Organic halogen compounds, excluding inert polymeric materials
Peroxides, chlorates, perchlorates and azides
Pharmaceutical and veterinary compounds
Phosphorus and phosphorus compounds
Selenium and selenium compounds
Silver compounds
Tarry materials from refining and tar residues from distilling
Tellurium and tellurium compounds
Thallium and thallium compounds
Vanadium compounds
Zinc compounds

PART II

Meaning of "dangerous to life"

1. Waste is to be regarded as dangerous to life for the purposes of these regulations if:
   (a) a single dose of not more than $5cm^3$ would be likely to cause death or serious tissue damage to tissues if ingested by a child of 20kg body weight;
   (b) exposure to it for fifteen minutes or less would be likely to cause serious damage to human tissue, by inhalation, skin contact or eye contact.
   (c) flash point of 21°C or less

1.1.2 Control of Pollution Act, 1974

The Act requires all Waste Disposal Authorities (WDAs) to prepare plans, for the Secretary of State for the Environment, for the disposal of all household, commercial and industrial waste likely to arise in their areas and to review and modify the plans as appropriate. The Waste Disposal Plan must include the kind and quantities of wastes arising, what the authority expects to dispose of itself and what it expects to export and import, the methods of disposal, sites and equipment being provided and finally an estimate of the costs involved. The Act requires authorities to consider reasonable arrangements for reclaiming waste materials.

The CoPA also introduces a comprehensive licencing system for the disposal of wastes over and above existing planning controls. It makes it an offence to deposit controlled waste on land or to use a waste disposal plant unless the land in question is licenced by the WDA. Applications for site licences can only be made if the required planning permission for the site is attained and the licence must be referred to the relevant water and collection authorities for comment. Site licences are made at the discretion of the WDA and may cover the following:-

- duration of the licence
- supervision by the licence holder of licenced activities
- quantities and nature of waste to be disposed
- record keeping
- precautions (e.g. security fencing)
- hours of site operation
- site preparation and upkeep.

Section 17 of CoPA implemented by the Control of Pollution (Special Waste) Regulations (1980) introduces the category of "special wastes" (defined in Section 1.1.1). The regulations provide for a control system for special wastes which include:-

- a requirement for waste producers to notify the receiving WDA of the intention to dispose of a special waste
- a consignment note system
- a record of dispatch, conveyance and disposal
- a permanent record of ultimate disposal location
- power for the Secretary of State to direct a particular site or plant to accept a specific waste

With the development of the legislation the DoE has published a series of Waste Management Papers (27 to date) as Codes of Practice and guidance notes for the WDA and to the disposers on acceptable practice and the scientific background to the subjects under discussion.

With the implementation of CoPA several committees have been set up to review the practice of waste disposal in the UK and the performance of CoPA. As a result of the suggestions of the House of Lords Select Committee on Science and Technology, 1981 (commonly known as the Gregson report) a central Hazardous Waste Inspectorate (HWI) was set up with the aim "........ to satisfy Environmental Ministers and, through them, Parliament and the Public at large, that what is being done in respect of hazardous waste management, especially disposal, is safe, environmentally appropriate, acceptable to reasonable public opinion and economical and efficient from the standpoint of the waste producers" (House of Lords Select Committee, Government Response, 1985). The HWI has now been subsumed under Her Majesty's Inspectorate of Pollution (HMIP).

The most recent review of waste disposal practice was made by the House of Commons Environment Committee (1989). The committee took evidence from a wide cross-section of the waste disposal industry and the final report was highly critical of waste disposal practice in the UK, it detailed wide ranging suggestions for modifications to the practice and legislation governing waste disposal. The committee's main criticisms of the present system for waste disposal were that:-

(i) The WDAs, created under CoPA, whose responsibility it is to operate waste disposal sites and also to regulate privately operated sites through a site licencing system, take these dual gamekeeper/poacher functions very lightly. Staff appointed by the authorities are poorly qualified and low in status and resources allocated to the disposal of controlled wastes are inadequate. The waste disposal plans which were required by legislation, enacted ten years ago, have not been submitted to the DoE by 56 out of the 76 English WDAs.

(ii) The Hazardous Waste Inspectorate, set up in 1983 after criticisms of the waste disposal system in the Gregson report, was grossly under-resourced with, until recently, only six inspectors responsible for overseeing more than 5000 disposal sites throughout the UK.

(iii) Delays in the enforcement of parts of CoPA and the enactment of regulations necessary for its implementation have added to the weakness of the Act and make enforcement difficult . For example, prosecutions for "fly tipping" are seldom successful because the tipper had literally to be "caught in the act" to ensure conviction. This loop-hole in CoPA is soon to be closed by the an Amendment to CoPA in a private members bill soon to be before Parliament but other inadequacies in CoPA remain.

(iv) Definitions of the wastes in CoPA are frequently confusing and inconsistent with the European Economic Community (EEC) recommendations.

(v) Waste Disposal Authority standards are inconsistent across the country and too frequently the standards are low.

(vi) Funding for research by the DoE needs to be reviewed and the allocation to waste management topics increased. The committee saw a need for fundamental research in the waste management field and for the development of new technology and processes for waste treatment.

1.1.3 EEC Policy on Waste Disposal

The EEC has issued a number of Directives pertaining to waste disposal. The major problem in Europe is that different countries have different interpretations of the definitions of dangerous and hazardous wastes in their national legislation (Mills, 1983). The EEC directives on disposal waste include:-

- Waste, framework Directive (1975)
- Disposal of Waste Oils (1975)
- Disposal of PCBs and PCTs (1976)
- Toxic and Dangerous Waste (1978)
- Transfrontier Shipment of Toxic Wastes (1984 - 87)

Each directive required compliance two years after the date of notification. In general the directives have little effect upon waste disposal practice in the UK as most of them are covered under existing legislation and indeed some of the directives seem to be modelled on CoPA. Pehaps the major contribution that the EEC directives have made to the UK's waste disposal practice is to generate pressure to introduce sections of CoPA without delay, and to clarify thinking on supplementary regulations (Haigh, 1987).

1.2 WASTE ARISINGS

1.2.1 United Kingdom

There are no reliable statistics on controlled wastes produced or disposed of in the UK, except for special wastes which require consignment notes prior to transportation and disposal, and so are quantified to some extent (House of Commons, 1989). Records on wastes kept by the WDA vary in quality and in the types of waste counted between the different authorities, so that even special waste figures may be inaccurate and include some other types of waste. An estimate of wastes disposed of in the UK by HWI (DoE, 1988) are shown in Table 1.2.

Table 1.2: Waste Arisings in the UK (1986/87)* - excluding liquid effluent discharged to sewers and water courses.

Waste Type	Amount (10^6tonnes/annum)
Agricultural	250.0
Mines and Quarries (including China Clay)	130.0
Industrial	50.0
(Hazardous and Special)	3.9
(Special)	1.5
Domestic and Trade	28.0
Sewage Sludge	24.0
Power Station Ash	14.0
Blast Furnace Slag	6.0
Building	3.0
Medical	0.2
	510.6

*From the evidence given by the Department of the Environment to the House of Commons Environment Committee 1989.

1.2.2 EEC Countries

EEC countries give many different interpretations to the definitions of toxic and dangerous waste in national legislation, hence comparable statistics are very difficult to obtain. Table 1.3 shows the figures estimated by Mills (1983) to be the annual hazardous waste arisings in Western Europe for that year.

Table 1.3: Hazardous Waste Arisings in Western Europe*

Country	Annual Hazardous Waste Arisings (tonnes)		
	In-house Disposal	External Disposal	Total
Austria	-	350,000	-
Belgium	>671,000	<429,000	1,100,000
Denmark	-	-	100,000
West Germany	15,000,000	3,000,000	18,000,000
France	1,500,000	500,000	2,000,000
Ireland	-	-	100,000
Italy	-	-	4,900,000
Luxembourg	-	-	-
Netherlands	260,000	240,000	500,000
Norway	61,000	66,000	127,000
Portugal	-	-	2,800,000
Spain	-	-	-
Sweden	241,000	279,000	520,000
UK	-	-	4,800,000
(England	1,500,000	2,200,000	3,700,000)

*From Mills (1983)

1.2.3 Import of Waste to the UK

The levels of import of special wastes for treatment and disposal in the UK has increased dramatically over the past six years (Figure 1.1). In 1986/87 130,000 tonnes of non-special wastes were also imported, consisting of mainly contaminated soils, gypsum and similar solid wastes for direct landfill. Special wastes imported into the UK originate from many countries. Figure 1.2 shows the countries of origin of wastes imported into the UK. The largest exporters to the UK are the Netherlands (55%), Eire and Belgium (12.5% each) (DoE, 1988).

Imported wastes, subject to the Control of Pollution (Special Waste) Regulations, 1980, are treated as if the wastes had arisen at the port of entry and consignment notes are dispatched by the importer from the port. Recent legislation to control the import of wastes under the Control of Pollution (Transfrontier Shipment of Waste) Regulations, 1988 has been enacted to comply with the EEC Directive 84/631/EEC..

1.3 DISPOSAL OF HAZARDOUS WASTES

1.3.1 Disposal Routes in the UK

The disposal routes for hazardous waste in the UK are shown in Figure 1.3. Landfill is the route adopted for the vast majority of wastes. Wastes which are solidified and ash from incineration also ultimately go to landfill. Marine disposal is the second most used route, but increasing concern about marine pollution is likely to reduce the availability and economic advantages of this route in the future.

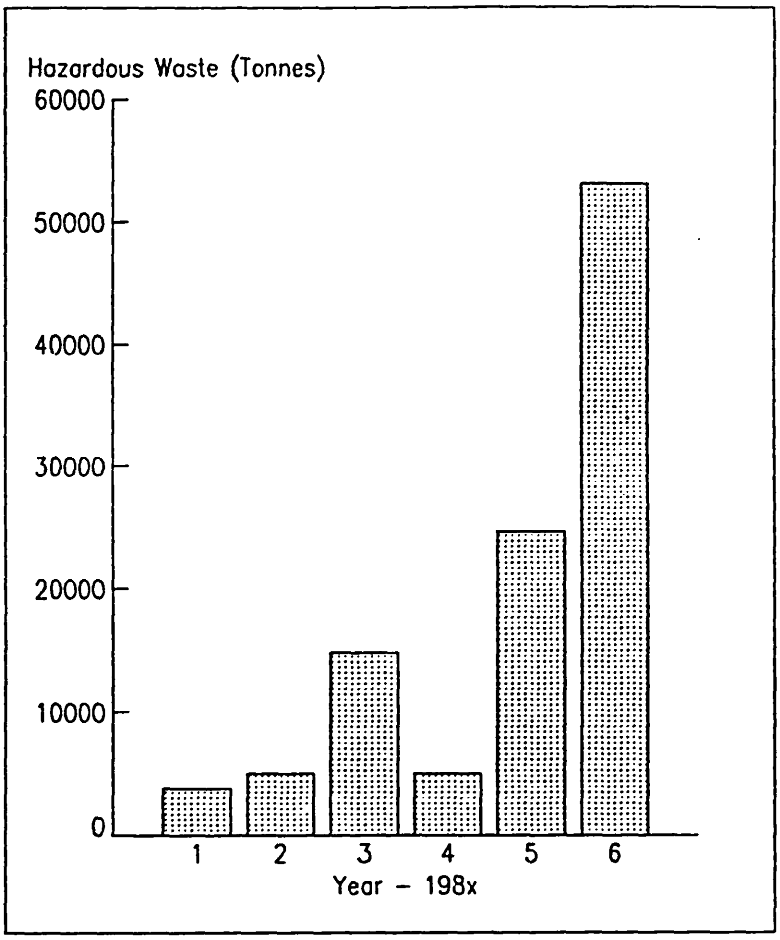


Figure 1.1: Hazardous Waste Imported into the UK, 1981 - 1986. (after HMIP, 1988)

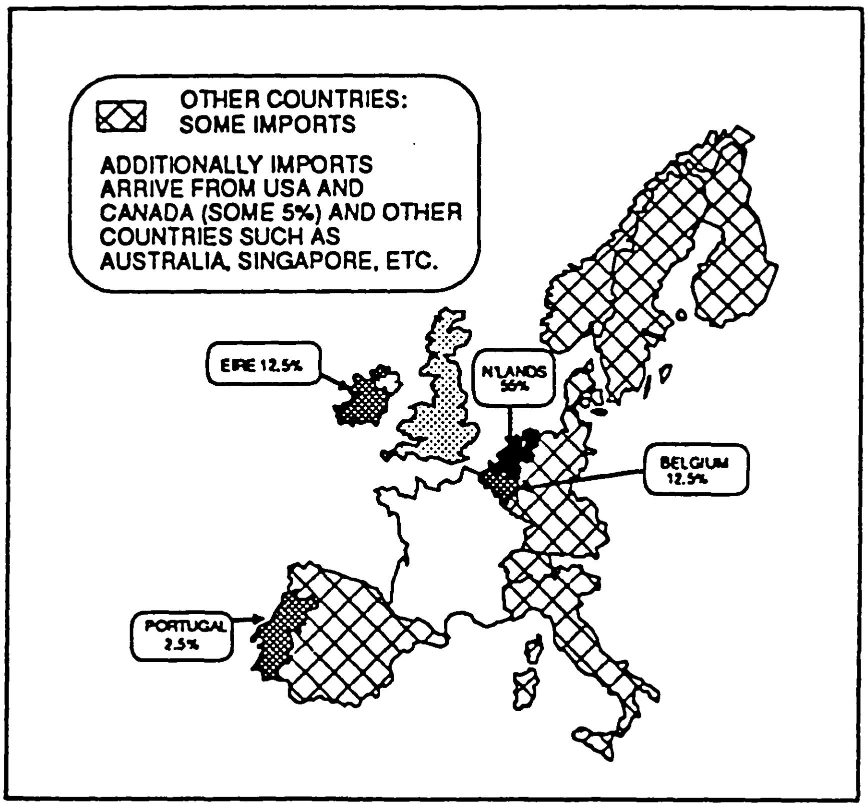


Figure 1.2: Waste Imported 1986/87: Countries of Origin (HMIP, 1988).

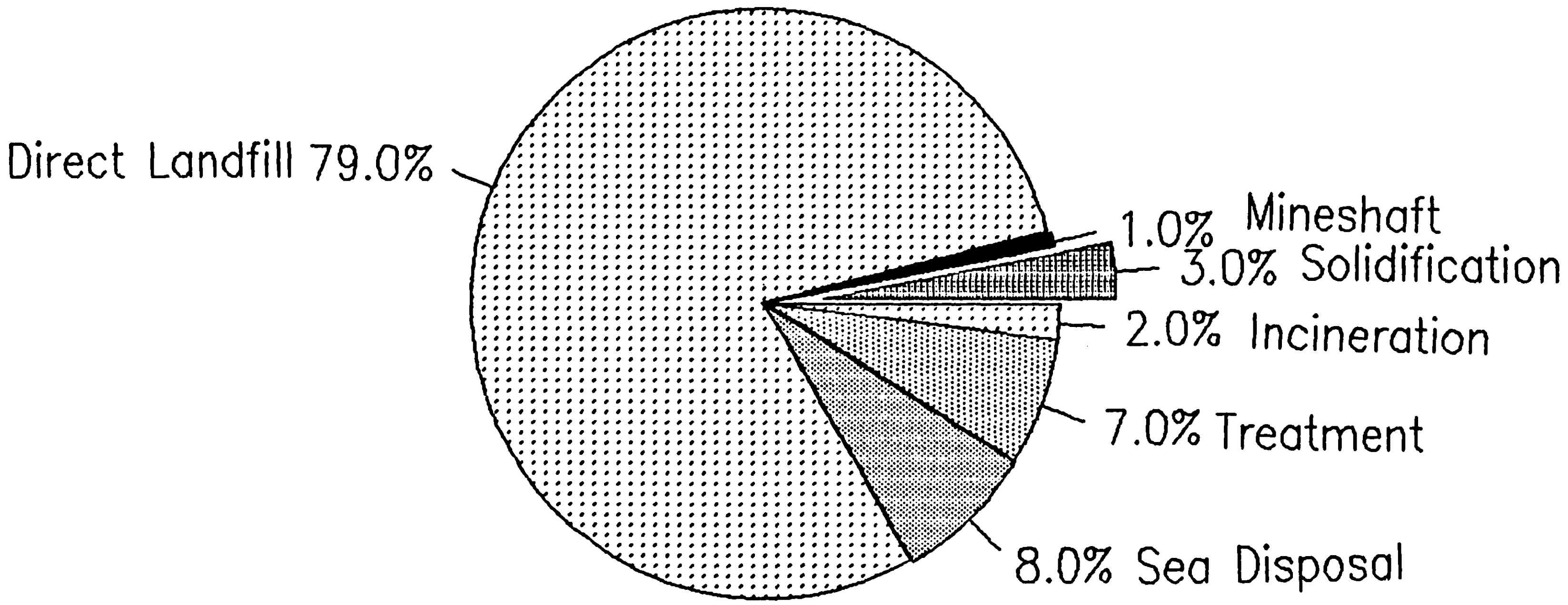


Figure 1.3: Hazardous Waste Disposal Routes in UK 1986/87 (HMIP, 1988).

1.3.2 Disposal on Land

(a) Landfill

Landfilling of wastes, in the UK, is usually the least expensive disposal route and until recently has caused little environmental and public concern. The disposal of hazardous wastes to landfill is, at present, the major ultimate disposal route for these wastes in the UK. Landfilling is the deposition of waste "en masse" either in the ground for the reclamation of quarries and gravel pits or on marginal lands such as marsh lands. Landfill sites must be situated and constructed so that waste disposal will (Crawford & Smith, 1985; DoE, 1986):-

- have no unacceptable impact on public health
- have no unacceptable impact on the quality of water resources
- have minimum nuisance to neighbours
- have minimum impact on the local environment
- enable eventual return of the land to some beneficial use.
- be economic

There are two idealised rationales for the development of sites suitable for hazardous waste disposal. Containment sites, as a result of their geology, hydrogeology and engineered structure, contain all of the deposited material and site leachates. Attenuate and disperse sites which allow slow migration of liquids so enabling the natural processes of attenuation and dispersion in and beyond the site to reduce the concentration of the pollutants (Sawhney & Kozloski, 1984). In practice landfill sites tend to conform to neither extreme but combine features of both (Knox, 1987).

Hazardous wastes may be deposited in either mono-disposal sites which contain only one particular type of waste, eg fly ash, or in co-disposal sites where domestic waste and industrial wastes (which may include hazardous wastes) are deposited together. Co-disposal optimises the effects of attenuation processes, such as microbial degradation, so, in well run sites, leachate from the site does not contain significant concentrations of the hazardous wastes and closely resembles that from domestic landfills (Ghassemi et al., 1984).

(b) Deep-Well Disposal

Deep-well disposal is an ultimate disposal method that injects liquid wastes far underground and away from freshwater sources. The method is particularly useful for the disposal of wastes which are difficult to treat such as salt-bearing solutions and wastewaters containing high concentrations of organic chemicals. This method is becoming increasingly unpopular as, too frequently, the wastes reappear in groundwater due to the difficulty in predicting the exact geological properties of the rock underlying the site (WHO Regional Publications, 1983).

1.3.3 Incineration

Incineration is a process for the thermal oxidative decomposition of gaseous, liquid and solid wastes at high temperatures (usually in excess of 1000°C) to destroy the organic fraction of the wastes and significantly reduce waste volume. The end products are gases which, after suitable cleaning and heat recovery, are discharged into the atmosphere, and slags or ashes, which are landfilled (Theodore & Reynolds, 1987).

Hazardous wastes suitable for incineration are non-reclaimable, have a high organic content (a high calorific value) and are, frequently, difficult to treat by alternative methods (Oppelt, 1986), for example halogenated hydrocarbons, pesticide wastes, mineral oil sludges, phenolic wastes and oily emulsions. Prior to incineration the wastes have to be well characterised and frequently chemical and physical pretreatment are necessary. Hazardous waste incinerators vary in design depending upon the type of waste which is to be treated (Table 1.4).

Table 1.4: Major Incinerator Designs and Wastes Treated*

	Furnace Design			
	Liquid Injection	Rotary Kiln	Fixed Hearth	Fluidised Bed
SOLIDS				
Granular, homogeneous		X	X	X
Irregular, bulky		X	X	
Low melting point	X	X	X	X
Organic compounds with fusible ash constituents		X		
Unprepared, large, bulky materials		X		
LIQUIDS				
High organic strength aqueous wastes	X	X		X
Organic liquids	X	X		X
SOLIDS/LIQUIDS				
Wastes containing halogenated organic compounds (1200°C)		X		X
Aqueous organic sludges		X		X
GASES				
Organic laden vapours	X	X	X	X

* Oppelt (1987).

The major features of hazardous waste incinerators are (Oppelt, 1987):-

- waste characterisation, pretreatment and feed
- combustion chamber(s)
- air pollution control
- residue/ash handling.

Careful controls on the temperature of combustion (>1000°C), the residence time in the furnace (>2 seconds) and the air flow through the furnace (>150% excess air) ensure good destruction of all the waste components. Flue gases from the furnace are quenched to cool them, passed through scrubbers to remove the particulate matter and acid gases prior to discharge of the gases from the stack.

1.3.4 Disposal at Sea

(a) Dumping at Sea

The disposal of waste at sea relies on the enormous dilution of the waste by sea water to reduce the concentration of toxic components to insignificant levels, and to allow degradation of the waste via natural biological and hydrolytic reactions.

The disposal of waste at sea is controlled internationally by the Oslo Convention, 1972 and the London Convention, 1975. In the UK dumping at sea is controlled by the Dumping at Sea Act 1974. Control is exercised by the issue of licences by the Ministry of Agriculture, Fisheries and Food, for every waste arising committed to this disposal route. The international conventions prohibit the dumping at sea of certain persistent hazardous materials (Annex 1, Oslo Convention 1972). For example, mercury, cadmium, organohalogen and organosilicon wastes are all banned as well as any toxic waste which demonstrates a tendency for bio-accummulation in aquatic species.

Dumping takes place either in deep water sites (>200m) beyond the continental shelf or in shallow waters. In deep waters the wastes are dumped in sealed containers which eventually corrode and rupture releasing the wastes. In shallower waters liquid wastes or sludges are discharged directly from the ship, usually into the propellor's wake to ensure immediate dilution and dispersal (Coleman, 1985).

(b) Incineration at Sea

Incineration at sea affords good economic advantages for the disposal of mainly, highly halogenated wastes, as gaseous emissions need not be subjected to expensive scrubbing systems prior to discharge. The acid halide by-product gases are released into the air where they are dispersed over a large area so they can be rapidly adsorbed and neutralised by the sea when they settle. Incineration at sea also has the advantages that the incinerators are not subject to planning permission or the hostility of local communities near the incineration site. The disadvantages of incineration are difficulties in controlling the destination of the highly acid flue gas clouds, the risk of transporting wastes over large distances to the port and onto the ship, the impossibility of recovering materials and energy from the combustion process as well asdifficulties in monitoring by regulatory authorities (Theodore & Renyolds, 1987).

Incineration at sea also comes under the control of the Oslo (1972) and London (1975) Conventions which strictly limit the wastes burnt and rigorously control the testing of the incineration vessels. Incineration at sea is becoming less acceptable as public awareness of the potential long term hazards to the aquatic environment increase, and this is increasing the pressure for tighter controls and an eventual world ban on incineration at sea.

1.3.5 Pretreatment

Hazardous wastes frequently require pretreatment prior to ultimate disposal. Pretreatment is carried out to either reduce the volume of the waste, to chemically render certain constituents of the waste less toxic or to reduce the overall toxicity of the waste to allow safer handling and to reduce the long term impact of the waste on the environment. There are four main categories of pretreatment (Landreth, 1974; NATO, 1981; WHO, 1983; Tucker & Carson, 1985; Schoen & Frega, 1987).

(a) Physical Treatment

The main aim of physical treatment is to reduce the volume of the waste by removal of, for example, the aqueous fraction which can then be discharged to the sewers. Phase separation is achieved by lagooning or tank storage of the waste which allow gravitational settlement. Other methods of separation include drying of sludges in beds, air flotation, filtration, centrifugation and flocculation of colloidal wastes.

(b) Chemical Treatment

Chemical treatment methods use specific chemical reactions to modify the chemical properties of the waste or more rarely to effect complete breakdown of the hazardous components of the waste into non-toxic gases and water.

Oxidation converts highly toxic cyanide wastes, for example, to cyanates or to nitrogen and carbon dioxide. Other compounds such as phenols, chlorinated organics and mercaptans can also be oxidised to less hazardous compounds. The oxidising agents used depend on the strength of oxidation required, but can include sodium hypochlorite or chlorine gas (for cyanide oxidation), ozone, hydrogen peroxide and potassium permanganate.

Reduction reactions are mainly used to convert the highly toxic and corrosive chromic acid (chromium VI) to the relatively non-toxic chromium (III) salt using sodium metabisulphate.

Precipitation of metals from solution is achieved by raising the pH of the waste solution using slaked lime (calcium hydroxide) or caustic soda (sodium hydroxide). The wastes can be "polished" by further sulphide precipitation as metal sulphides are generally more insoluble than the corresponding metal hydroxides.

Neutralisation of wastes is frequently achieved commercially by the mixing of acid and alkaline waste streams. Addition of slaked lime or carbon dioxide is used to neutralise acid wastes, whilst sulphuric acid is used for alkaline wastes. Neutralisation is often accompanied by evolution of gas, precipitation of pH sensitive coupounds and a rise in temperature of the waste. Neutralisation may not make a waste less hazardous but it will make the waste easier to handle, less corrosive and possibly suitable for biological degradation.

(c) Biological Treatment

Certain organic materials can be degraded into relatively innocuous derivatives by micro-organisms which "feed" on the organic material (Coleman, 1985). Biological treatment is frequently used for in-house treatment of dilute organic wastes and wastewaters. Methods used are similar to those for conventional sewage treatment, but for well characterised waste streams micro-organisms have been developed that selectively degrade toxic chemicals.

Composting by mixing wastes with top soil or sewage sludge makes use of the soil's natural microbes to degrade the waste. Composting has been used for the treatment of contaminated land, where the top soil would otherwise require removal and ultimate disposal (Anon, 1987).

1.4 STABILISATION/SOLIDIFICATION

Stabilisation/solidification (S/S) is used to treat wastes prior to landfill. Stabilisation refers to a process by which a waste is converted to a more chemically stable form. This may involve the formation of insoluble compounds that entrap the toxic wastes in an impervious polymer, or the formation of a barrier between the waste and the environment (Wiles, 1987). Solidification is a treatment process that produces a solid monolithic or soil-like mass from a liquid waste, The resulting product has improved structural integrity and physical characteristics (Montgomery et al., 1988). The objectives of S/S are (Wiles, 1987):-

- to produce a solid from liquid wastes
- to improve handling characteristics of all wastes
- to decrease the surface area across which the transport of waste constituents may occur
- to limit the solubility of contaminants when exposed to leaching fluids.
- to reduce the permeability of the material
- to increase the strength and stiffness of the material
- to increase the resistance to chemical and biological degradation

Stabilisation/solidification is divided into three main categories which indicate the mechanisms of treatment or the mechanisms involved in stabilisation (Wiles, 1987).

1. <u>Sorption</u> is a solidification technique. It involves the addition of dry adsorbent solids to liquid wastes or sludges to remove free liquid and so improve handling characteristics.

2. <u>Encapsulation</u> of waste takes two main forms, microencapsulation and macroencapsulation. In the former the wastes, usually solids, are distributed within an encapsulating material and each particle of the waste surrounded by the polymer. In

macroencapsulation, the wastes, in containers such as drums, are coated with a jacket of inert polymer.

3. Inorganic Fixation methods are the most widely used group of S/S techniques. Inorganic fixation generally requires readily available inexpensive raw materials, a low energy input and relatively unsophisticated equipment. Inorganic fixation can be used to treat a wide range of inorganic wastes especially those with a high concentration of cations.

1.4.1 Sorption

Sorption is widely used in the United States for the disposal of liquid wastes because the disposal of liquids to landfill is illegal, but the technique is less common in the UK. Ideal adsorbents are inert, non-degradable and non-reactive solids. Dry wastes such as pulverised fly ash (PFA), cement kiln dust, lime kiln dust and soils are used to adsorb the liquids. There is no evidence of stabilisation of the waste components by these solids. Specially designed adsorbents such as activated carbons, clays and zeolites are being developed, they provide satisfactory stabilisation, however, they are expensive (Sell, 1988).

The advantages of sorption are that the technique eliminates free liquids, improves handling, can modify the pH and redox potential of treated wastes and is inexpensive if dry wastes are used as adsorbents. Wastes which can be treated by sorption techniques are liquid wastes with high water contents.

The disadvantages of sorption techniques are that wastes can leach readily from the solid, as physical adsorption is the only retention mechanism. The additives increase the volume of waste and specialist adsorbents are expensive and unproven. Wastes cannot be treated it they are highly reactive or flammable.

1.4.2 Encapsulation

Encapsulation processes are generally expensive and require specialist equipment and trained staff. The techniques were developed mainly for use in the disposal of radioactive wastes or problematic hazardous wastes.

(a) Thermoplastic Processes

These microencapsulation processes blend wastes with organic thermoplastic polymers, such as asphalt, bitumen, polyethylene and wax, which reversibly soften on heating and harden on cooling. For treatment, wastes are dried, heated and dispersed through the heated plastic polymer and cooled in containers to give a convenient shape (Doyle, 1979; Berennerr & Rugg, 1982).

The advantages of thermoplastic processes are that they can solidify very soluble toxic wastes which, if processed dry, may result in an overall volume reduction of the product. The migration rates of waste constituents in the solid are low and the solidified product is resistant to leaching. Thermoplastics adhere well to dry wastes, and reclamation of waste constituents after solidification is possible. Wastes which can be treated by thermoplastic processes are inorganic wastes such as electroplating sludges, paint residues and refining sludges. Radioactive wastes can also be treated.

The disadvantages of thermoplastic processes are that they require expensive equipment and skilled labour. The wastes must be dried prior to processing and if volatile components are present great care must be taken. Thermoplastic materials are flammable and oxidise explosively. Wastes which cannot be treated by this method are organic wastes containing solvents and strong oxidants (DoE, 1989).

(b) Organic Polymers

A monomer is thoroughly mixed with either dry waste or waste sludge in a container such as a steel drum. An initiator is added to the mix which causes polymerisation of the monomer. The polymer forms a hardened cross-linked material which entraps the waste. This microencapsulation technique does not chemically bind with the waste. Any liquid associated with the treated waste must be removed from the solid prior to ultimate disposal. The most common processes use urea formaldehyde, polyester and polyvinyl chloride (Lubowitz et al., 1977; Unger & Lubowitz, 1988).

The advantages of polymerisation are that only small quantities of additives are required to cause setting and air curing polymers do not require heating. The wastes treated are inorganic wastes which in solidified form are usually less dense than cement-based solidification processes.

The disadvantages of organic polymers are that the waste must be treated in containers and the wastes are only entrapped, not bonded, in the matrix. Initiatiors of polymerisation are often corrosive and require special handling, and fumes from polymerisation can be harmful. Uncombined water must be removed from the solidified product as it is often highly acidic and contaminated with toxic metals. Wastes which cannot be treated by this process are acidic wastes, strong oxidants and organic wastes.

(c) Vitrification

Extremely hazardous materials may be mixed with silica and fused at high temperatures to form glass. This form of microencapsulation, unlike other techniques discussed above, uses inorganic materials. Crystalline silicate and ceramics can also be used (Anon, 1988).

The advantages of vitrification are that the wastes are subject to a high degree of containment and the additives are relatively inexpensive. Wastes which can be treated by this process are radioactive wastes and highly contaminated soils.

The disadvantages of vitrification are that the process is energy intensive and requires specalist equipment as the charge must be heated to >1350°C to produce a melt. Some components of the waste, for example metals, may vapourise causing a health hazard to personnel, hence highly trained operators are required. Wastes which cannot be treated by vitrification are wastes with high or low electrical resistivity (Cullinane et al., 1986).

1.4.3 Inorganic Fixation

(a) Cement-Based Processes

Cement is an anhydrous clinker which, when hydrated by water forms a solid amorphous mass of low permeability. Aqueous wastes may be used to hydrate cement and solid wastes incorporated as "bulking" materials. Cement is highly alkaline so many multivalent metal ions will be incorporated into the matrix as their insoluble hydroxides. Other wastes may also be trapped in the matrix (Hill, 1986). Cement-based S/S processes will be discussed further in Section 1.5.

The advantages of cement-based S/S are that the technique is well established using cheap readily available materials and entails low equipment and running costs. The alkalinity of the cement helps to neutralise acidic wastes and precipitate metals. Liquid in the wastes can be used in the cement hydration process and additives to the process can increase retention of specific waste components. The final product has a low permeability and leaching from the solid is low. Wastes which can be treated by cement-based S/S are inorganic wastes, particularly those containing metal cations.

The disadvantages of cement-based solidification are that the process requires large amounts of raw materials which significantly increase the weight and volume of the waste. The mechanism of cement hydration is not well understood and certain compounds act as inhibitors to hydration. Under acidic conditions the solidified product is vulnerable to attack resulting in leaching of waste components. Wastes which cannot be treated by cement-based S/S processes are organic wastes or inorganic wastes containing certain mobile anions (Cullinane et al., 1986).

(b) Pozzolanic Processes

Aqueous solutions of hazardous materials are mixed with lime and fine-grained pozzolanic (siliceous) materials to form a pozzolanic concrete. Natural pozzolanas include volcanic ash and lava. Pozzolanas commonly used are themselves wastes such as PFA, blast furnace slag and cement-kiln dust. All classes of quicklime and hydrated lime, including waste lime, react well with pozzolanic materials. Generally finer pozzolanic materials will produce stronger end products (Tittlebaum, 1985).

The advantages of pozzolanic processes are that the additives are widely available, inexpensive and are often waste materials themselves. The equipment for processing is simple and the characteristics of pozzolanic reactions are well known. Dewatering of the waste is not required because water is required for hydration of the pozzolanic materials. Inorganic wastes can be treated by pozzolanic S/S.

The disadvantages of pozzolanic processes are that the additives increase the volume and weight of the waste and may require compaction on final deposition. The setting rates of pozzolanic processes are generally slower than for cement-based processes. Pozzolanic S/S are vulnerable to leaching under acidic conditions. Wastes which cannot be treated by pozzolanic processes include organic wastes, or those containing mobile anions.

(c) Self-Cementing

Wastes containing calcium sulphate or calcium sulphite (eg flue gas cleaning or desulphurisation sludges) can be solidified using their self-cementing properties. Small portions of the waste (8 - 10%) are dehydrated and calcined to produce cementitious material. This material is re-introduced into the rest of the waste and water added if necessary. The waste hardens to a plaster-like solid (Valiga, 1979).

The advantages of self-cementing are that no major additives have to be made or transported to the treatment site. The waste does not require dewatering and has a faster setting rate than lime-based systems. The final product is stable, non-flammable and non-biodegradable. Wastes which are suitable for self-cementing are sulphate or sulphite wastes.

The disadvantages of the self-cementing process are that the process can only be applied to a limited type of waste. Processing requires skilled labour and the equipment for calcining the waste is expensive and has a high energy requirement. The final product is vulnerable to leaching especially under acidic conditions.

1.5 CEMENT-BASED STABILISATION/SOLIDIFICATION

A wide range of cement-based S/S processes have been patented for the treatment of industrial wastes. At present only one process, the "Sealosafe" process (Chappell, 1977; Schofield, 1979) is used in the UK's two operators. In the USA a much wider range of cement-based S/S processes are operated, many of which contain the operators own "patent" solidifying agents; however, the basic principles of cement-based S/S remain the same (Cullinane et al., 1986).

There are five main stages for the treatment of a waste from its reception to its ultimate disposal (Clements & Griffiths, 1985)

1. Analysis
2. Pretreatment
3. Addition of binders and solidifying agents
4. Quality control of end product
5. Disposal of end product

Initial analysis of the wastes, carried out at the treatment site, determines a wide range of properties of the incoming wastes such as pH, solids content, organic and metals contents etc. The aim of analysis is to determine if the waste contains any constituents that make it unsuitable for cement-based S/S, for example, certain organic contaminants will inhibit the hydration of cement.

Pretreatment processes for waste streams, as described in Section 1.3.5, are frequently carried out on-site and can often be achieved by mixing different wastes. For example, acid wastes can be neutralised by the addition of alkaline wastes. After pretreatment the wastes are formed into a slurry with a solids content of approximately 30 to 40%. The solids being necessary to give an adequate strength to the product (Sollars & Perry, 1988). The solids content of the slurry can be increased by, for example, centrifugation of the slurry to remove excess liquid or by the addition of inert solids. The slurry is then well mixed with the solidification agents and placed in the final disposal site. Solidification of the product begins as soon as mixing ceases. The rate of setting, however, usually allows transport to a disposal site away from the treatment plant.

Quality control of the solidified material must be related to the primary objectives of cement-based S/S i.e. to produce a solid with improved structural integrity, decreased surface area and limited solubility of waste components. The UK has, at present, no formal national testing procedures for solidified wastes. The production of a Waste Management Paper proposed by the DoE (House of Commons, 1989) will lay down codes of practice for solidified waste testing and disposal. A range of five tests give a good overall picture of the required properties of the solidified wastes. These tests are (Rushbrook et al., 1989)

- a cone penetrometer test to measure the rate of setting
- a mechanical press to measure compressive strength
- laboratory techniques to measure permeability
- laboratory techniques to measure leaching of the waste components
- laboratory techniques to observe and measure supernatant formation

Standards to which the solidified materials must conform are dependent upon the final disposal site for the solidified waste and the end use of that site; however, ultimately the objective must be to produce a material which can be described as non-hazardous and which has a good structural integrity.

The costs of cement-based S/S of hazardous wastes depend upon a wide range of factors, for example, the type of the waste, the toxic species present and the form the waste is in. Typical treatment costs for one of the American cement-based solidification processes range from $40 to $260 depending upon the form that the waste is in (Hill, 1986).

1.5.1 Cement Hydration Chemistry

The properties of cement-based S/S depend upon the properties and behaviour of the cement additives and how they react with the wastes. Much work has been done to investigate the chemical and physical characteristics of ordinary Portland cement (OPC) hydration and this information provides a good foundation for the development of an understanding of the processes occurring in cement-based S/S.

Ordinary Portland cement is a hydraulic cement; it sets, hardens and does not disintegrate in water (Helmuth, 1987). Anhydrous OPC consists of angular particles (usually about 20 μm) with the following major constituents (Neville, 1981):-

- tricalcium silicate	(C_3S)	≈ 54%
- dicalcium silicate	(C_2S)	≈ 17%
- tricalcium aluminates	(C_3A)	≈ 11%
- alumino-ferrite	(C_4AF)	≈ 9%
- gypsum	($C\bar{S}H_2$)	≈ 4%

where C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, $\bar{S}$ = SO_3 and H = H_2O in cement chemist's nomenclature.

The hydration of C_3S is the dominant mechanism in the overall hydration and hardening process of OPC. The general hydration reaction can be written as :-

$$C_3S + (1.3 + x)H = C_{1.7}SH_x + 1.3\ CH \qquad - (1)$$

$C_{1.7}SH_x$ is calcium silicate hydrate and CH is calcium hydroxide (Bye, 1983). Calcium silicate hydrate (C-S-H) is an ill defined, poorly crystalline solid.

Several distinct stages in the hydration of C_3S have been identified (Birchall et al., 1978, 1979, Jennings & Pratt, 1978). When OPC is dispersed in water calcium ions are rapidly leached from the solids to form a solution of mainly CH (stage I, Figure 1.4) (Birchall et al 1978). The aqueous CH is thought to react with silicic acids on the surface of the cement to form a gelatinous semi-permeable membrane of C-S-H around the cement grains (Powers, 1961; Double & Hellawell, 1976; Jennings & Pratt, 1980). This semi-permeable membrane causes a dormant phase in the hydration process as the osmotic pressure inside the membrane increases (stage II, Figure 1.4). These stages can be observed experimentally by isothermal conduction calorimetry (Figure 1.4). The osmotic pressure inside the membrane causes it to rupture with the development of new C-S-H radiating from the anhydrous grain (stage III, Figure 1.4). The rupture of the gelatinous membrane is thought to occur by a scaling (exfoliation) mechanism (Bye, 1983). The previous rupture mechanism was thought to be an "osmotic pumping" mechanism which formed tubules of C-S-H (Double et al., 1977, 1978). Barnes et al. (1981), however, have shown that the "tubules" are associated with the hydration of C_3A and C_4AF in the presence of gypsum. The early stages of the hydration process are shown schematically in Figure 1.5. Stage III of the hydration process is also characterised by the initial CH crystallisation (Young et al., 1977) and by the transformation of C-S-H gel which exposes additional surface area of the anhydrous particles. Deceleration of the diffusion controlled reactions typify stages IV and V (Figure 1.4).

The hydration of C_3A, while not critical to initial strength development, is vital in determining cement setting times and the characteristics of stages I and II (Hansen, 1959). Hydration of C_3A in the absence of sulphate can be represented as :-

$$3C_3A + 21H \;=\; \underbrace{C_4AH_{13} + C_2AH_8}_{\text{metastable hexagonal hydrates}} \;=\; \underbrace{2C_3AH_6 + 9H}_{\text{stable hydrates}} \qquad - (2)$$

Most OPCs contain small quantities of sulphate in the form of gypsum (calcium sulphate) to prevent flash setting of the cement due to the reaction of C_3A (Equation 2). This modifies the hydration of C_3A to :-

$$C_3A + 3C\bar{S}H_2 + 26H \;=\; \underbrace{C_3A.3C\bar{S}.H_{32}}_{\text{ettringite}} \qquad - (3)$$

$$C_3A.3CS.H_{32} + 2C_2A + 4H \;=\; \underbrace{3(C_3A.CS.H_{12})}_{\text{monosulphoaluminate}} \qquad - (4)$$

The formation of ettringite (Equation 3) slows the hydration of C_3A by precipitation onto its surface. Ettringite forms both long prismatic crystals with hexagonal cross-sections, and amorphous layers. The formation of ettringite brings a volume increase, which, if the ettringite is formed after initial set, disrupts the structure causing an increase in permeability with the concomitant loss in strength (Wieldeman, 1982). In time the ettringite crystals may

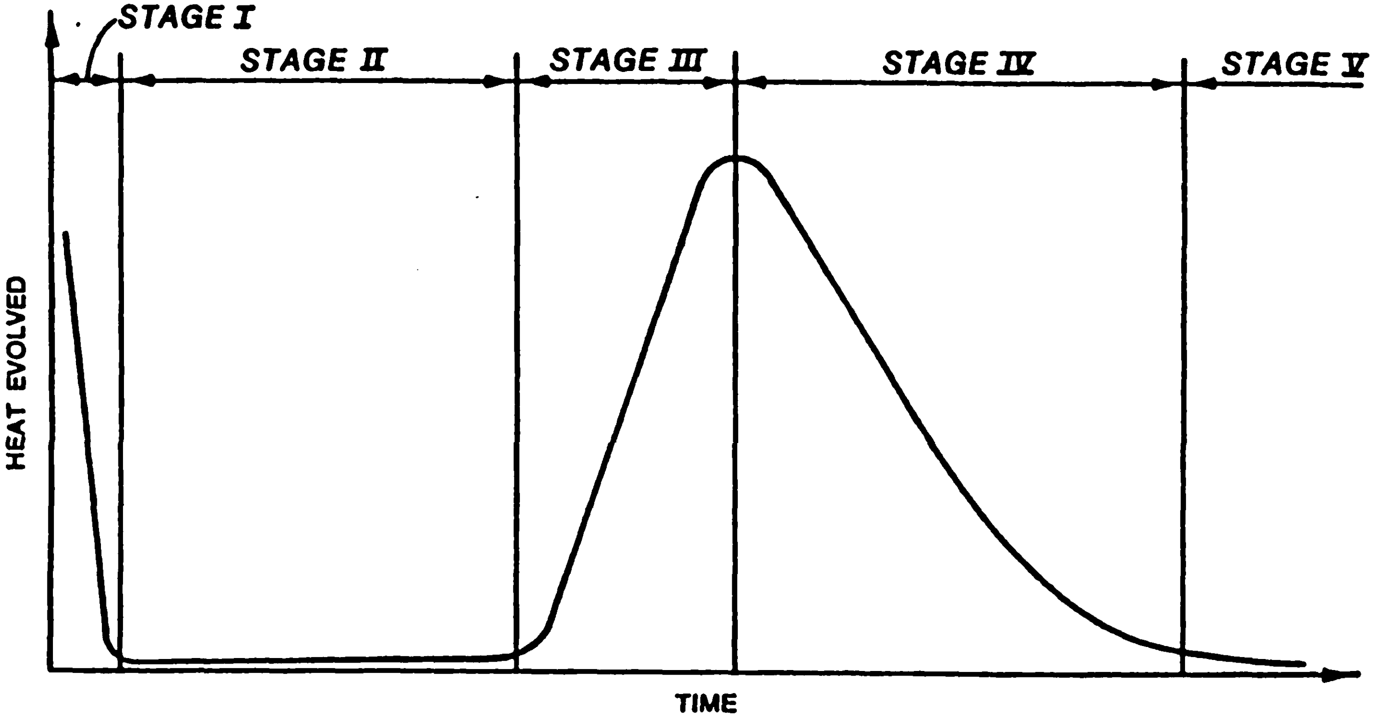


Figure 1.4: Heat Liberation Curve for the Hydration of Tricalcium Silicate, Determined by Isothermal Conduction Calorimetry (after Kondo & Daimon, 1969).

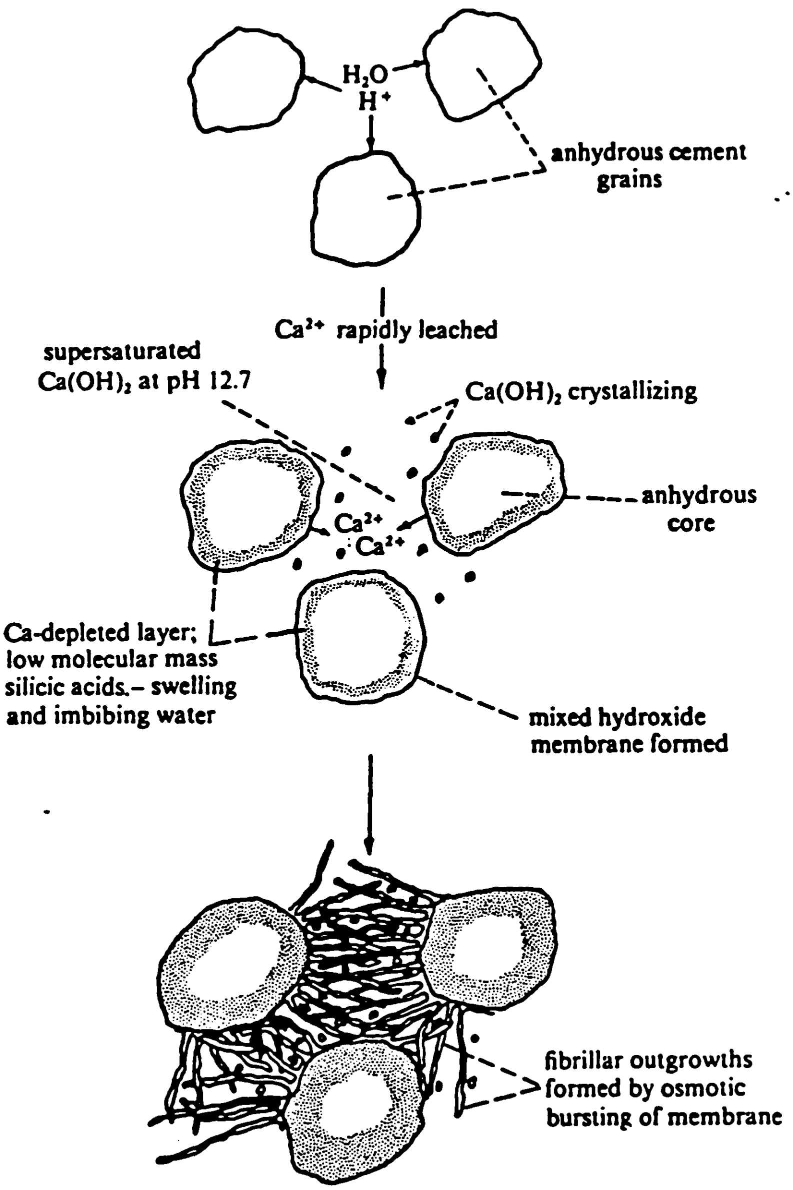


Figure 1.5: Schematic model for the hydration and setting of Portland Cement (Birchall et al., 1978).

react with the dicalcium aluminate according to Equation 4, to produce monosulpoaluminate. Monosulphoaluminate makes up 15 to 20% of the total solids volume of hydrated OPC and is the main constituent which is vulnerable to sulphate attack.

1.5.2 Interactions of Waste and Ordinary Portland Cement

Cement-based S/S has been widely used for the treatment of hazardous wastes; but a major problem with this form of waste treatment is chemical interference by the waste of the cement hydration process. In the cement and construction industry experience has shown that small amounts of some chemicals can significantly affect the strength and setting characteristics of cement. Stringent controls have been developed by the industry to ensure the quality of the cement, aggregate, water and additives used (Jones et al. 1986). A general list of constituents unacceptable in wastes for cement-based S/S are shown in Table 1.5. Limited scientific work has been carried out on the effects of specific waste components on the physical and containment properties of the final S/S waste product. The complexity of the hydration reactions of cement and the wide variety of constituents in even a single waste stream make prediction of the effect of a waste on a S/S mix highly complex (Jones 1988).

Of particular concern to cement-based S/S technology is the affect of organic compounds on the strength and contaminant immobilisation characteristics of the final product (Cullinane et al., 1987). Wastes which contain more than 1 to 2% organic compounds are difficult to solidify and the product is often weak and the organics easily leached (Montgomery et al., 1988).

(a) Research on Organic/Cement Interactions

The effect of small concentrations of some organic compounds on cement strength and hydration is well documented (Ashworth, 1965;

Young, 1972; Ramachardran, 1976; Lorprayoon & Rossington, 1981; Chandra & Flodin, 1987). Recently studies of organic/cement mixtures

Table 1.5: Components of Wastes which are Unacceptablė for Commercial Cement-Based S/S Processes as Single Waste Streams.*

	Waste Characteristic	Reason for Unacceptability
	INORGANIC WASTES	
1.	High soluble salt content eg. sodium chloride	Affect cement setting and may cause cracking
2.	High toxic anion content eg. borates	More easily leached than cations
3.	High content of cement setting retarders, eg. sulphates	Affect strength of final product e.g. spalling of surface
4.	Production of toxic gases not destroyed during processing eg. Hydrogen sulphide	In-plant health hazard
5.	Production of toxic/hazardous gases on contact with water or alkali e.g. metal carbides	In-plant health/safety hazard
6.	Production of toxic dust	
	ORGANIC WASTES	
6.	Contain flammable/explosive materials	In-plant safety hazard
7.	Contain biologically active compounds e.g. pesticides	May leach readily from final product
8.	Contain compounds known to inhibit cement e.g. sugars	Affects strength of final product
9.	Contain volatile components	In-plant safety
10.	Contain organics that are toxic in low concentrations	In-plant safety and risk of leaching into groundwater
11.	Contain carcenogenic material	In-plant safety and risk of into groundwater

*Clements & Griffiths (1985) and Sollars & Perry (1988) have been directed towards the effects of typical constituents of organic wastes upon cement hydration. Smith (1985) looked at the effects of phenol on the long term strength of cement paste and found that even low loadings (0.2% by volume) had an adverse effect upon the strength development. Riaz & Zamorani (1989) measured the effect of 1,3,5-trichlorobenzene on cement's physical properties. They found that although the strength and mean pore diameter of the cement pastes were reduced, the release of the organic during leach tests was low. Work on mixtures of pure organic compounds in cement has been carried out by Clarke et al. (1982), El Korchi et al. (1986) and Cullinane et al. (1987). All of these workers showed that for the organic compounds tested there was an appreciable reduction in the strength and setting rate of the solidified mixes unless additional solid binders were used to adsorb the organics. El Korchi et al. (1987) also looked at the effect of three organic compounds on the microstructure of the cement. They found that methanol and phenol inhibited the formation of ettringite whilst trichloroethylene seemed to stimulate it.

A major contribution to the data on the microstructural behaviour of cement with selected organic compounds has been make by workers at Louisana State University, USA (Tittlebaum, 1985; Chalasani et al., 1986; Roy et al., 1986; Skipper et al., 1986, 1987; Eaton et al. 1987; and Walsh et al. 1986). Over the past five years they have been working on the effect of ethylene glycol, parabromophenol and parachlorophenol on cement hydration using a wide range of microstructural, and some macrostructural, techniques. They have shown that ethylene glycol has a retarding effect upon the cement and occupies three distinct sites in the hydrated cement matrix. Ethylene glycol altered the microstructure of the cement, producing grainy nodular surfaces which lacked crystallinity. Walsh et al. (1986) postulated that the ethylene glycol molecules may be small enough to substitute for water in the hydration process so causing deformation of the products. Parabromophenol was found to react with the C-S-H gel which then underwent phase separation forming a concentrated crystalline phase. Parabromophenol had no overall effect upon the cement hydration products. Parachlorophenol was found to cause morphological changes in the cement hydration products and was shown to be closely associated with the C-S-H gel and is homogeneously distributed within it.

(b) Organic Wastes

In general, conventional cement-based S/S processes are unsuitable for the treatment of wastes which contain organic compounds. In recent years, hovever, a limited number of bench scale and pilot studies have been reported on wastes containing significant concentrations of organic compounds. The details of many processes reported are, unfortunately, "veiled in mystery" as they contain proprietary trade name products, the contents and structures of which are not reported.

Conner (1984), Myers & Zappi (1987), Shively & Crawford (1987) and Anon (1988) each reported the successful treatment of a range of organic containing wastes, on laboratory and pilot plant scales, by proprietary cement-based S/S techniques. Belteker et al. (1986) compared the treatment of contaminated dredge material by two proprietary processes and by cement alone. They showed that all three processes successfully stabilised the metal contaminants, but that the cement mix was the most successful technique for the containment of polychlorinated biphenyls in the waste. Montgomery et al. (1988) used an OPC/silicate mix to solidify heavy metal contaminated sewage sludge, and found that most metals were well stabilised, although copper and nickel were thought to complex with organic ligands present and were readily leached.

Kyles et al. (1987) investigated a range of conventional and novel techniques for the S/S of four wastes. Each waste contained considerable organic contamination; for example, an electroplating filter cake contaminated with chlorinated solvents and an acid tar residue from petroleum manufacture which contained high concentrations of entrapped oils and grease. Kyles et al. found that although most of the techniques tested produced solid products only the novel methods, which involved the use of, for example, acrylic jacketing of the solidified waste or the adsorption of the organic fraction of the wastes by powdered activated carbon prior to solidification, immobilised the organic constituents so they were not vulnerable to leaching.

Pichat (1983) and Millot et al. (1986) examined S/S techniques for the treatment of acidic organic wastes arising principally from the manufacture of fine chemicals. The authors used techniques which relied upon the reaction of strong acids with silicates, such as clays, to produce silicic acids and eventually silicate polymers. Van Keuren et al. (1987) also worked on acidic organic sludges, but used OPC together with spent Fullers earth to achieve a satisfactory S/S mix. Escher and Newton (1985) similarly used an OPC/clay mix to solidify three wastes spiked with cyanide and phenol. They showed that the presence of the clay gave good organic immobilisation during extensive leach testing. Lin & Mackenzie (1983) surveyed a range of adsorbents with a view to cement-based S/S of oily wastes. They found that all of the adsorbents tested could be saturated with up to 30% of the oily waste and successfully solidified with OPC. Newton (1988) described work on patent adsorbents containing sodium magnesium fluorolithosilicate and sodium bentonite reacted with a quaternary ammonium compound. Newton claimed to have successfully solidified organic containing wastes using these clay-based adsorbents and solidification by cement-based S/S. Cement/clay grouts have also been investigated by Spooner et al. (1984) who showed that they were suitable for cement-based S/S of a range of organic contaminated wastes.

1.6 CLAYS

Clay minerals have great potential as adsorbents for the pretreatment of organic contaminated wastes prior to cement-based S/S (Warren et al., 1986). Clays interact with a wide range of organic compounds (Theng, 1974; Lagaly, 1984) and are compatible with cement's silicate matrix (Grim, 1962). Clays have been used, for a number of years, for waste disposal in the nuclear industry (Holcomb, 1979) and as liners for hazardous waste containment landfill sites (Daniel, 1985; Buchler, 1986) due to their low permeability and high adsorption capacity for many metals and cationic species.

1.6.1 Reactions of Clays with Organic Compounds

Research on the reactions of clays with organic compounds is a fairly recent field as its development relied upon the detailed understanding of clays' mineralogical structure (Gard, 1971; Theng, 1974). Early experiments involving simple organic chemicals and pure bentonite clays showed that the inorganic cations could be replaced by organic cations (Giesking, 1939) and that uncharged polar compounds could enter the interlamellar space of the clay without the cations being released (MacEwan, 1948; Green-Kelley, 1955).

Clay-organic reactions were initially characterised by observation of the x-ray diffraction structure of the clays with organic compounds and calculation of electron density maps to obtain the orientation of adsorbed molecules (Brindley, 1956; Bradley et al., 1963). Clays have been found to adsorb most types of organic compounds ranging from anions such as oxalic acid (Siffert & Espinasso, 1980), neutral polar molecules such as ethylene glycol (Nguyen et al., 1987) and cations such as pyridine (Breen et al., 1985).

Over the years, studies of clay-organic interactions have been extensive and a wide range of techniques used in order to understand the mechanisms of adsorption and the properties of the organo-clays (Raussell-Colom & Serratosa, 1987). Extensive reviews of organo-clay chemistry are given by Theng (1974 & 1982), van Olphen (1977), MacEwan & Wilson (1980) and Raussell-Colom & Serratosa (1987).

Organo-clay complexes have found specialist industrial applications to produce thixotropic properties in paints and waxes, as gelling agents for lubricants and as additives to tars, plastics, ointments and cosmetic preparations (Lagaly, 1984). Recent developments in the field of organo-clays have focussed principally on their application as catalysts for a wide range of reactions (Barrer, 1984; Theng, 1982) particularly where the orientation of the reagents is paramount (Adams, 1985).

1.6.2 Structure of Montmorillonite

Smectites are a group of clays that have been widely investigated and found to have the ability to adsorb numerous inorganic and organic compounds (Barrer, 1984). The montmorillonite sub-group has the three layer sheet silicate structure, common to the whole group, with a central dioctahedral layer. Figure 1.6 shows the preferred "Wyoming" type structure for montmorillonite, although alternative structures have also been proposed (Grim, 1968). Montmorillonite occurs naturally in many different forms, for example, calcium montmorillonite as Fullers earth and sodium montmorillonite as Wyoming bentonite.

The major structural features of montmorillonite clays are their expandable interlamellar volume. This feature is due to trivalent aluminium, present in the clay lattice, being replaced by divalent iron or magnesium. The substitution results in an excess of negative charge which is compensated for by the adsorption of cations such as calcium or sodium. The compensating cations are too large to be accommodated in the lattice so they are held in the interlamellar space of the clay and can therefore easily be exchanged in aqueous solutions for other cations. The cation exchange capacity (c.e.c.) varies for each different type of clay, and a typical value for montmorillonite is 76.4 miliequivillants per 100 g of clay (Van Olphen & Fripiat, 1979).

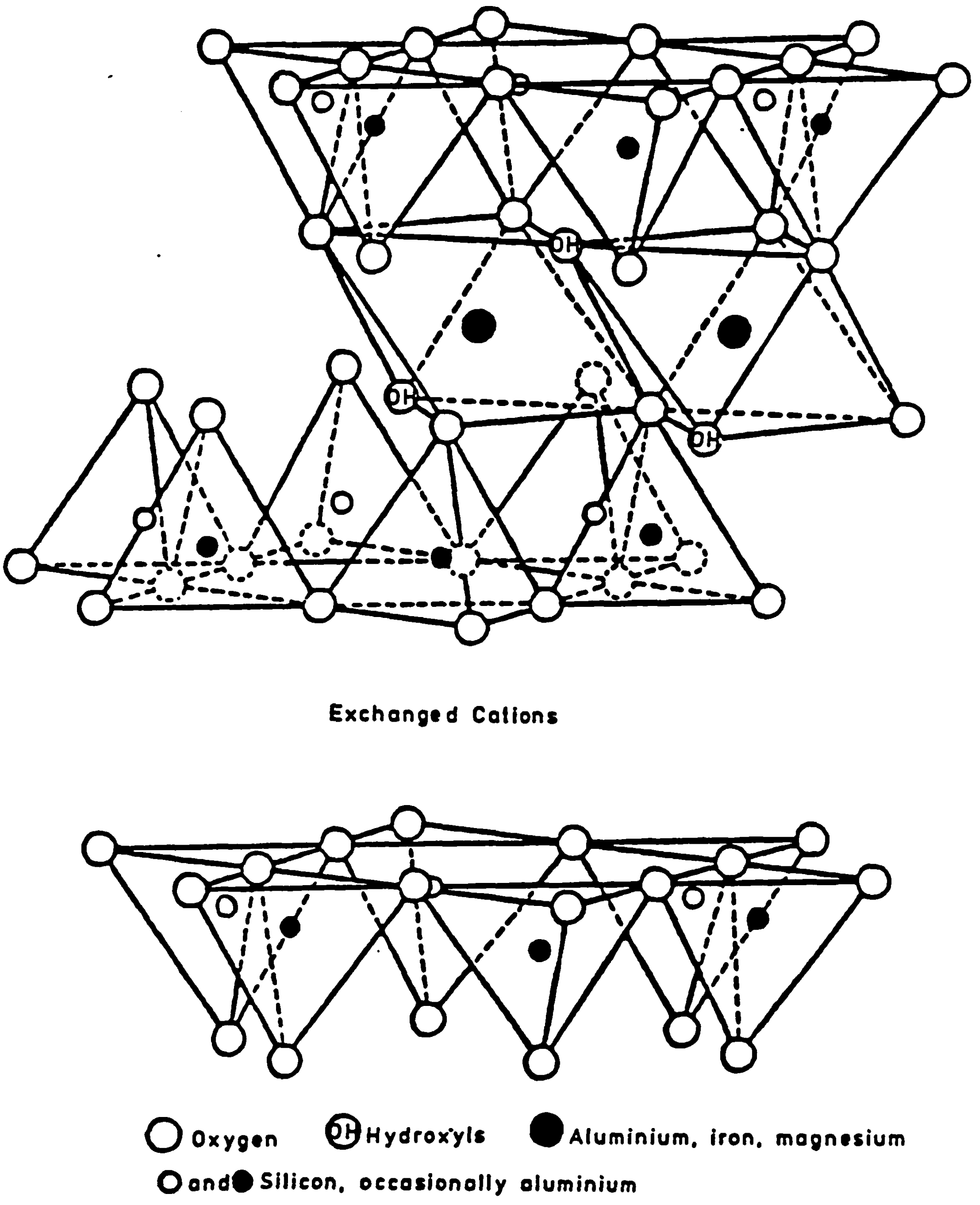


Figure 1.6: Sketch of the Structure of Montmorillonite (after Grim, 1968).

1.6.3 Cation Exchanged Montmorillonite

Organic cations can be adsorbed into montmorillonite from aqueous solution by the replacement of the exchangeable inorganic metal ions. The cation exchange capacity determined by small organic molecules corresponds closely to that obtained by inorganic cations (Hendricks, 1941). Conversely larger organic molecules, such as codeine, are adsorbed in smaller quantities than predicted from their basicities. This "cover up" effect is observed when the size of the adsorbed organic molecules exceeds the area per exchange site, 0.8 nm^{-2} for montmorillonite (Theng, 1974). The kinetics of the exchange processes have been studied by several groups, for example Midsuf et al. (1970) and Mackintosh et al. (1971). They found that the extent of displacement of inorganic cations and the reaction rates were dependant upon the structure and characteristics of the clay and the pH, temperature and, to some extent, the concentration of the organic cations in solution.

Research on the adsorption of longer chain alkylammonium compounds by montmorillonite has shown that those with chain lengths above C_{10} can be adsorbed in excess of the exchange capacity of the clay (Cowans & White, 1958; Theng et al., 1967 and Johns & Sen Gupha, 1967). Electro-neutrality is maintained by simultaneous adsorption of inorganic anions. Smaller cations can be removed from the clay by copious washing (Garnett & Walker, 1962) but the larger cations cannot (Furkawa & Brindley, 1973).

As the organic cations are adsorbed by the clay the interlamellar spacing increases to accommodate them. Jordan (1949) measured the basal spacing of alkylammonium montmorillonite complexes of varying chain lengths. He found that for amines containing 3 to 10 carbon atoms the basal spacing remained constant at 1.36 nm and for amines with carbon chain lengths of 12 to 20 carbons the spacing increased to 1.76 nm (Figure 1.7). Jordan postulated that the smaller cations could form monolayers in the interlamellar space while the larger cations overlapped to form a quasi-double layer. Figure 1.8 shows the stepwise change in the interlamellar spacing

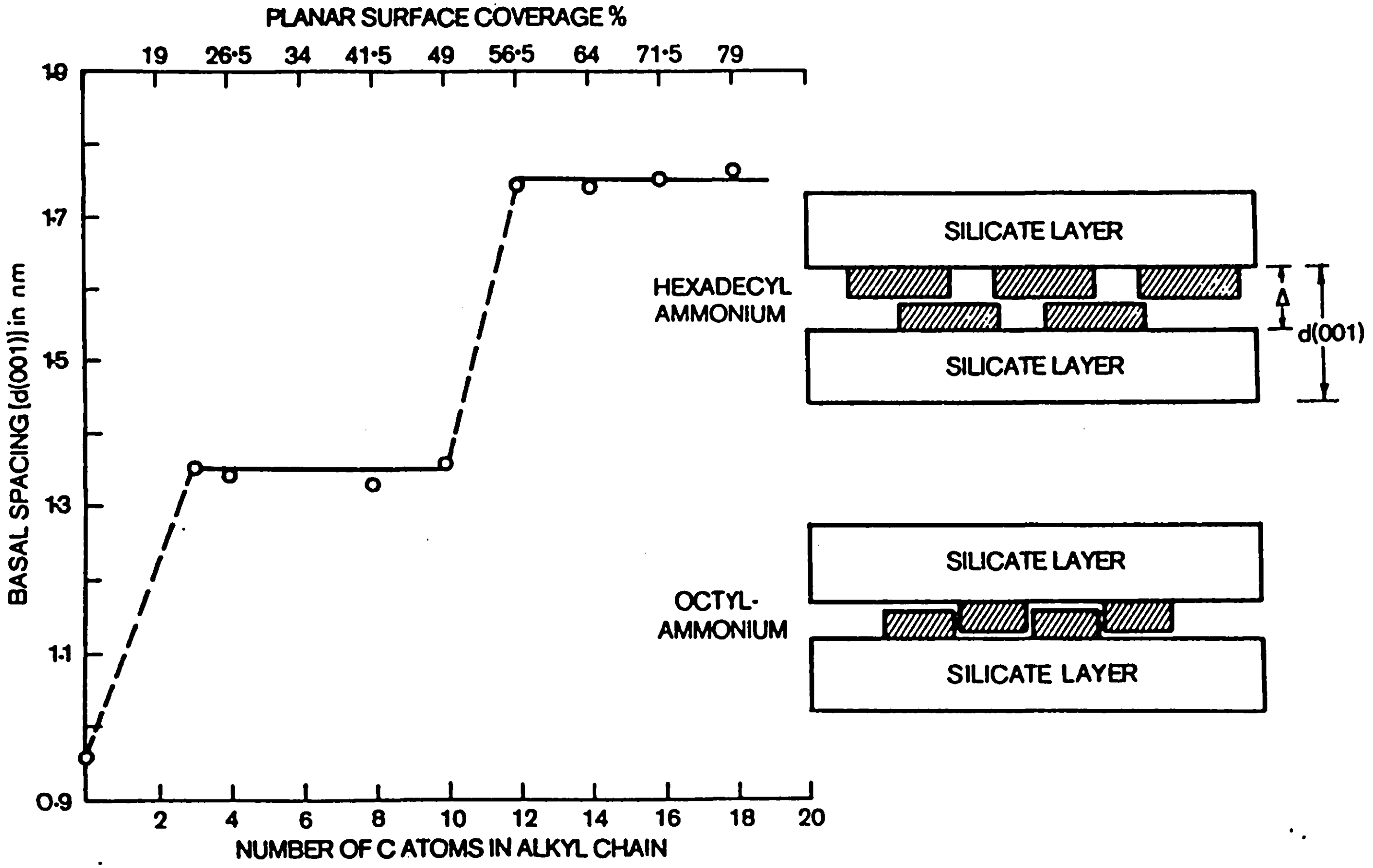


Figure 1.7: Variation in Basal Spacing with Number of Carbon Atoms in Alkyl Chain and with Percentage of Internal Basal plane Area Occupied by the Cation, in Complexes of Montmorillonite with Primary N-Alkylammonium ions (after Jordan, 1949).

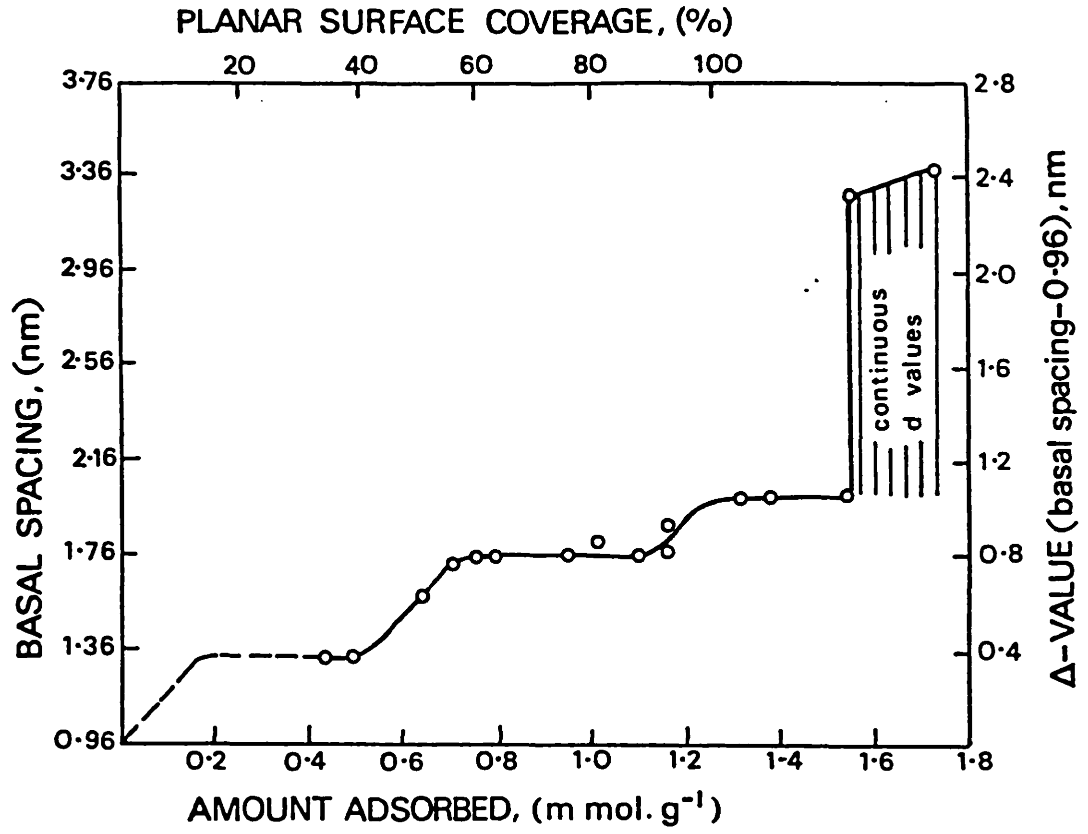


Figure 1.8: Changes in Basal Spacing of Montmorillonite Complexes with Increasing Amounts of N-Octadecyl Ammonium Ions Adsorbed (after Jordan et al., 1950).

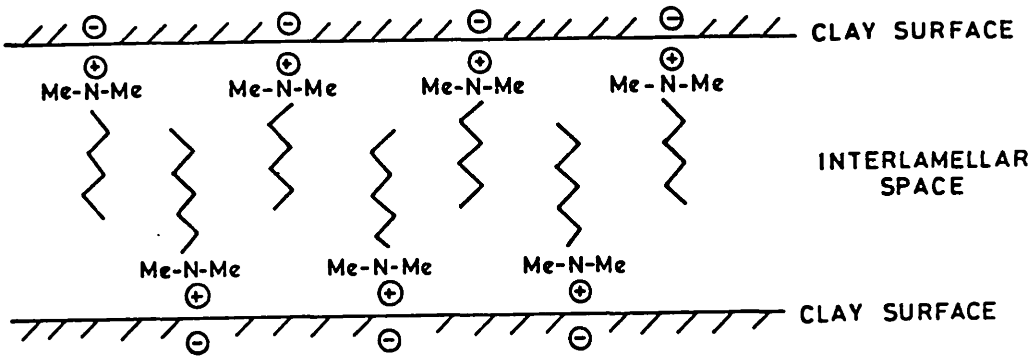


Figure 1.9: Schematic Representation of a Quaternary Ammonium Exchanged Clay (NOTE: One methyl group has been omitted from each QAS for clarity)

which is observed when long chain cations are adsorbed in amounts up to twice the exchange capacity of the clay (Jordan, 1950). Weiss (1954) showed that at low charge densities the hydrocarbon chains lay parallel to the clay's interlamellar surface, but with increasing charge density the chains tended to overlap and so were forced into a near-upright position with respect to the clay surface (Figure 1.9).

The bonding, in alkylammonium montmorillonites, between the organic cations and the charged silicate surface is mainly due to long range electrostatic forces, although physical, non-coulombic forces also contribute to adsorption. The free energy of adsorption, in the exchange process, has been found to decrease in the direction $R_3NH^+ > R_2NH_2^+ > RNH_3^+$ (Theng et al., 1967; Tahoun & Mortland, 1966). The increasing preference for the higher molecular weight species, with the largest number of alkyl groups, was thought to be due to the increased contribution of van der Waals forces to the adsorption energy (Theng, 1967). Work by Vansat & Uytherhoven (1972) has shown that the exchange was ruled mainly by entropic effects and that van der Waals forces play little part. They concluded that the increased affinity for larger cations was due to their greater disruptive effect on the structure of the hydration shell around the interlayer sodium ions.

Fixation is favoured if the organic cations contain radicals capable of interaction by hydrogen bonding with the surface oxygens of the silicate (Martin-Rubi et al., 1974). There is no conclusive evidence to show the hydrogen bonding of the methylene or terminal methyl groups to the surface oxygens (Fripiat et al., 1962). Gonzalez-Carreño et al. (1977), however, used infra-red spectroscopy to demonstrate a splitting of the symmetric deformation vibration band of the methyl group at $1380cm^{-1}$. They interpreted this as indicative of terminal methyl groups having their C_3 axes perpendicular to the clay surface and of a weak interaction between these groups and the silicate-oxygen atoms. The fixation of the organic cations in the clay are due to a combination of forces which contribute to a greater or lesser extent depending upon the structure of the organic cation. The stability of the complex formed will depend upon the combined strengths of all of the operating bonding mechanisms.

1.6.4 Adsorption of Organic Compounds by Alkylammonium Montmorillonite

Alkylammonium montmorillonites can adsorb neutral organic molecules on to the interlamellar space of the clay, from the vapour phase, from pure liquids or from aqueous solutions. Work on the adsorption of organic compounds, in the vapour phase, was originally carried out by Barrer & Macleod (1955) and Barrer & Reay (1957). They found that the alkylammonium montmorillonites had greatly increased adsorptive capacities compared to the unexchanged clays, and molecules such as paraffins and aromatic hydrocarbons were freely adsorbed. They also showed that short chain alkylammonium montmorillonites had a greater affinity for smaller molecules and the longer chain clays a greater affinity for the larger molecules. The length of the alkyl chains in alkylammonium montmorillonites govern the magnitude of adsorption of the organic compounds.

Cowans and White (1962) tested a range of alkylammonium bentonites and found that dodecylammonium bentonite best adsorbed phenols from aqueous solution. Alkylammonium montmorillonites possess areas of both hydrophilic and organophilic properties, the balance between the hydrophilic silicate surface and the organophilic amine chains being crucial to adsorption. Phenols possess a localised centre of high electron density, while the remainder of the molecule is essentially nonpolar. Cowans & White proposed that adsorption of the phenols on the alkylammonium montmorillonites occurred by electrostatic hydrogen bonding between the organophilic centres. Asymmetric hydrogen bonding to the organic cations occurs if the adsorbed molecules contain functional groups capable of acting as electron donors (Farmer and Mortland, 1965). Spectroscopic evidence for hydrogen bonding was obtained by Doner & Mortland (1969) who observed shifts in the carbon-oxygen and carbon-hydrogen stretching frequencies of the adsorbed amides and alkylammonium ions.

The greater the electronegavity of the amides the greater the frequency shift i.e. the stronger the hydrogen bonds formed.

Alkylammonium cations, capable of solvating the adsorbed organics, form van der Waals interactions between the cations and the adsorbed molecules (Raussell-Colom & Serratosa, 1987). Accommodation of the adsorbed molecules in the interlamellar space may affect the orientation of the alklyammonium cation so causing swelling of the complexes. In montmorillonites the alkylammonium cations and adsorbed organics arrange themselves with their longitudinal axes perpendicular to the silicate surface. For short chain alkylammonium complexes, adsorption with lattice expansion is only possible for the alkyl chain cations whose chains lengths exceed a critical length that is inversely related to the layer charge of the clay. The structural ordering of the bimolecular films in alkylammonium clays has been extensively studied by Lagaly et al. (1976). They found that the molecules in the film are able to undergo conformational changes by rotation about the carbon-carbon bonds so that the chain's structure is slightly modified.

Long chain alkylammonium montmorillonites can be dispersed in polar organic liquids to form thixotropic gels with very high liquid contents. Development of good organophilic character requires more than half of the available clay surface to be covered by the alkylammonium cations and the separation to be approximately 0.8 nm. Maximum swelling occurs with organic liquids such as nitrobenzene or benzonitrile which combine high polarity and high organophilicity. Complexes with unsymmetric tetra-alkylammonium cations, with two long aliphatic chains, are more organophilic because a larger proportion of the silicate suface is covered, hence they are able to adsorb less polar liquids, swelling even in unsubstituted hydrocarbons (Weiss, 1963).

The adsorption of organic compounds by clays from aqueous suspensions may be very different from the adsorption from non-aqueous systems, because water molecules will tend to compete readily for coordination sites on strongly solvating exchange cations (McBride et al., 1977).

Qualitative studies of the adsorption of alcohols from dilute aqueous solutions onto alkylammonium montmorillonites were carried out by Stul et al. (1979). They found that for adsorption the interlamellar phase of the clay acted as a solvent and the partition of the alcohol between the clay and aqueous solution was similar to the distribution of alcohols between alkanes and water in bulk solution. The alcoholic adsorption was found to be more dependant upon the alcohol chain length than on the alkylammonium cations.

The adsorption of phenol, benzene and chlorobenzene on to tetramethylammonium montmorillonite was studied by McBride et al. (1977). They found that solvent interactions with phenol, due to hydrogen bonding, were greater than with benzene so there was less tendency for phenol to penetrate the interlamellar regions. There was, however, a direct correlation in magnitude between benzene and phenol adsorption suggesting similar mechanisms of adsorption for both aromatics. Infrared studies by Fenn & Mortland (1972) have shown that alkylammonium montmorillonites adsorb phenol by ion-dipole interactions between the cations and the phenol molecules in a non-aqueous environment as well as by π-electron interactions with the silicate surface. The presence of water probably prevents ion-dipole interactions. McBride et al. also showed that chlorobenzene was poorly adsorbed from aqueous solution because it was too large to enter the interlamellar region of the clay. Mortland et al. (1986) studied a range of quaternary ammonium cations exchanged onto smectite as adsorbents for phenols. They found that complexes containing the longer chain cations were most hydrophobic and adsorbed phenols from water in proportion to their hydrophobicities which increased with chlorine addition. In less polar solvents (eg n-hexane) the trend in phenol adsorption was reversed.

Boyd et al. (1988a) showed that pentachlorophenol, a compound commonly used in treatment of wood, was well adsorbed by long chain quaternary ammonium exchanged clays (exchanged clays) from water.

They found, like Stul et al., that the partition of pentachlorophenol between the aqueous phase and the organophilic interlamellar clay surface was similar to that in a water:hexane system. The pentachlorophenol could be removed from the exchanged clay by treating the clay with a less polar solvent such as methylene chloride. Boyd et al. (1988b) extended their work to look at the adsorption of benzene and trichloroethane from aqueous solution onto hexadecyltrimethyl ammonium exchanged clay. They suggested that such sorptive organo-clay complexes would be useful to enhance the containment capabilities of clay landfill liners and for the treatment of the organic contaminants in leachates from landfill sites.

Wolfe et al (1985 & 1986) investigated the use of three quaternary ammonium exchanged bentonites for the aqueous adsorption of eleven organic compounds which commonly occur as pollutants in surface and ground waters in the USA. They found that the exchanged clays adsorbed all eleven organic compounds, to varying extents depending on the polarity and hydrophobicities of the molecules. X-ray diffraction studies of the organics adsorbed onto the exchanged clays showed that at high organic concentrations dodecylammonium ions were able to dissolve in the adsorbed organics and orientate perpendicularly to the silicate surface, greatly expanding the clay layers. At lower organic concentrations, the propylammonium montmorillonite had a larger free interlamellar volume and thus became a better adsorbent.

2. OBJECTIVES OF RESEARCH

Cement-based stabilisation/solidification has been used for the treatment of inorganic industrial wastes for a number of years. The fundamental objectives of the S/S process are to stabilise the waste in a impermeable monolithic matrix to prevent it from entering the environment. One of the major drawbacks of cement-based S/S, however, has occurred when trying to treat organic wastes or inorganic wastes with organic contents greater than 1 to 2 %. This is due, generally, to the poor interaction between organic hydrophobic compounds with the inorganic cement matrix. Organic compounds which do interact and cement tend to have a retarding effect on cement hydration and adversely affect the microstructural and hence the engineering properties of the final product.

The objectives of this study were to:-

- Characterise an adsorbent for the adsorption of the organic components from industrial waste streams.

- Use the adsorbent in the cement-based S/S process to solidify model and real organic-containing hazardous wastes which would otherwise be untreatable by conventional cement-based techniques.

- Study the solidification products:-
(a) Macrostructurally, to determine the physical characteristics of the materials and the chemical stability of the adsorbed organics.
(b) Microstructurally, to characterise the effect of the organic contaminants on the different phases of cement hydration in the absence and presence of the adsorbent.

- Investigate the potential use of the adsorbent in the reclamation of contaminated land either by stabilisation of the hazardous contaminants in the soil, or by use in cement-based S/S of the soil.

Studies on the topics of the adsorption of organic compounds by clays, cement-based stabilisation/solidification, the microstructrual properties of the S/S matrix, the application of the S/S process to industrial wastes and the clean up of contaminated land, have each been dealt with in separate self-contained chapters including results and a summary. This approach has been adopted because of the sequential design of the experimental work in which each separate section follows logically on from the preceding topic.

3. ADSORPTION STUDIES

3.1 INTRODUCTION

Organophilic clays have long been recognised as adsorbents for organic compounds. A major group of these clays are montmorillonites exchanged with quaternary ammonium salts (QAS). Extensive research has been carried out on the exchange of QAS cations onto montmorillonite. Adsorption studies and microstructural analysis has determined the degree of adsorption and the orientation of the QAS on the clays (Cowans and White, 1958; Theng et al., 1967; Martin-Rabi et al., 1974; Wolfe, 1981). The adsorption of small organic molecules from solution onto the QAS-exchanged clays has recently been investigated by several workers (Wolfe, 1985; Mortland et al., 1986; Sheriff et al., 1987).

This study investigated the use of specifically tailored QAS-exchanged clays to adsorb either single organic compounds or mixtures of inorganic and organic compounds from aqueous solution with a view to stabilisation of hazardous mixed organic/inorganic wastes prior to cement-based solidification and ultimate disposal.

The exchanged clays which gave best adsorption were assessed by determining the aqueous adsorption isotherms for three phenolic compounds by a wide range of exchanged clays. Phenolic compounds were chosen to screen the exchanged clays because:

- phenols are relatively soluble in water, so a wide range of concentrations could be prepared to produce the isotherms. (Solubilities:- Phenol = 9.3 g/100 ml; 3-chlorophenol = 2.7 g/100ml and 2,3-dichlorophenol = 0.49 g/100ml water at 25°C).

- the range of phenols, by introducing more chlorine substituents, showed the effect of increasing the hydrophobicity and acidity of the organic molecules

- phenols occur widely as hazardous pollutants in industrial wastes and in wastewaters (Patterson and Kadukala, 1981). Annual production of phenol is approximately 1.25 million tonnes (Chem. Eng. News, 1980). Phenol is the basic structural unit for many synthetic organics and is the degredation product of several common pesticides. Chlorophenols are produced form the degredation of chlorinated phenoxyacetic acid herbicides (Boyd, 1982).

- complex phenolic compounds are widely used as agricultural chemicals, for example, the pesticide pentachlorophenol.

The exchanged clay which was found to be the best adsorbent of the phenols was tested as an adsorbent for a wide range of common pollutants with differing structures, such as chlorinated solvents and aromatics. The stability and adsorptive capacity of the exchanged clay was tested over a wide range of pH and over long time periods. These tests assessed whether the clays would be suitable for use as adsorbents for industrial wastes, which are often highly corrosive, and determined whether the clays would break down in the highly alkaline cement matrix.

3.2 MATERIALS AND METHODS

3.2.1 Materials

Wyoming bentonite and Fulmont Première acid activated montmorillonite were supplied by Laporte Industries, Widnes, UK. Wyoming bentonite comes from rocks of the Cretaceous era, composed of shales, marls and argillaceous sandstones. Wyoming bentonite is composed mainly of sodium and calcium montmorillonite with impurities of quartz and calcite. The Fulmont acid activated montmorillonite is produced from a typical calcium montmorillonite, from Redhill in Surrey, activated by treatment with sulphuric acid. The chemical and physical properties of both of these clays are shown in Table 3.1.

Table 3.1: Analysis of Wyoming Bentonite and Acid Activated Montmorillonite

	Wyoming Bentonite*	Acid Activated Montmorillonite*
Chemical Analysis (% by weight of sample dried at 105°C)		
Silicon dioxide (SiO_2)	62.90	62.50
Alumina (Al_2O_3)	19.60	12.00
Titanium dioxide (TiO_2)	0.09	0.60
Ferric oxide (Fe_2O_3)	3.35	5.10
Ferrous oxide (FeO)	0.32	0.00
Manganese oxide (MnO)	0.01	0.00
Magnesium oxide (MgO)	3.05	2.20
Calcium oxide (CaO)	1.68	4.00
Sodium oxide (Na_2O)	1.53	0.20
Potassium oxide (K_2O)	0.53	0.60
Phosphorus pentoxide (P_2O_5)	0.05	0.00
Sulphur (S) or sulphate (SO_4^{2-})	0.05	6.60
Fluoride (F^-)	0.11	0.00
Loss on heating	4.47	6.20
Surface Area (m^2/g	31.82 ± 0.22	240.00
Cation Exchange Capacity (meq/100 g)	76.60	50.00

*Data supplied by Laporte Industries, UK.

Quaternary ammonium salts (QAS) were obtained from:-

Sigma Chemical Company Ltd, UK (Tetradecyltrimethyammonium chloride (TDTMA-Cl), Hexadecyltrimethyammonium chloride (HDTMA-Cl)).

AMB Chemicals, UK (Octyltrimethyammonium chloride (OTMA-Cl)).

Akzo Chemie, UK (Octadecyltrimethyammonium chloride (ODTMA-Cl), Benzyloctadecydimethylammonium chloride (BODDMA-Cl), Cocobis(2-hydroxyethyl)methylammonium chloride (CB2-HE-Cl), Oleylbis(2-hydroxyethyl)methylammonium chloride (OB2-HE-Cl), Polyoxyethylene(15)cocomethylammonium chloride (POE(15)C-Cl), Polyoxyethylene(15)stearylmethylammonium chloride (POE(15)S-Cl)).

Fluka Chemie AG, Switzerland; (Dioctadecyldimethyammonium chloride (DODDMA-Cl), Tetraoctyldecyl ammonium chloride (TODA-Cl)).

The activated carbons used in the adsorption experiments were obtained from The British CECA Co. Ltd., UK (CXV and 3SA); Chemviron Carbon, UK (Chemviron); Sutcliffe Speakman Carbons Ltd., UK (SS203C/P, SS207C/P and SS338C/P).

All other reagents were obtained from BDH Chemicals Ltd, UK and were AnalaR grade unless otherwise stated.

3.2.2 Preparation of Quaternary Ammonium Salt Exchanged Clays

Unexchanged Wyoming bentonite (100 g) was ground in a ball mill, sieved to give a particle size of less than 200 µm, dried at 105°C for 24 hours, and cooled in a desiccator. Samples (75 g) of the desiccated clay were weighed out and suspended in 1.5 l of aqueous 0.1 M quaternary ammonium salt (QAS) solution which was being rapidly stirred on a magnetic stirrer. The formulae, relative molecular masses of QAS and the acronyms of the exchanged clays used are shown in Tables 3.2 and 3.3.

Table 3.2: Structure of Quaternary Ammonium Salts Exchanged onto Wyoming Bentonite.

Chain Length	Structural Formula of Cation	Name of Cation	Acronym of QAS Clay	RMM of Cation
1	$(CH_3)_4\ N^+$	Tetramethylammonium	TMAM	74
1	$(CH_3)_3\ N^+\ C_6H_5$	Trimethylphenyl -ammonium	TMPAM	124
8	$(CH_3)_3\ N^+\ (CH_2)_7CH_3$	Octyltrimethyl -ammonium	OTMAM	172
14	$(CH_3)_3\ N^+\ (CH_2)_{13}CH_3$	Tetradecyltrimethyl -ammonium	TDTMAM	256
14	$(CH_3)_2\ N^+\ (CH_2)_{13}CH_3$ $CH_2C_6H_5$	Benzyldimethyltetra -decylammonium	BDMTDAM	284
16	$(CH_3)_3\ N^+\ (CH_2)_{15}CH_3$	Hexadecyltrimethyl -ammonium	HDTMAM	318
18	$(CH_3)_3\ N^+\ (CH_2)_{17}CH_3$	Octadecyltrimethyl -ammonium	ODTMAM	312
18	$(CH_3)_2\ N^+\ (CH_2)_{17}CH_3$ $CH_2C_6H_5$	Benzyloctadecyl -dimethylammonium	BODDMAM	388
18	$(CH_3)_2\ N^+\ ((CH_2)_{17}CH_3)_2$	Dioctadecyldimethyl -ammonium	DODDMAM	550
18	$((CH_2)_{17}CH_3)_4\ N^+$	Tetraoctadecyl -ammonium	TODAM	1026

Table 3.3: Structure of Modified Quaternary Ammonium Salts (QAS) Exchanged onto Wyoming Bentonite.

Structural Formula of Cation	Name of Cation	Acronym of QAS Clay	Molecular Mass of Cation
$R\ N^+\ (C_2H_4OH)_2$ CH_3	Cocobis(2-hydroxyethyl) -methylammomium	C/12	298
$(C_2H_4O)_xH^*$ $CH_3\ N^+\ R$ $(C_2H_4O)_yH^*$	Polyoxyethylene(15)stearyl -methylammonium	C/25	841
R = 3% C_8; 5% C_{10}; 50% C_{12}; 19% C_{14}; 10% C_{16}; 10% C_{18}.			
$R\ N^+\ (C_2H_4OH)_2$ CH_3	Oleylbis(2-hydroxyethyl) -methylammonium	O/12	360
R' = 1% C_{12}; 4% C_{14}; 12% C_{16}; 82% C_{18}; trace C_{20}			
$(C_2H_4O)_xH$ $CH_3\ N^+\ R''$ $(C_2H_4O)_yH$	Polyoxyethylene(15)coco -methylammonium	HT/25	903
R'' = 1% C_{12}; 4% C_{14}; 31% C_{16}; 64% C_{18}; trace C_{20}.			

* $x + y = 15$

To obtain homogeneous solutions of the higher chain length QAS compounds, it was necessary to heat the salts to around 60°C to enable them to dissolve. The solutions were kept between 60 and 70°C whilst exchange was taking place to allow maximum penetration of the clay by the QAS (Mifsud et al. 1970; Mackintosh et al. 1971). The 5% w/w clay suspensions were stirred for 48 hours to allow exchange to take place. After 48 hours, the suspension were filtered, under vacuum, through a Whatman No. 1 paper, care being taken to exclude the final 100 ml of the suspension which contained the black quartz and calcite impurities. The filter cakes, which contained predominantly exchanged montmorillonite, were re-suspended in approximately 2 l of distilled water, stirred until a homogeneous suspension was obtained and then re-filtered. This washing process was repeated three times to remove the excess QAS from the outer surface of the clays. After the final washing the filter cakes were dried at 105°C for 48 hours, cooled in a desiccator and ground manually in a pestle and mortar to a particle size less than 500 µm. For TODAM and DODMAM the drying procedure was modified as the salts were heat sensitive; hence, after the final washing the filter cakes were dried under vacuum for approximately 7 days.

3.2.3 Adsorption of Phenols from Water

The adsorbents (exchanged clay or activated carbon, 1.0 g) were weighed into 250 ml polypropylene screw-top containers. Aliquots (100 ml) of the required solutions containing a range of phenol concentrations between 5 mM and 20 mM were added to the clays and phenol concentrations between 1 mM and 50 mM added to the activated carbons. The containers were rotated end-over-end for 3 hours until the equilibrium had been reached between the adsorbent and the phenolic solutions (the method for measuring the equilibrium point is described latter in this section). The suspensions were filtered through Whatman No. 1 paper and the filtrate analysed for the phenol concentration either colourimetrically (APHA-AWWA-WPCF, 1980) or by measurement of the filtrate ultraviolet (UV) adsorption on a Pye-Unicam spectrophotometer using 10 mm quartz cells. The wavelengths used for this were 269 nm for phenol, 274 nm for 3-chlorophenol, and 272 nm for 2,3-dichlorophenol.

The amount of the phenols adsorbed by each exchanged clay and by activated carbon were determined in three separate samples per concentration and the results presented as the mean of the adsorption data.

The average time taken for equilibrium to be reached had been previously determined by adsorption experiments with aqueous solutions of phenol, 3-chlorophenol and 2,3-dichlorophenol using three representatative exchanged clays. The clays chosen were montmorillonite exchanged with the QAS containing the TMA, BODDMAM and C/12 cations (Tables 3.2 amd 3.3 respectively). The equilibrium point in these experiments was determined by analysing the residual concentration of each of the three phenols at regular time intervals (15 minutes) until no significant further adsorption took place (3 hours). The adsorption experiments were then continued for BODDMAM up to 56 hours with samples taken at 1 hour intervals.

3.2.4 Stability of Quaternary Ammonium Salts on Montmorillonite Clay

Two experiments were carried out to determine the stability of the exchanged clay. The first experiment investigated the stability of the QAS on the clay in aqueous suspensions at high pH. One set of clay samples were exchanged with BODDMA-Cl to below the maximum exchange capacity of the clay. The other set of samples was exchanged with excess BODDMA-Cl, the excess being adsorbed by the clay.

The clays were prepared by suspending 75 g of Wyoming bentonite in 1.5 l of 0.05 M BODDMA-Cl solution for exchange below the clay's capacity and in 0.1 M solution for the exchange above the clay's capacity. The suspensions were stirred for 48 hours to allow adsorption to take place. The clay suspensions were filtered, under vacuum, and a sample of each removed for analysis. The clays were washed by resuspending the filter cake in 2 l of water and filtering between each of the three washings. Samples of clay were preserved after the final wash. The two washed filter cakes were divided into four portions each and the portions suspended in 2 l of either (i) distilled water, (ii) ammonium hydroxide buffer at pH 9, (iii) sodium hydroxide at pH 10, (iv) sodium hydroxide at pH 11. The clay suspensions were stirred for 3 hours, then filtered and analysed for

QAS concentration. Analysis for the QAS on the clay samples was carried out by carbon-hydrogen-nitrogen (CHN) analysis.

The second experiment investigated the stability of the QAS, on the clay, to leaching over a 56 day period. Exchanged clay (1.0 g) was added to 100 ml distilled water or 0.1 M sodium hydroxide in polypropylene containers. The containers were rotated, end-over-end, for 56 days. Samples of the supernate were collected at regular intervals by allowing the containers to stand for 1 hour to allow the clay to settle prior to removal of 1.5 ml of supernate using a syringe. The supernate samples were stored at -18°C in glass vials prior to analysis for Total Organic Carbon. Total Organic Carbon (TOC) analysis was carried out on a DC-80 analyser (Envirotec Dohrmann). The DC-80 is a general purpose laboratory analyser utilizing the ultraviolet-promoted acid persulphate oxidation technique to oxidize organic carbon to carbon dioxide. The concentration of carbon dioxide in the out-flow gas is measured by UV analysis. The concentration of QAS in the samples was calculated from the weight of carbon found in the samples which was found to be all due to QAS. Three replicates of each experiment were performed.

3.2.5 Effects of pH

To test the effect of pH on the exchanged clays twelve samples of BODDMAM were weighed into polypropylene containers and 100 ml of pH adjusted buffer added. The containers were shaken for 3 hours and the contents filtered. Analysis of the filtrates for QAS concentration was carried out using a TOC analyser.

To determine the effect of pH on the adsorption of phenols, a series of adsorption experiments were carried out at a range of pHs. For each of the three phenols under test twelve samples (1.0 g) of BODDMAM were weighed into polypropylene containers and 100 ml of the aqueous phenolic solution added, as in the previous adsorption experiments (Section 3.2.3). The containers were shaken for 3 hours to allow adsorption to take place. The pH of each sample was then adjusted to that required using 0.1 M hydrochloric acid (pH 2, 3 and 4); 0.5 M phosphate buffer (pH 5, 6 and 7); 0.5 M ammonium hydroxide (pH 8, 9 and 10); 0.1 M potassium hydroxide (pH 11 and 12). The containers were shaken for a further 3 hours, the pH of each sample was checked at regular intervals during the experiment and the pH adjusted, if necessary, to maintain the selected value. After 3 hours the suspensions were filtered and analysed. The volume of acid or base added to obtain the required pH was recorded, and when the samples were analysed the dilution of the supernatant by the buffers was included in the calculation.

3.2.6 Co-adsorption of Group IIB Metals with 3-Chlorophenol onto BODDMAM

The adsorption experiments were carried out as in the previous adsorption experiments (Section 3.2.3) except that the phenolic concentration was held constant at 1.0 mM of 3-chlorophenol per 100 ml of solution. To the aqueous 3-chlorophenol solution was added zinc nitrate ($Zn(NO_3)_2.3H_2O$), cadmium nitrate ($Cd(NO_3)_2.H_2O$), and mercuric chloride ($HgCl_2$), in varying quantities, to give a range of metal concentrations from 1 mM to 100 mM. The clay suspensions were shaken for 3 hours, filtered and analysed for the 3-chlorophenol and metal concentrations. Analysis for 3-chlorophenol was carried out by measuring the ultraviolet adsorption at λ = 274 nm using 10 mm quartz cells. Analysis for metals was carried out using a Perkin Elmer 5000 series atomic absorption spectrophotometer (A.A.).

3.2.7 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared analysis (FTIR) enhances the sensitivity of the infrared spectra by reducing the background noise. This effect is achieved by signal averaging all of the resolution elements of the spectrum which are measured simultaneously. The FTIR analysis was carried out on five powdered samples (the preparation of which was described in Sections 3.2.2 and 3.2.3), unexchanged Wyoming bentonite, BODDMA-Cl, BODDMAM, and BODDMAM with 0.5 m mol. and 1.5 m mol. of 3-chlorophenol adsorbed. The instrument used was an "Sigma" Alpha Centauri instrument made by Mattheson Instruments, UK, analysis was carried out between the wavelengths 3500 to 750 nm.

3.2.8 Thermal Analysis

Thermal analysis was carried out using a Stanton Redcroft STA-780 series thermal analyser (Stanton Redcroft, UK). Thermogravimetric analysis (TGA) continuously records the mass of the sample as its temperature is increased. The plot of mass as a function of the temperature provides information on the decomposition of the sample. In differential thermal analysis (DTA), the heat absorbed or emitted by a chemical system is observed by measuring the temperature difference between that system and an inert reference compound (alumina) as the temperatures of both are increased at a constant rate. DTA provides qualitative information of phase changes in the sample and energy changes during decomposition or reaction of the sample.

The samples were analysed under a flow of purified nitrogen (87 ml/min) at a heating rate of either 15°C/min or 25°C/min over a temperature range of 25 to 530°C. The heating took approximately 35 minutes or 21 minutes respectively and the furnace was then held at 530°C for a further 10 minutes. To determine the total amount of carbon present, the samples were first heated in nitrogen to 530°C at a heating rate of 40°C/min. Air was then pumped into the furnace at a rate of 60 ml/min whilst heating continued. The samples were then heated further to 1000°C in air, the temperature being held constant for five minutes at values of 500°C, 760°C and 840°C respectively to allow the sample temperature to equilibrate with that of the furnace.

3.2.9 Adsorption of Organic Compounds by ODTMAM

(a) Adsorption From Water

The adsorption experiments were carried out over a wide range of concentrations. For example naphthalene, had a maximum organic concentration of 2.5 mM due to its low solubility in water, whilst others could be tested up to 25 mM. The range of concentrations of the organic compounds in water used in these experiments and their solubilities in water are shown in Table 3.4.

Table 3.4: Range of Concentrations of Organic Compounds used in Adsorption Experiments and Analytical Wavelengths.

Compound	Solubility* (mg/l)	Concentration Range (mM) From	To	Wavelength (nm)
Phenol	93,000	5.0	25.0	266
3-Chlorophenol	27,000	5.0	25.0	270
2,3-Dichlorophenol	4,900	5.0	25.0	272
Methyl Orange	<100,000	0.1	20.0	450
Methylene Blue	<100,000	0.1	20.0	658
Phthalic Acid	5,000	0.1	10.0	274
Toluene	460	1.0	10.0	254*
Aniline	37,000	5.0	10.0	274
Acetone	<100,000	0.9	10.0	>190*
Benzene	1,900	1.0	2.0	198*
Naphthalene	32	0.1	2.0	270
Chloroform	8,200	0.1	2.0	198*

* = Analysed by TOC
* = at 20°C in Aqueous Solution.

The clay used for all of the experiments was octadecyltrimethylammonium montmorillonite (ODTMAM), which does not contain an aromatic group as in BODDMAM which would interfere with the UV analysis of the organic species. The protocol for the adsorption experiments was the same as for the phenol adsorptions from water (section 3.2.3). The exchanged clay (1.0 g) was weighed into a container and 100 ml aliquots of the required solution added. The clays were allowed to adsorb for 3 hours before they were filtered and analysed. Analysis was carried out using a Lambda 3 Perkin Elmer UV spectrophotometrer the wavelengths shown in Table 3.4. For compounds where the adsorption maxima overlapped the adsorption of the ODTMA cation (254 to 210 nm) the Total Organic Carbon content of the filtrate was measured and compared to a control solution to allow for the possible release of ODTMA cation into the leachate. The absolute concentration of all of the original solutions was checked using TOC analysis, to ensure that no evaporation of the organic compounds had taken place .

(b) Adsorption From Hexane

Many organic compounds are only sparingly soluble or are insoluble in water, so to test the ability of exchanged clays to adsorb a wider range of organic compounds, hexane was chosen as an alternative solvent.

The adsorption experiments were carried out in hexane using the same protocol as the adsorption experiments from aqueous solution (Section 3.2.3), except that the adsorption of the exchanged clays was tested at only one concentration (10 mM). The organic compounds tested were benzene, chlorobenzene, naphthalene, 1-chloronaphthalene, biphenyl, 4-chlorobiphenyl, 4-hydroxybiphenyl, naphthol, 4-chloro-1-naphthol and 2,4-dichloro-1-naphthol.

3.3 RESULTS

3.3.1 Adsorption of Phenols from Water

A range of fourteen QAS with carbon chain lengths from C_1 to C_{18} and with several substituents were exchanged onto Wyoming bentonite to form a series of exchanged clays. Adsorption studies were carried out using these exchanged clays to produce adsorption isotherms for phenol, 3-chlorophenol and 2,3-dichlorophenol from aqueous solution. The results of these studies, (Figures 3.1, 3.2 and 3.3) illustrate the adsorption by 1.0 g of the exchanged clay of between 0.5 and 2.0 m mol. of phenol or chlorinated phenols from 100 ml of the solutions. These results, when compared with the adsorption of the phenols by unexchanged Wyoming bentonite, and with acid activated montmorillonite (not shown) show greatly improved adsorption ability. The results were also compared with the adsorption of the phenols by a range of eight activated carbons commonly used in wastewater treatment (Figure 3.4).

The general trends of phenol adsorption demonstrated by the unsubstituted exchanged clays were increased adsorption with increasing chain length, i.e. ODTMAM >> OTMAM >> TMAM. The substitution of a benzyl group for one of the N-methyl groups had a slightly beneficial effect upon the adsorption capacity compared with that of the trimethyl alkyl QAS-exchanged clays. The addition of two or four aliphatic chains to the exchanged clays greatly reduced the ability of the clays to adsorb the phenols. This effect was considered to be due to either the inability of the larger QAS to be effectively exchanged into the interlamellar space of the clay, or to the ability of the larger branched molecules to completely fill the interlamellar spacing so preventing the phenols entering the structure. The magnitude of adsorption of both 3-chlorophenol and 2,3-dichlorophenol by the exchanged clays was very similar. They were adsorbed best by the long chain exchanged clays, over 90% being adsorbed by BODDMAM (Figures 3.2(III) and 3.3(III)). Phenol,

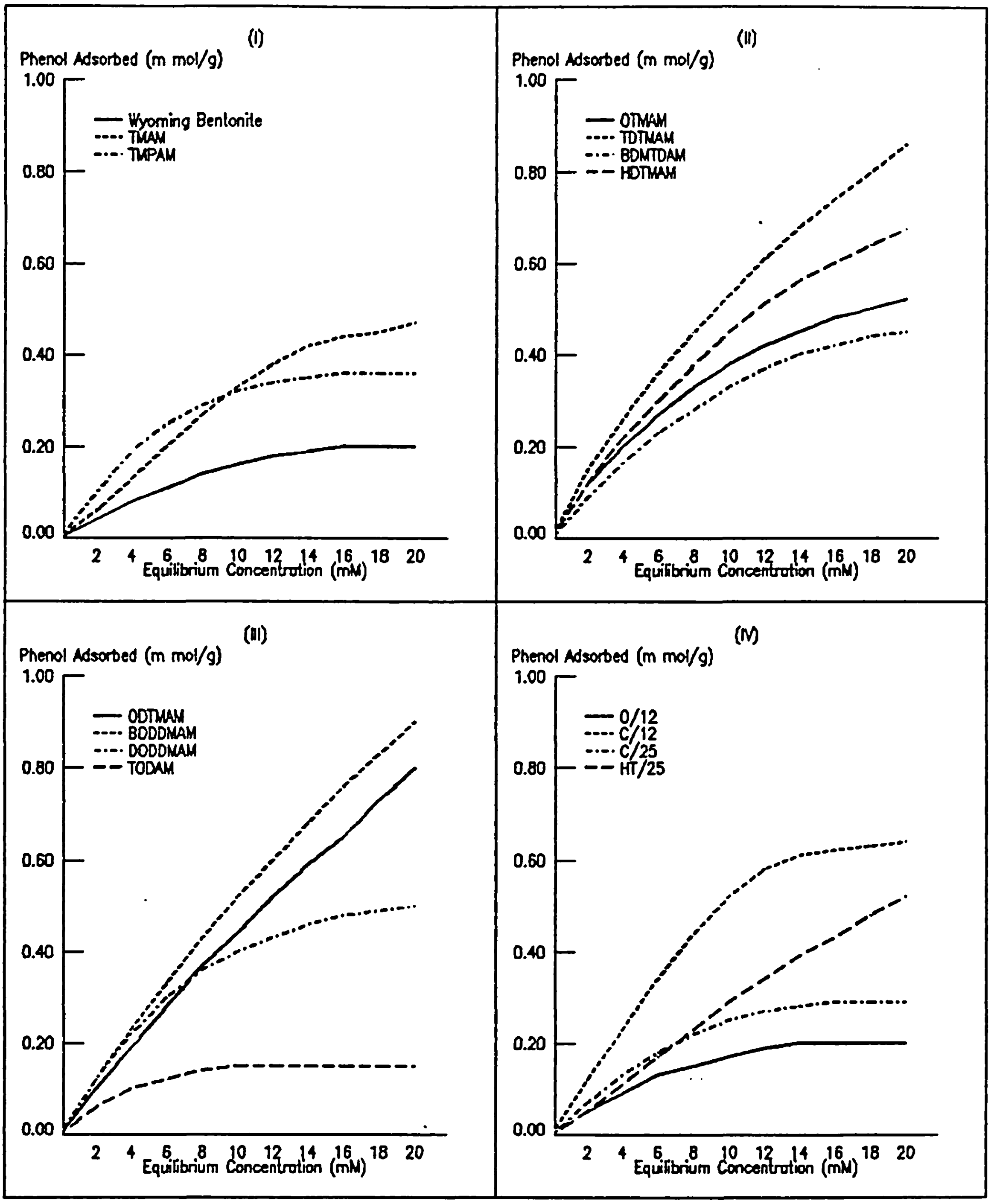


Figure 3.1: Adsorption of Phenol by the Exchanged Clays.

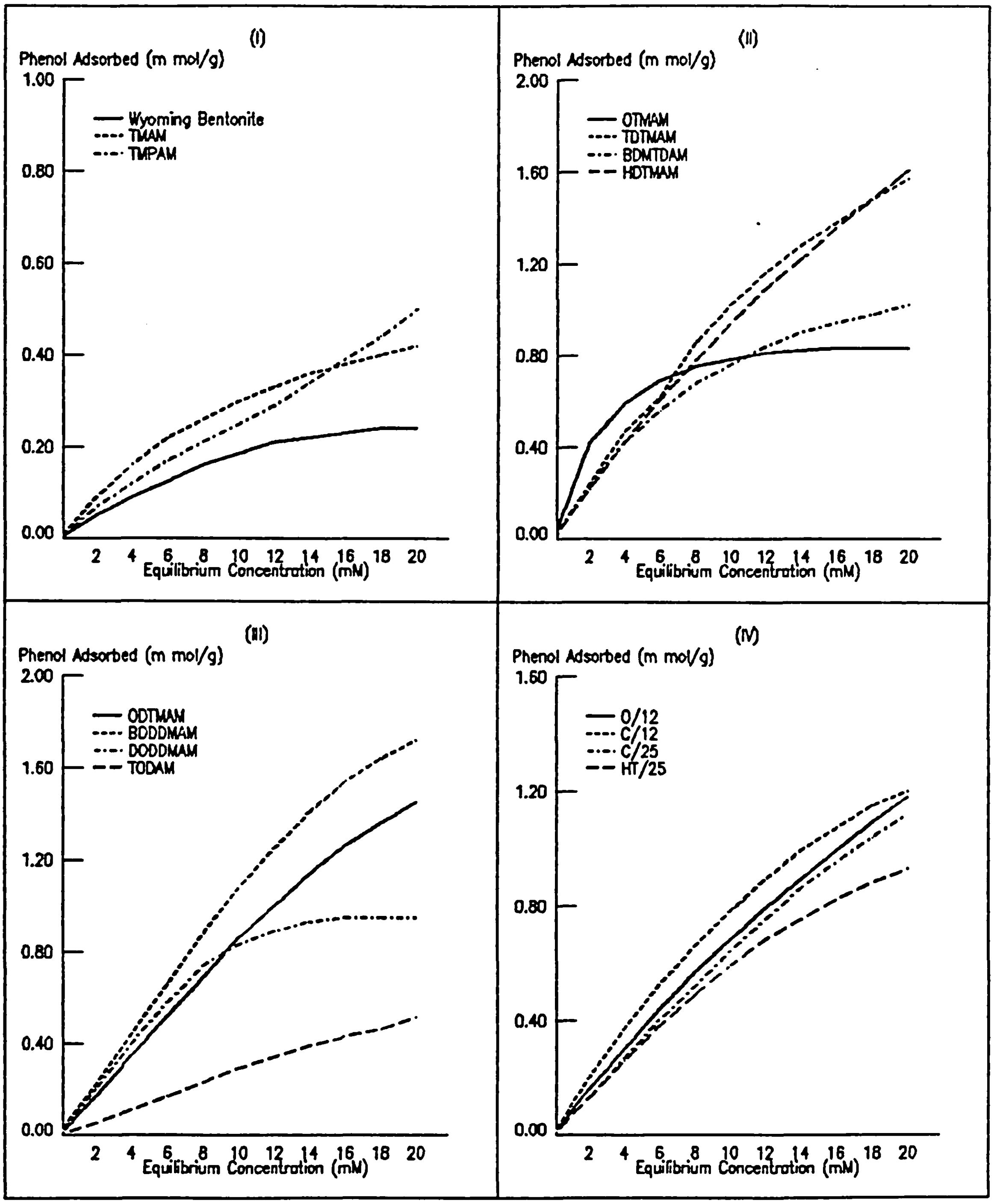


Figure 3.2: Adsorption of 3-Chlorophenol by the Exchanged Clays.

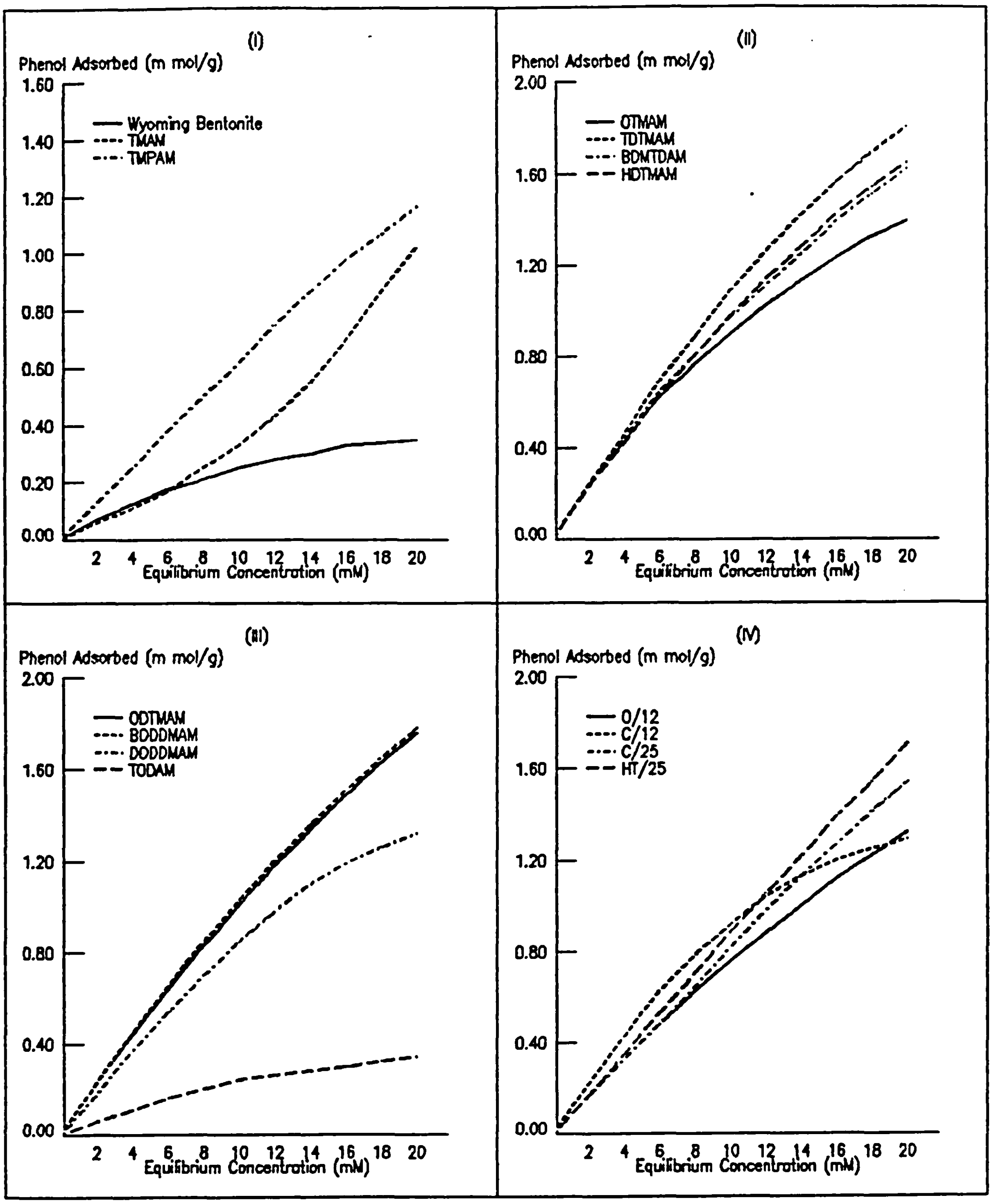


Figure 3.3: Adsorption of 2,3-Dichlorophenol by the Exchanged Clays.

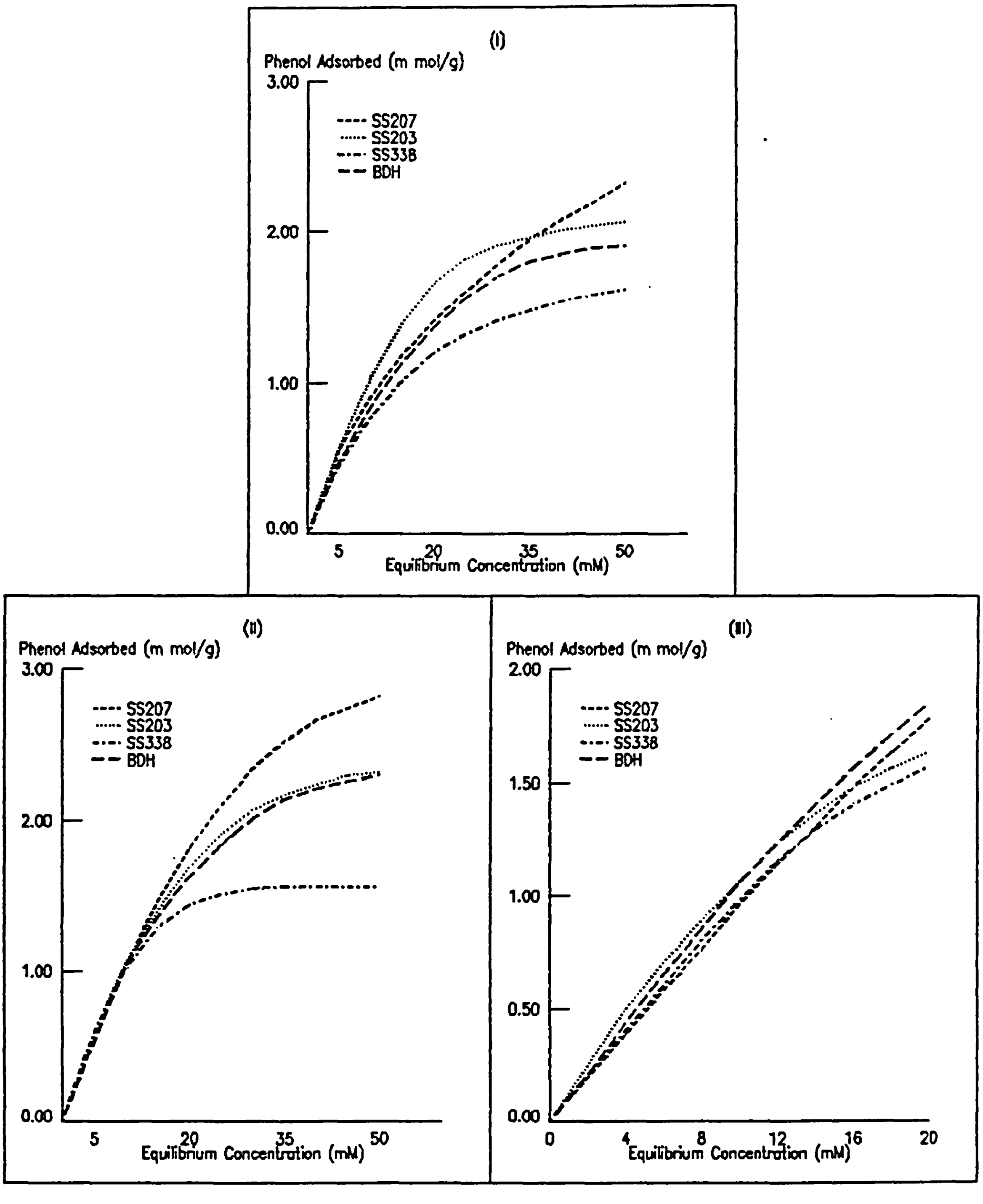


Figure 3.4: Adsorption of (I) Phenol, (II) 3-Chlorophenol and (III) 2,3-Dichlorophenol by Activated Carbon.

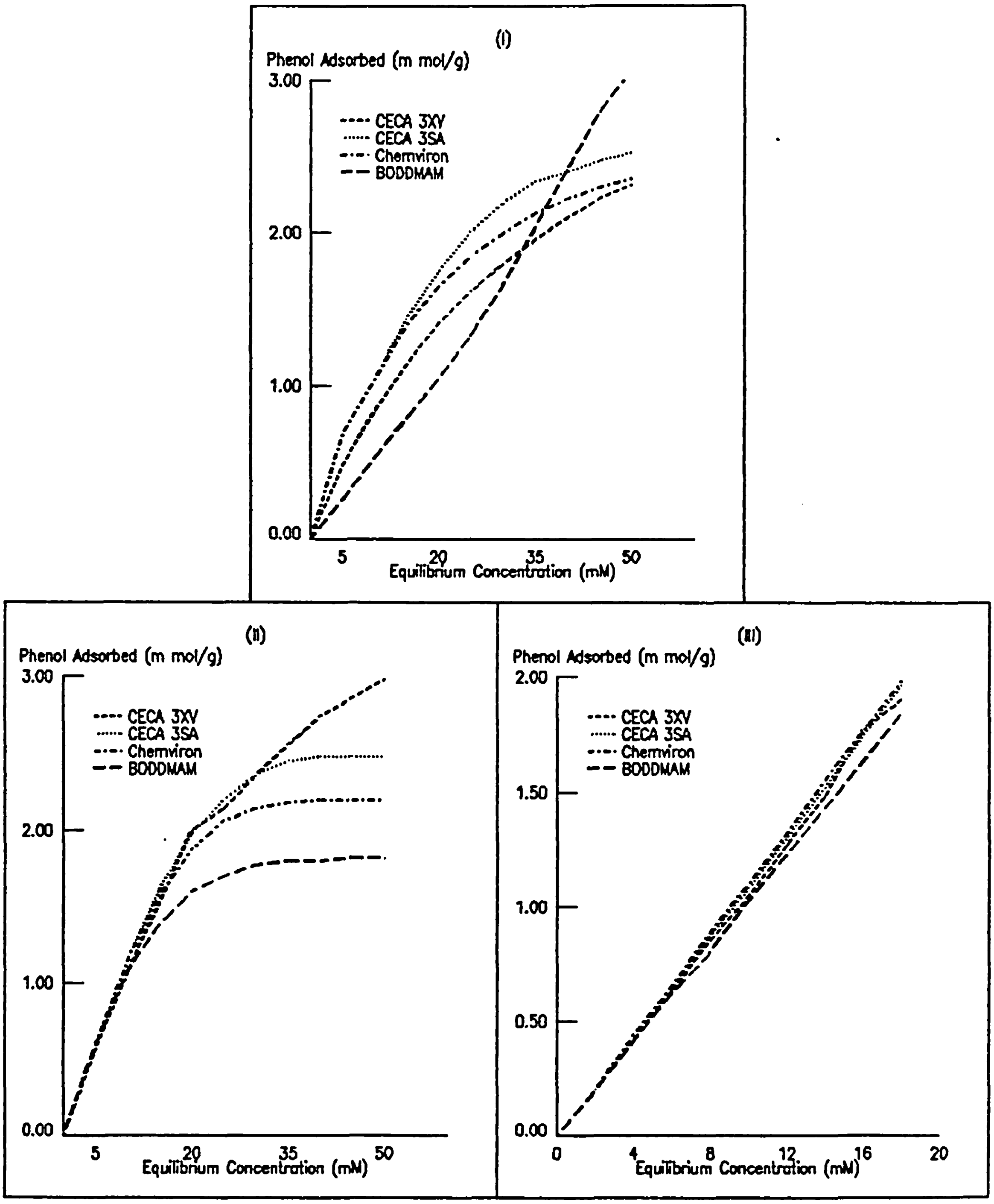


Figure 3.4 cont'd: Adsorption of (I) Phenol, (II) 3-Chlorophenol and (III) 2,3-Dichlorophenol by Activated Carbon.

however, was less well adsorbed by all of the exchanged clays except those with short chain QAS. The adsorption of phenol by TMAM and TMPAM was similar in magnitude to the adsorption of 3-chlorophenol by the same clays (Figures 3.1(I) and 3.2 (I)).

Adsorption of the phenolic compounds by the exchanged clays was believed to be facilitated by hydrogen bonding between the hydroxy group of the phenol and either the clay's silicate surface or the aliphatic chain of the QAS. In an attempt to enhance the potential for hydrogen bonding between the adsorbed organic compounds and the QAS aliphatic chains, hydroxy and ethoxy groups were introduced into the QAS aliphatic chain. The results of the phenol adsorption experiments are shown in Figures 3.1(IV), 3.2(IV) and 3.3(IV). The ethoxy and hydroxy QAS-exchanged clays showed no enhanced adsorption compared to BODDMAM, for 3-chlorophenol or 2,3-dichlorophenol (Figures 3.2(IV) and 3.3(IV) and adsorption of phenol was reduced (Figure 3.1(IV).

The adsorption of the phenols by the commercially produced activated carbons designed to adsorb organic molecules from wastewaters are shown in Figure 3.4. The results were compared, on the figure, to the adsorption of the phenols by BODDMAM, the "best" exchanged clay. The adsorption of the phenols by the carbons varied greatly, some carbons showing a great affinity for the small phenol molecules (CXV and SS203), whilst others show a greater affinity for the larger 2,3-dichlorophenol (3SA and Chemviron). The adsorption capacity of activated carbons for each of the compounds depends upon the specific microporosity and surface activity of each activated carbon. Comparison of the adsorptions of the activated carbon with those of the exchanged clays showed that the clays did not demonstrate the high degree of specificity of the activated carbon but had good overall adsorption of different sized molecules.

3.3.2 Desorption with Time

Experiments were initially performed to determine the time taken for the exchanged clay suspensions to reach equilibrium with the phenol solutions. These experiments measured the amount of phenol adsorbed by the clay at time intervals between 0.5 and 56 hours. The results showed that, for all of the systems tested, equilibrium was reached rapidly, maximum adsorption occurring in less than 3 hours.

Figure 3.5 shows the results of extending the adsorption studies using 1.0 g of BODDMAM in 100 ml of 10.0 mM aqueous solution of the phenols over a 56 hour period. It can be seen that after 56 hours there was a slight decrease in the amount of the phenol and 3-chlorophenol adsorbed, although the loss was small compared to the total phenol concentration. This effect was believed to be due to washing out of the QAS/phenol molecules adhering to the edge of the crystals and to the outer surface of the clay.

3.3.3 Stability of the Quaternary Ammonium Salt on the Montmorillonite Clay

The aim of the first desorption experiment was to determine the stability of the exchanged clays at high pH. The experiment also attempted to show that, below the exchange capacity of the clay, the QAS was well adsorbed but above the exchange capacity the QAS was easily removed from the clay. The results of the first desorption experiment are shown in Table 3.5. The results showed that for the exchanged clay with 0.05 M of QAS, below the exchange capacity of the clay, the QAS remained firmly bound onto the clay even after vigorous washing at high pH. The excess QAS on the over-exchanged samples was partially removed by the high pH wash, suggesting that some of the excess QAS was less well adsorbed by the clay, pehaps on the crystal edges or on the outer silicate surface. An excess of QAS still remained on the surface of the clay, however, even after the washing. This effect has also been observed by Furukawa & Brindley (1973) for QAS-clay complexes with carbon chain lengths greater than fourteen. They found that even with vigorous washing of the clay with organic solvents the excess QAS remained on the clay surface.

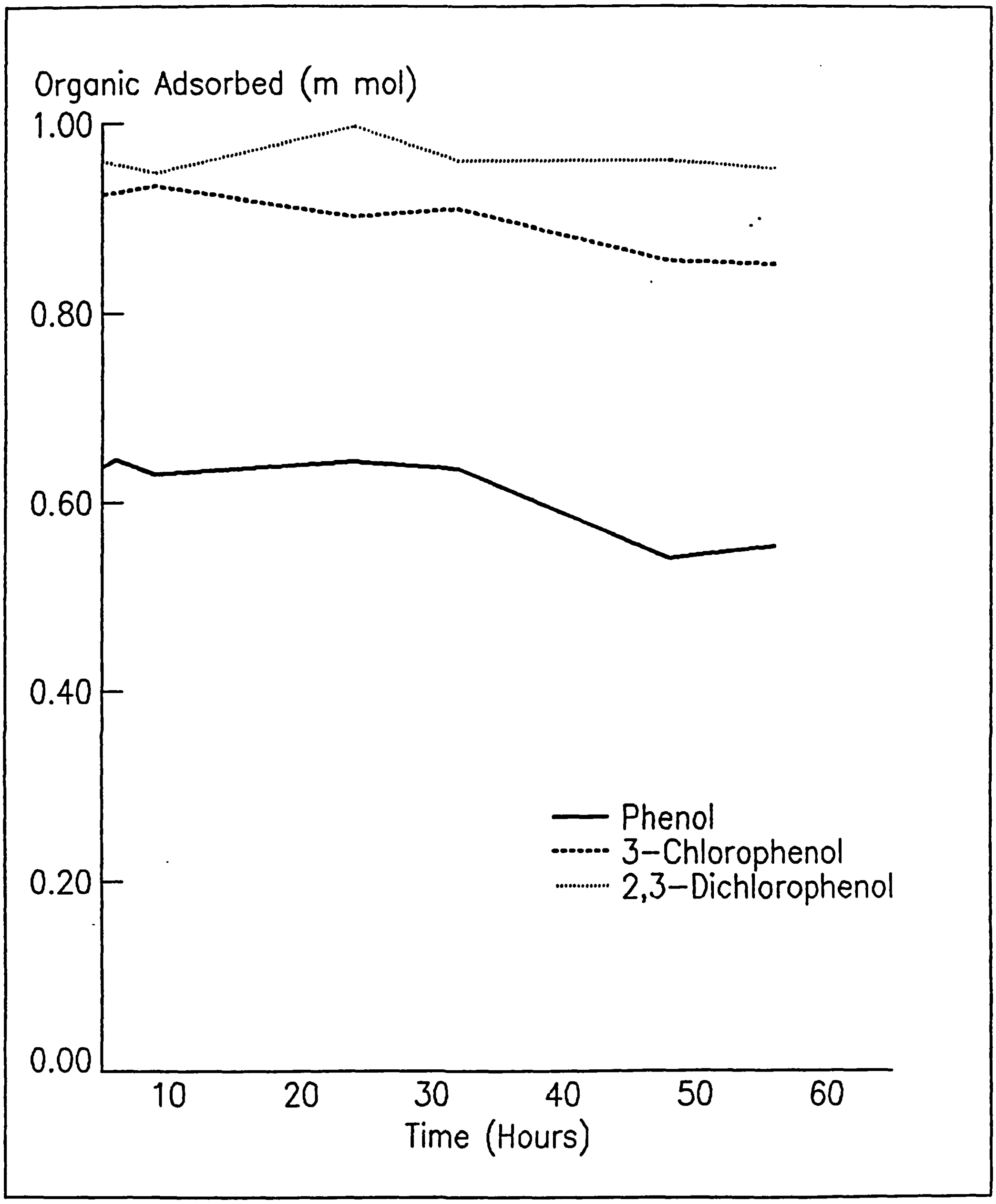


Figure 3.5: Desorption of Phenols from BODDMAM over 56 Hours.

Table 3.5: Stability of QAS on Montmorillonite

Sample	Weight of QAS on 100g Clay (m mol.)	Percentage QAS Lost Compared to Unwashed Clay
Wyoming Bentonite	0	---
<u>0.05 M QAS on Clay</u>		
Unwashed	69	---
Water Washed	69	0.0
Suspend in Water	70	0.0
Suspend at pH 9	66	4.3
Suspend at pH 10	69	0.0
Suspend at pH 11	71	0.0
<u>0.1 M QAS on Clay</u>		
Unwashed	106	---
Water Washed	106	0.0
Suspend in Water	96	9.4
Suspend at pH 9	94	11.3
Suspend at pH 10	95	10.4
Suspend at pH 11	95	10.4

The results of the second experiment to determine the stability of the QAS on the clay over a long time period are shown in Table 3.6. The results suggest that the QAS was, initially, released from the clay into the solution (days 1 - 14 in water and day 1 for sodium hydroxide solution) and was then gradually readsorbed (day 14 onwards for water and day 2 onwards for sodium hydroxide).

Table 3.6: Release of QAS by BODDMAM into Water and 0.1 M Sodium Hydroxide.

Day	Aqueous Leachate		Sodium Hydroxide Leachate
	pH	QAS Concentration (mM)	QAS Concentration (mM)
1	9.22	3.7 ± 0.1	6.3 ± 0.2
7	9.48	5.1 ± 0.2	3.2 ± 0.1
14	9.82	6.3 ± 0.3	1.9 ± 0.3
21	9.52	2.9 ± 0.3	1.8 ± 0.1
28	9.20	2.2 ± 0.1	2.0 ± 0.1
56	9.10	2.1 ± 0.1	1.9 ± 0.1

3.3.4 Effect of pH

The effect of pH on the release of QAS from BODDMAM is shown in Figure 3.6. The results show that the maximum release of QAS occurred at pH 8.4, the release, over the complete pH range, being only a very small amount of QAS compared with the total weight of QAS present (1.06 x 10^{-3} moles).

The effect of pH on the adsorption of phenol, 3-chlorophenol and 2,3-dichlorophenol onto 1.0 g of BODDMAM can be seen in Figure 3.7. The maximum amount of phenol was adsorbed at pH 10, the adsorption falling off rapidly at higher and lower pH values. The high adsorption of phenol at pH 10 was probably due to the acidic nature of the phenol, which would be deprotonated at this pH and would be able to interact with both the intercalated aliphatic chain and with

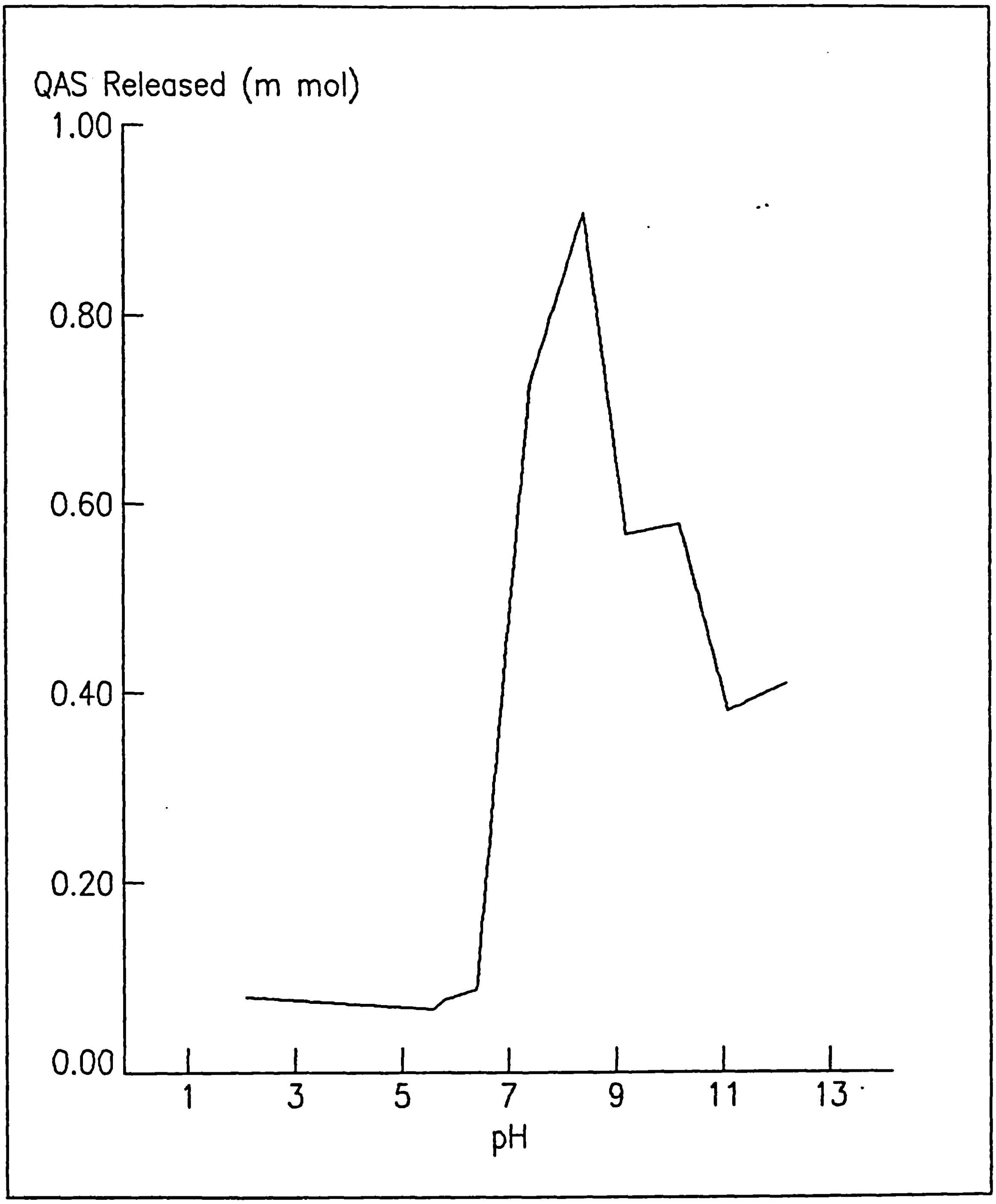


Figure 3.6: Release of QAS by BODDMAM as a Function of pH.

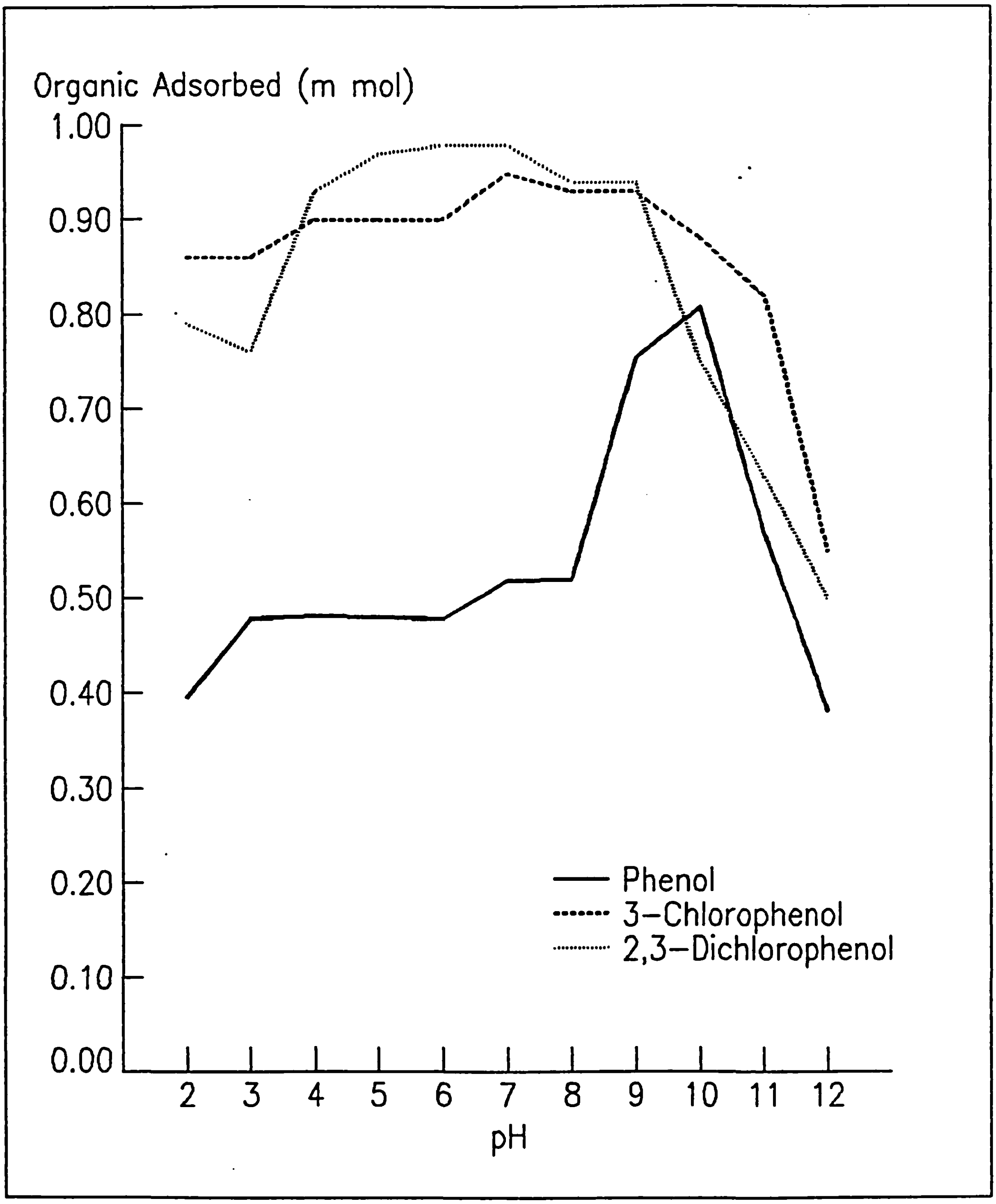


Figure 3.7: pH Profiles of the Adsorption of the Phenols by BODDMAM from Aqueous Solution.

the cationic nitrogen of the QAS. 3-Chlorophenol showed a maximum adsorption at pH 7, a pH close to that of the aqueous clay suspension (6.45). The maximum adsorption of 2,3-dichlorophenol occurred over the range pH 5 to 8, with significantly lower values evident at higher and lower pH values. The results suggest that to maximise the adsorption of all three phenols the pH must be kept in the range pH 4 - 9.

The effect of three different pHs on the adsorption isotherms of phenol, 3-chlorophenol and 2,3-dichlorophenol are shown in Figure 3.8. Three pH values were selected for testing, pH 3 (acid), pH 7 (neutral) and pH 11 (basic). Figure 3.8 shows that the pattern of adsorption over an increasing concentration range remained the same at the different pHs with only the magnitude of adsorption varying.

3.3.5 Co-adsorption of Group IIB metals with 3-chlorophenol onto BODDMAM

The adsorption of heavy metals by montmorillonite clay has been reported by several workers (Netzer & Ghanayem, 1984; Haas et al., 1986; Garcia-Miragaya, 1986). They looked at the adsorption of heavy metals such as cadmium and zinc onto clay with the aim of obtaining a closer understanding of the behavoiur of metals in clay soils. The adsorption, which was found to be greatest at high pHs, was thought to be due to metal hydroxide precipitation onto the surface of the clay particles. At lower pHs, the metals were thought to be absorbed onto the outer surface of the clay (Netzer & Ghanayem, 1984).

For these studies, the Group IIB metals, Zn, Cd and Hg were chosen as simulated pollutants because they commonly occur in industrial wastewaters from, for example, battery manufacture and electroplating works. The salts chosen (zinc nitrate, cadmium nitrate and mercuric chloride) were all stable in aqueous solution, zinc and cadmium forming mainly ionic solutions whilst mercuric chloride is covalent.

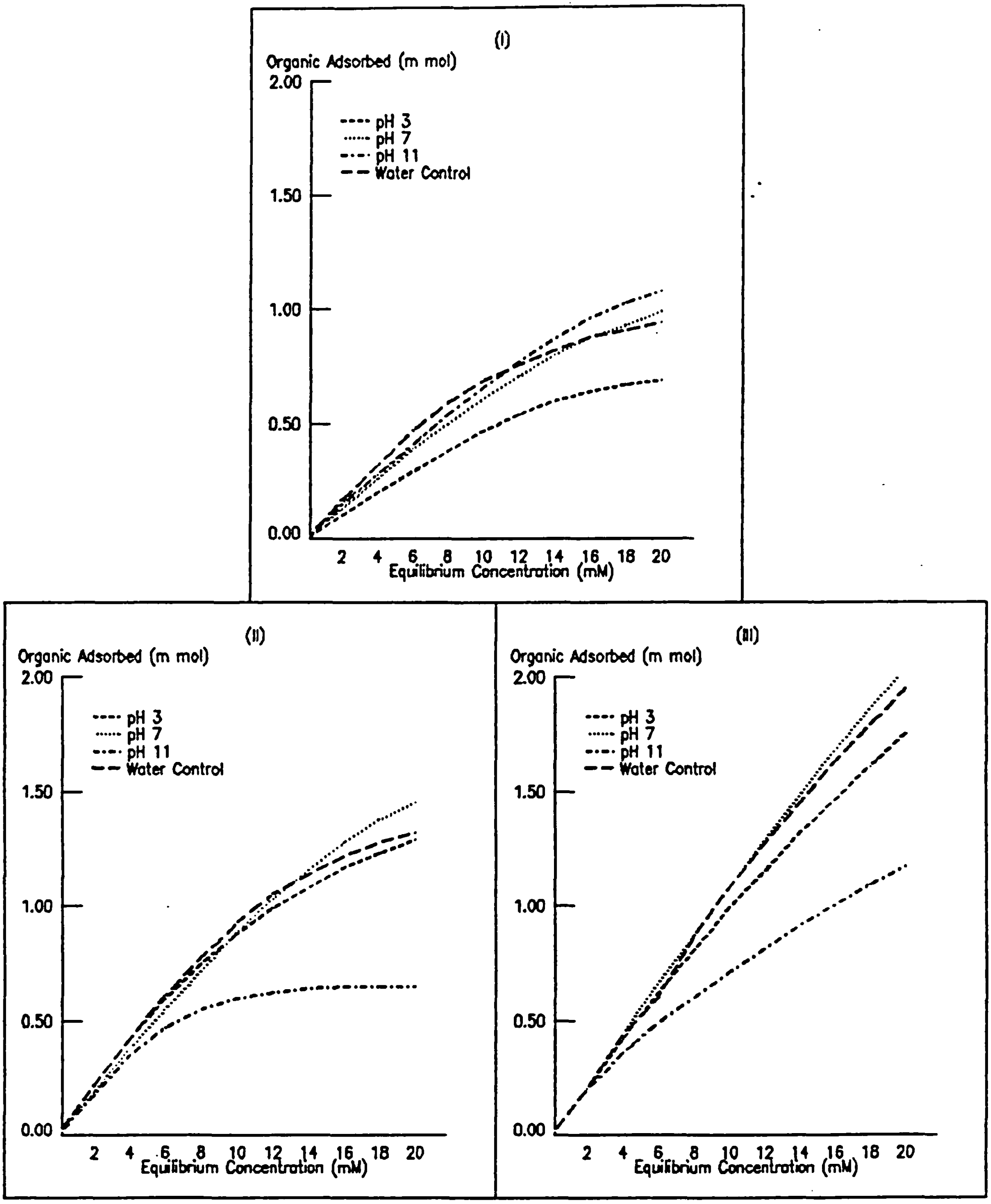


Figure 3.8: Effect of pH on Adsorption of (I) Phenol, (II) 3-Chlorophenol and (III) 2,3-Dichlorophenol.

In this set of experiments work was carried out to determine whether co-adsorption of the phenols and metals from aqueous solution by the exchanged clays was possible. The results shown in Figure 3.9 are for the co-adsorption of 1.0 m mol. 3-chlorophenol and either zinc, cadmium or mercury at the concentrations shown, onto 1.0 g of BODDMAM.

The results show that in the presence of increasing zinc concentrations, the amount of 3-chlorophenol adsorbed onto BODDMAM decreased and the amount of zinc adsorbed increased by approximately the same amount. This suggests that the zinc and the 3-chlorophenol were competing for the same adsorption sites. but that zinc could displace the 3-chlorophenol or the QAS only at high concentrations. Cadmium was slightly adsorbed onto the exchanged clay and, simultaneously inhibited the adsorption of the 3-chlorophenol. Mercury was adsorbed well by the exchanged clay. The adsorption of mercury by BODDMAM caused the partial displacement of 3-chlorophenol, suggesting some competition for the adsorption sites occurred between mercury and 3-chlorophenol.

3.3.6 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy has been widely used in the investigation of clay organic complexes (Fripiat et al., 1969; Serratosa et al., 1970; Martin-Rubi et al., 1974; Nguyen, 1986). Infrared spectroscopy provides valuable information about molecular orientation in the interlamellar space, and about the mechanisms of interaction between the adsorbed molecules and the silicate surface, the interlayer cations and the residual water, and also between the molecules themselves.

The spectra obtained from the FTIR analyses are shown in Figure 3.10. The region of the spectrum studied lay between 3500 and 750 nm. At high wavenumbers the spectra became obscured by the strong absorption bands of water, and at lower wavenumbers the silicon-oxygen and the hydroxyl deformation peaks obscured the spectrum. The

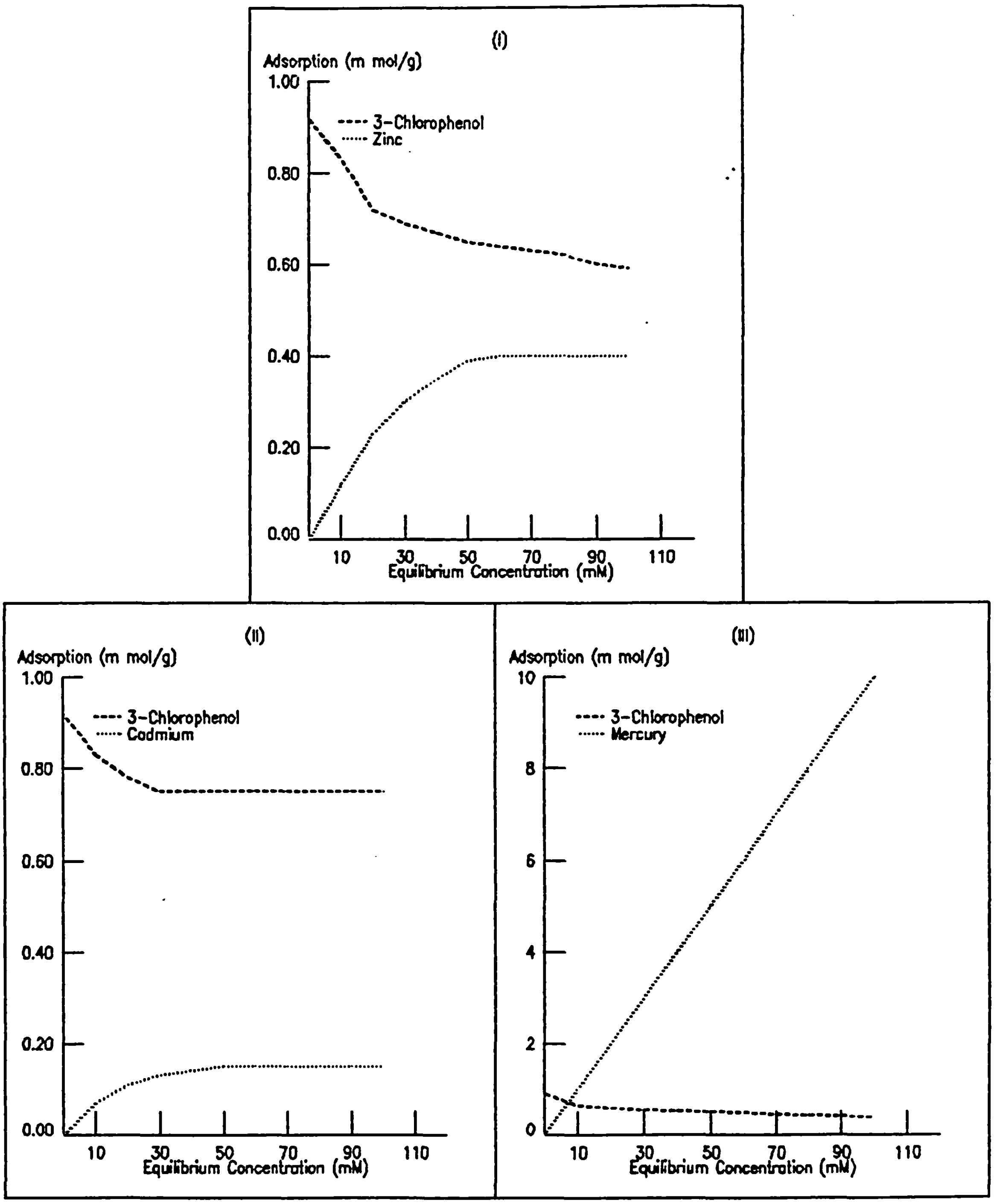


Figure 3.9: Co-adsorption of 3-Chlorophenol and (I) Zinc, (II) Cadmium or (III) Mercury onto BODDMAM.

spectra show the characteristic peaks of carbon dioxide and water from the air in the instrument. The aim of this series of spectroscopic determinations was to confirm microstructurally that the QAS was adsorbed onto the clays and to determine if any bonding was taking place between the QAS and the phenols. .In the presence of high concentrations of 3-chlorophenol, the vibrations of the aliphatic chain of the QAS were measured to see if any change in the frequency occurred resulting from crowding. Figures 3.10(I) and 3.10(II) give the spectra of the unexchanged Wyoming bentonite and the solid BODDMA-Cl. The only major peaks from Wyoming bentonite that occurred in the region studied were those due to the carbonate stretches at 1425cm^{-1} and silicate stretches at 1077 and 1042 cm^{-1}, but these were hardly visible. Figure 3.10(III) shows the spectrum of BODDMAM clay, and the carbon hydrogen stretches and bends of the QAS are clearly visible. Figure 3.10(IV) and (V) show the spectra of BODDMAM with 0.5 m mol. and 1.5 m mol. of 3-chlorophenol adsorbed onto it respectively. From these spectra the carbon-hydrogen adsorption of the QAS aromatic ring and the phenolic ring can be seen. The carbon-carbon aromatic stretch is also visible although whether it is due to the QAS or the 3-chlorophenol, or both, is uncertain. Figure 3.10(VI) gives the spectrum of 1.5 m mol. 3-chlorophenol in the clay environment by subtracting the spectra of Figure 3.10(III) from that of 3.10(V). The most characteristic absorption visible is the carbon-carbon bond from the aromatic ring of the 3-chlorophenol. No additional interactions between the QAS and the 3-chlorophenol could be observed.

3.3.6 Thermal Analysis

Thermal analysis was carried out on a wide range of QAS and exchanged clays to examine and compare the surface reactions in the absence and presence of 3-chlorophenol. The objective was to study any interactions occurring between the QAS and the 3-chlorophenol or the organic part of the QAS and the clay surface.

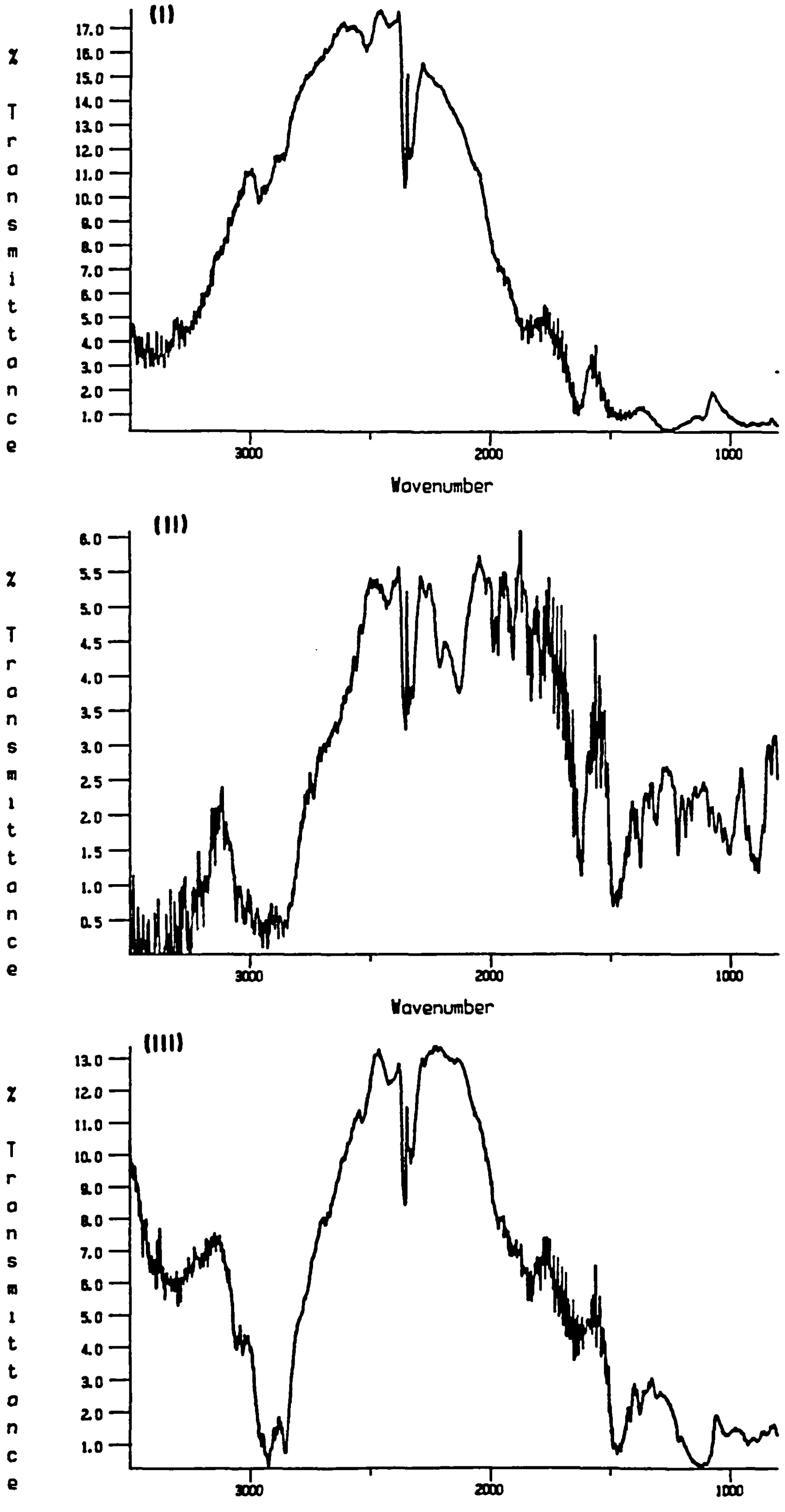


Figure 3.10: Fourier Transform Infrared Spectra of (I) Wyoming Bentonite, (II) BODDMA-Cl Cation and (III) BODDMAM.

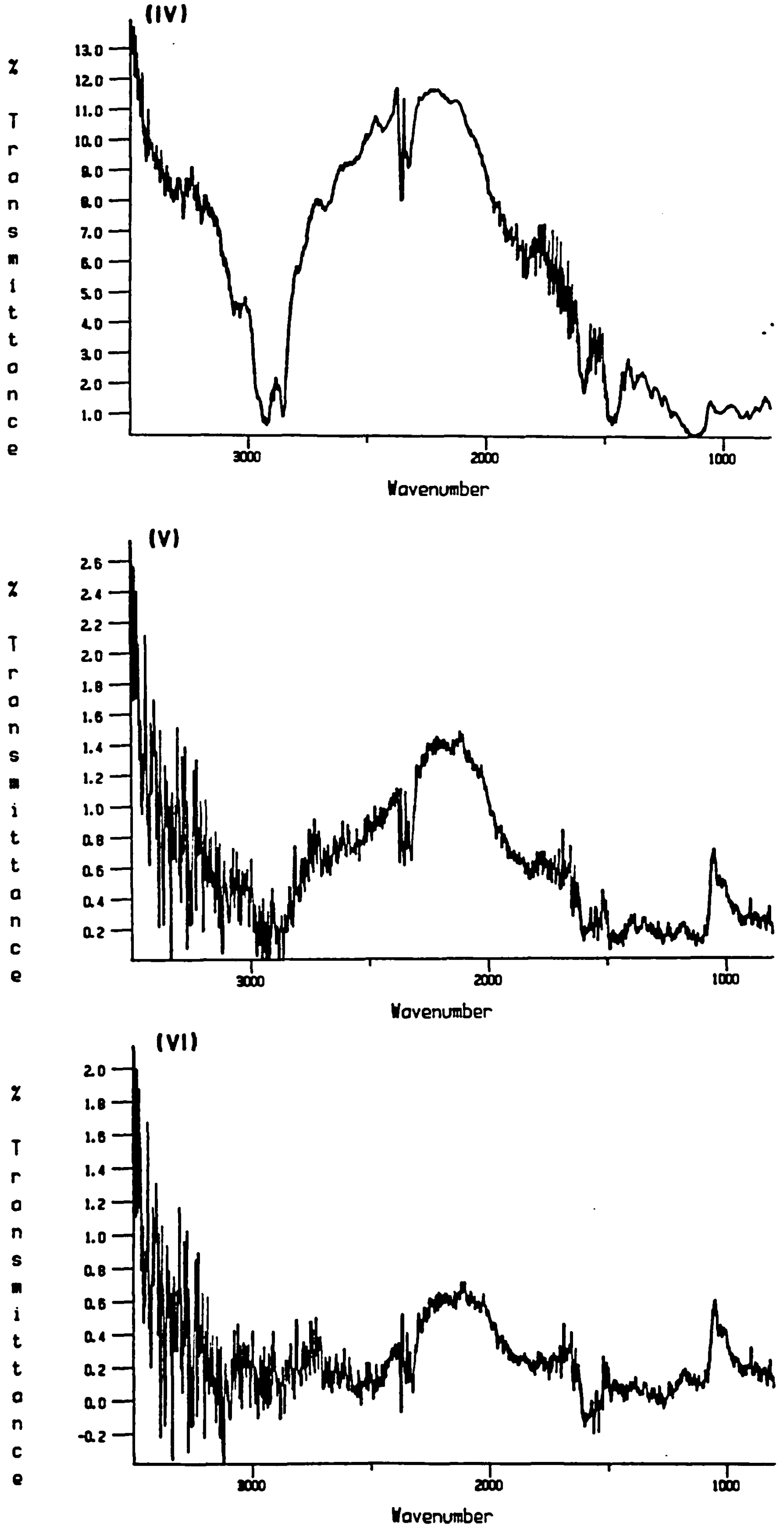


Figure 3.10: Fourier Transform Infrared Spectra of (IV) BODDMAM + 0.5 m mol 3-Chlorophenol, (V) BODDMAM + 1.5 m mol 3-Chlorophenol and (VI) 3-Chlorophenol in Clay Environment (V - III).

Figure 3.11 shows the differential thermal analysis (DTA) of three QAS. The DTA results compared with thermogravimetric analysis (TGA) results (not shown) revealed the following transitions. Figure 3.11(I) shows TMPA-Cl, which exhibited one endotherm at 244°C which corresponded to the sublimation of the QAS. Figure. 3.11(II) shows the DTA of ODTMA-Cl, (melting point 119°C). The QAS started to decompose at 230°C, possibly forming shorter chain products in a similar way to those observed by Durant et al (1972). The two major reactions, both endothermic, occur at 292°C and 316°C, with all of the weight being lost by 370°C. The DTA of BODDMA-Cl (Figure 3.11(III)) closely resembled that of ODTMA-Cl (Figure 3.11(II)). This must be expected since the QAS differs in structure from ODTMA-Cl only by the replacement of one methyl group for a benzyl group. The DTA of BODDMA-Cl shows a melting point at 73°C and its maximum weight loss, due to reaction of the aliphatic chains, between 260° and 350°C. An additional series of endothermic peaks occurred around 216°C due to the breakdown and reaction of the benzyl group fragment of the QAS.

Figure 3.12(IV) gives the DTA of 3-chlorophenol, showing the melting point at 42°C and the boiling point 207°C. Figure 3.12(V) shows the effect of mixing 3-chlorophenol with BODDMA-Cl (a) in the ratio of 1:10 and (b) in the same ratio, but after fusing the mixture at 100°C for 30 minutes to allow the molten salts to combine. Both of the DTAs showed similar patterns of reaction and weight loss, the melting point of the mixture being depressed with respect to the pure compounds. The endotherm at 219°C corresponded to the similar endotherm in the pure BODDMA-Cl, which was also accompanied by a substantial weight loss, hence this peak was due to the QAS. Endothermic peaks occurred around 252°C and were accompanied by a significant weight loss and occurred in both the mixed and fused samples. It is thought that the endotherms around 252°C were the result of the reaction of the 3-chlorophenol with fragments of QAS. It should be noted that the 3-chlorophenol seemed to remain liquid to temperatures far in excess of its boiling point (207°C) or the elevated temperature expected for the mixed compounds. Figure

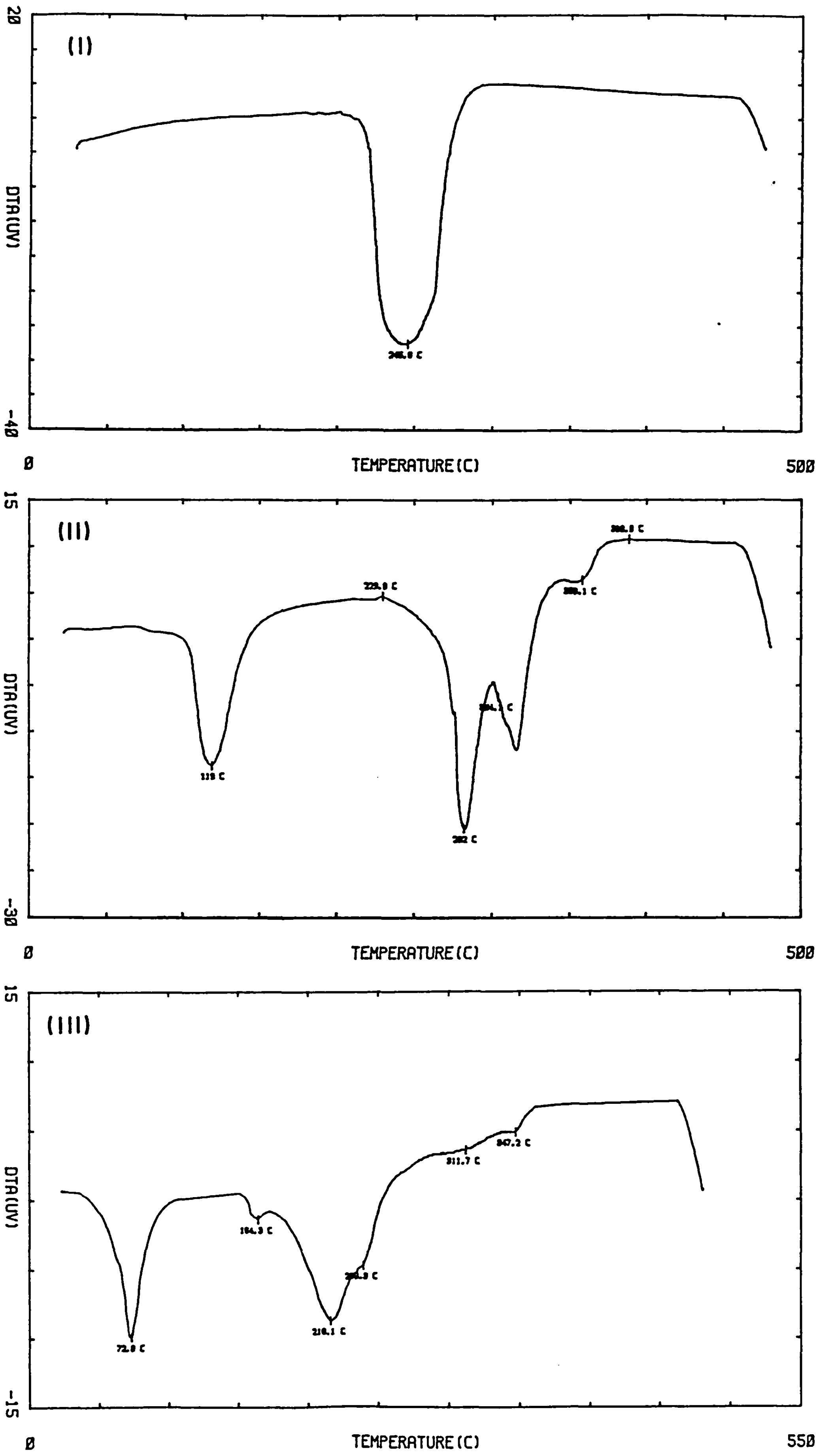


Figure 3.11: DTA of the Quaternary Ammonium Salts (I) TMPA-Cl, (II) ODTMA-Cl and (III) BODDMA-Cl.

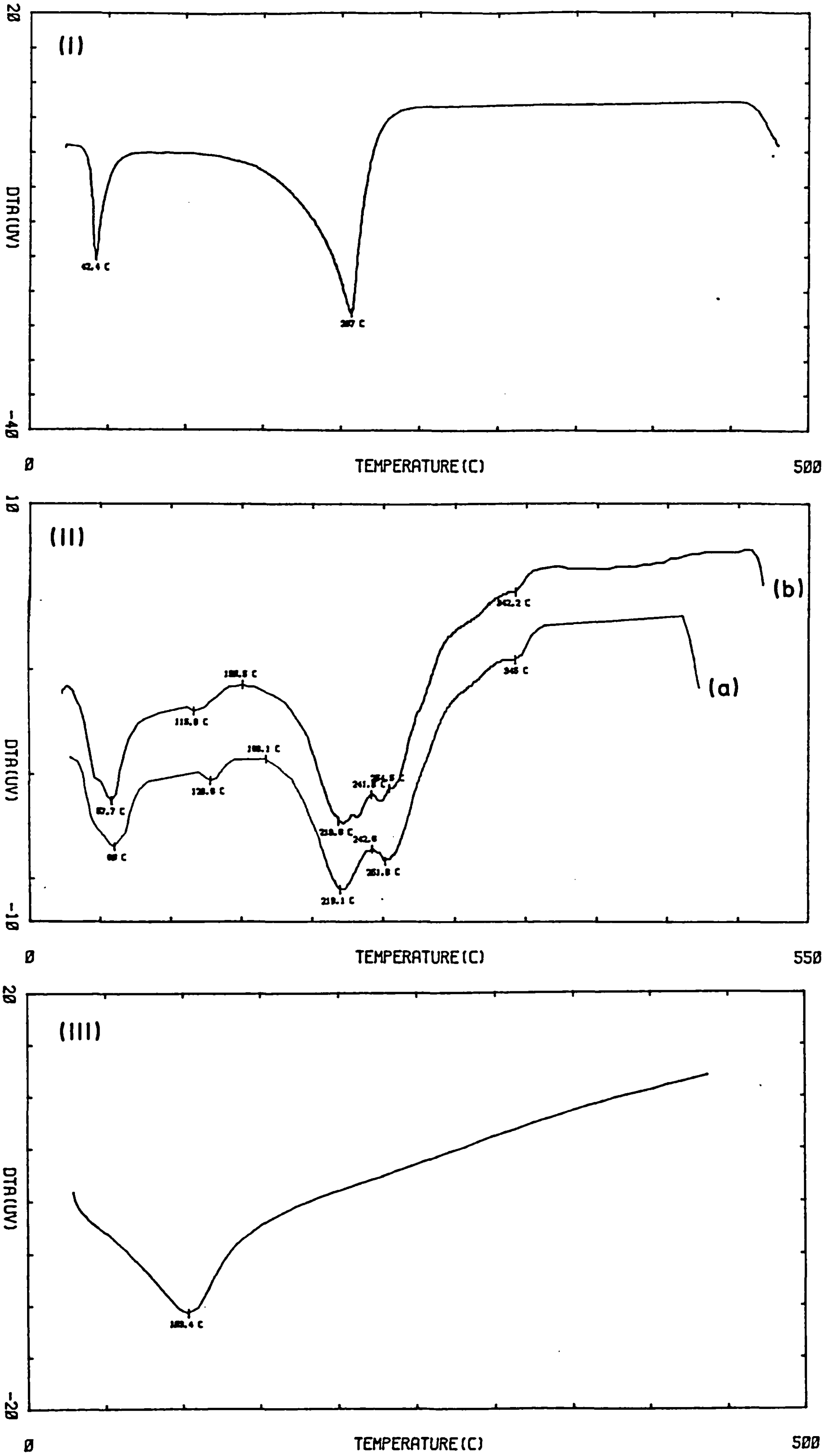


Figure 3.12: DTA of (I) 3-Chlorophenol, (II) 3-Chlorophenol + BODDMAM (a) Mixed in a 1:10 Ratio, (b) Fused at 100°C for 30 Minutes and (III) Wyoming bentonite.

3.12(VI) shows the DTA of unexchanged Wyoming bentonite which exhibits one endotherm resulting from the loss of adsorbed water.

Figures 3.13(I), (II) and (III) give the DTA curves of the three QAS shown in Figures 3.11(I),(II) and (III) exchanged onto Wyoming bentonite (TMPAM, HDTMAM AND BODDMAM). The DTA of TMPAM (Figure 3.13(I) shows one major exotherm at 337°C, the major weight losses occurring at the tail of the peak and around 426°C. This analysis clearly demonstrated the effect of the clay surface on the spectra of TMPAM compared to the spectra of the pure salt TMPA-Cl (Figure 3.11(I) which showed only one endotherm. The clay surface acts as a catalyst in the breakdown of the QAS and the subsequent reaction of the fragments. Figure 3.13(II) shows the spectra of OTMAM, the major endotherm and corresponding weight losses, resulting from the breakdown and reaction of the QAS occurring at 320°C and 450°C. Figure 3.13(III) shows the DTA of BODDMAM, in which the first endotherm at 60°C corresponds to the melting of the QAS. The major weight losses occurred at 320° and 450°C, which is a much higher temperature than those of the QAS alone, and once more lends support to the concept of the catalytic role of the clay surface. The exothermic peaks at 450 and 526°C represent dehydrogenation and initial oxidation of hydrocarbon chains of the alklyammonium ion. The magnitude and position of these peaks indicates the strength with which the alkylammonium ions were held in the interlamellar space. The endotherm at 760°C represents dehydroxylation of the clay and the burning off of the carbon residue from the oxidation of the alklylammonium chains.

When 3-chlorophenol was adsorbed onto the exchanged clay (Figure 3.14(I)), the endotherms show a similar shift to that seen when the 3-chlorophenol was mixed with the QAS (Figure 3.12(II)). The major differences between the exchanged clay in the presence and absence of 3-chlorophenol were the magnitude of the weight loss and the temperature at which the loss occured. In Figure 3.14(I) the weight losses occur at 290°C and 414°C and are of similar magnitude. Figure 3.13(III) shows the weight loss occurring at 320° and 450°C. This depression of reaction temperature is due to the presence of the

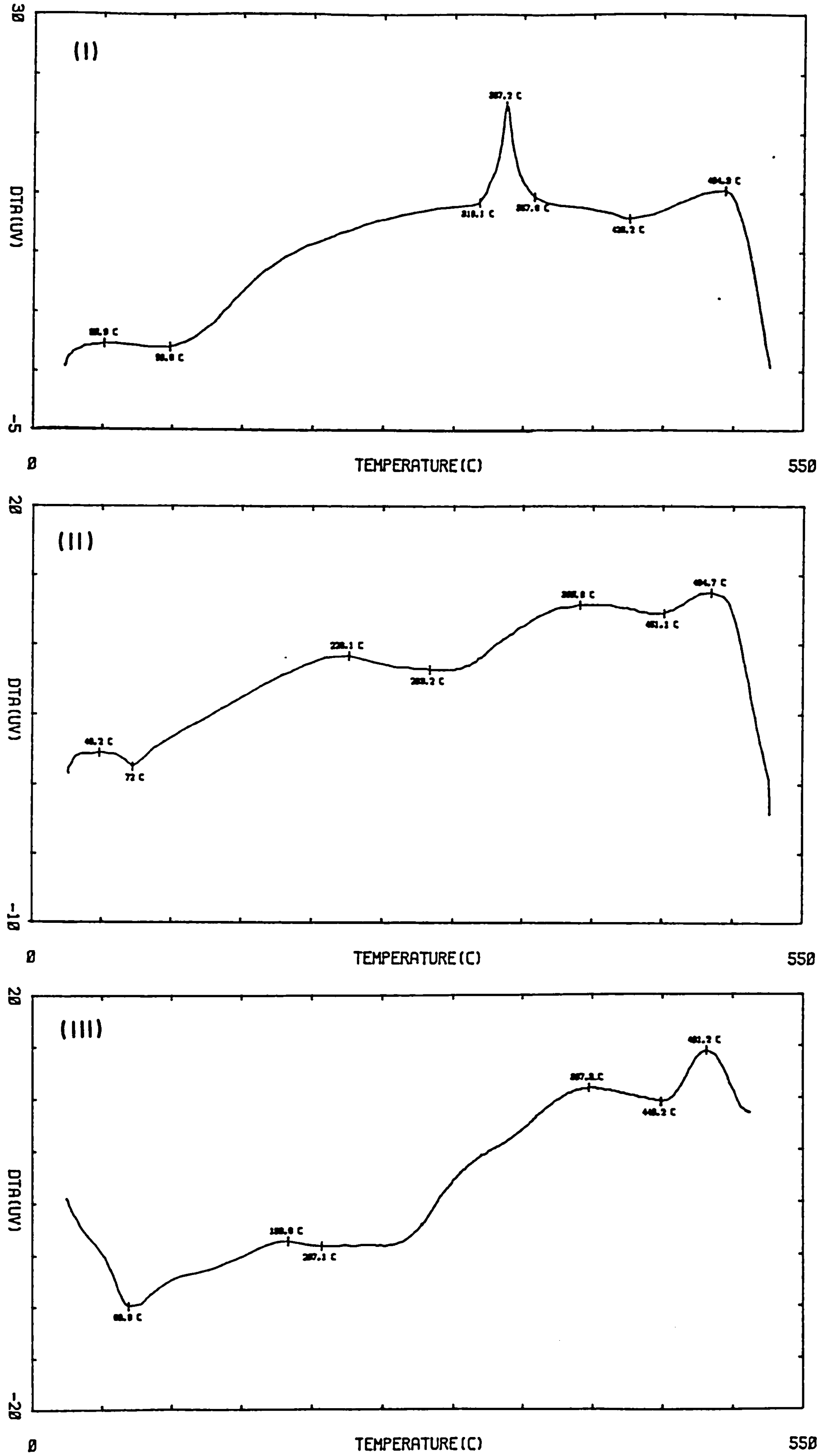


Figure 3.13: DTA of the Exchanged Clays (I) TMPAM, (II) ODTMAM and (III) BODDMAM.

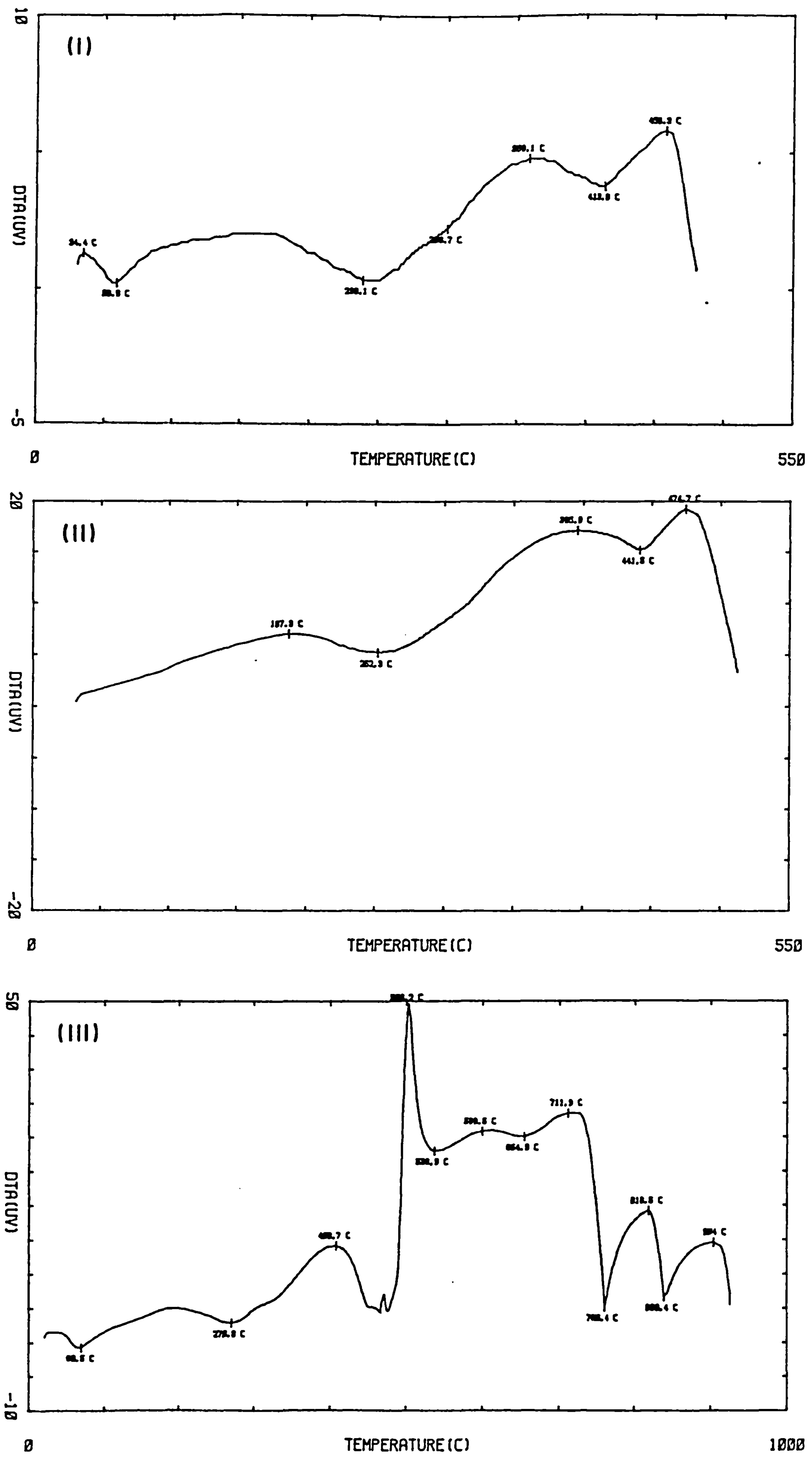


Figure 3.14: DTA of BODDMAM with adsorbed 3-Chlorophenol
(I) 0.5 m mol (II) 1.5 m mol and (III) 0.5 m mol heated in air to 1000°C.

3-chlorophenol and its reaction with the fragments of the QAS. With a higher loading of the 3-chlorophenol (Figure 3.14(III)) the major weight loss occurs at 280°C, although no distinct endotherm is observed. Figure 3.14(III) shows the effect of burning off the residual carbon fragments in air after the sample has been heated to 500°C in nitrogen. The DTA shows the effect of the reaction of the oxygen with the organic carbon and hydrogen to form carbon monoxide, carbon dioxide and water, resulting in a large exotherm at 500°C. A continuous heating cycle was followed up to 1000°C with temperature holds at 760° and 840° to allow the sample temperature to equilibrate with that of the furnace. A gradual weight loss of 4% by weight occurred over this period and the sample, when removed from the furnace, was a creamy white colour indicating that most of the carbon had been lost.

3.3.8 Adsorption of Organic Compounds by the Exchanged Clays

(a) Adsorption from Water

Previous adsorption experiments have concentrated on the adsorption of phenolic compounds from aqueous solutions. These compounds were chosen because of their prevalance in industrial wastes and their relatively high solubility in water. To extend the study of exchanged clays, a wider range of organic compounds has to be studied, particularly, for later applications of the clays, those organics which are commonly found in industrial waste streams. The organic compounds chosen were among those found by Patterson and Kadukala (1981) to occur most regularly in a survey of over 3100 individual waste streams from the chemical industry in the USA e.g.

Phthalates	(ubiquitous)	Benzene	(26 %)
Chloroform	(37 %)	Phenol	(24 %)
Methylene Chloride	(36 %)	Naphthalene	(10 %)
Toluene	(28 %)		

The concentrations of the aqueous solutions tested depended upon the solubility of the chosen compound in water. The adsorption isotherms for the removal of a range of organic compounds by BODDMAM from water are shown in Figure 3.15.

Figure 3.15(I) shows the adsorption isotherms of chloroform, which although only sparingly soluble in water, was well adsorbed at the concentrations tested. The adsorption isotherm for acetone showed that it was also well adsorbed. Figure 3.15 (II) shows the adsorption isotherms of benzene and naphthalene which were well adsorbed at the concentrations tested. The adsorption of these sparingly soluble compounds reflects the beneficial effect of the hydrophobic nature of the clay which solvates the organic in the organophilic interlamellar spacing.

The two dyes tested (Figures 3.15(III) and (IV)) were well adsorbed up to a saturation point where the adsorption tailed off. The dyes tested were large polar molecules which contained functional groups that could be ionised. The cationic form of the dyes could be adsorbed into the clay by attraction to the anionic silicate surface.

Aniline was poorly adsorbed (Figure 3.15(III)), the percentage adsorbed dropping to almost zero above 10 mM, when the saturation point of the clay had been reached. Phthalic acid was adsorbed (Figure 3.15(IV) but at higher concentrations only 50 % of the weight was removed from the aqueous solution.

This study has shown that a wide range of organic compounds can by adsorbed by BODDMAM from aqueous solution, although the concentration adsorbed varies depending upon the structure of the organic compound.

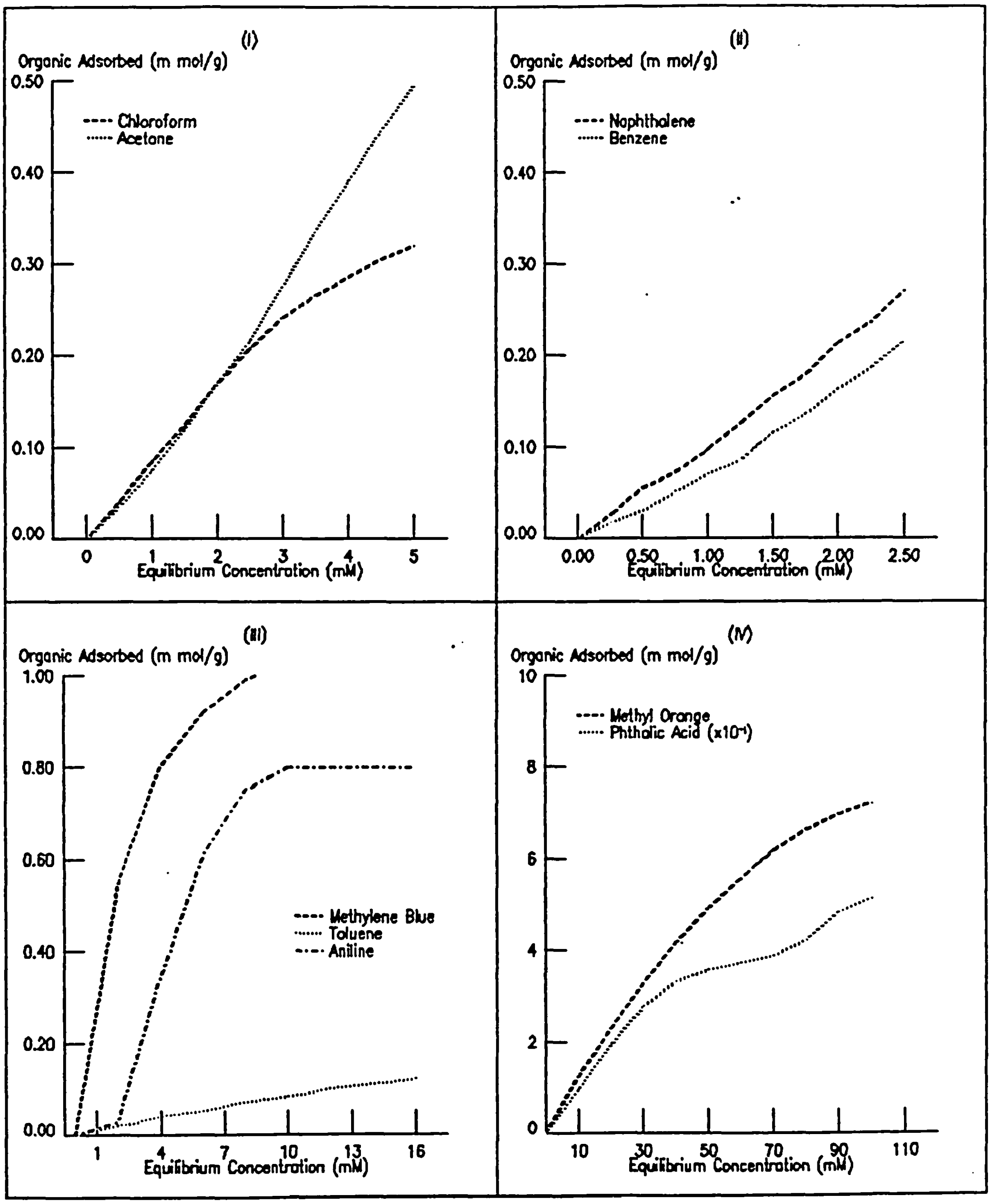


Figure 3.15: Adsorption of (I) Chloroform and Acetone, (II) Benzene and Naphthalene, (III) Methylene Blue, Toluene and Aniline and (IV) Methyl Orange and Phthalic Acid from Water by BODDMAM.

(b) Adsorption from Hexane

Table 3.7 shows the adsorption of a range of organic compounds from a 10 mM solution in hexane by 1.0 g of BODDMAM. The adsorptions of benzene and similar aromatic compounds, such as naphthalene and biphenyl were poor compared with the adsorption of the analogous hydroxylated compounds i.e. phenols, naphthols and hydroxy biphenyls. This effect suggests that the hydroxy group plays an important role in either the initial adsorption from hexane or the bonding of the organics in the exchanged clays.

The adsorption of the three phenolic compounds by the exchanged clays demonstrated the opposite order of adsorption compared to the adsorption from water, the order of adsorption from hexane being phenol > 3-chlorophenol > 2,3-dichlorophenol. The three naphthols also demonstrated as similar increase in adsorption as the chlorine substitution decreased. Figure 3.16 shows the adsorption profile of the phenols (in the concentration range of 5.0 to 20.0 mM) from hexane onto BODDMAM. The opposing trends in adsorption are considered to be due to the solubility of the phenols in the solvent. In water the solubilities decrease in the order phenol > 3-chlorophenol > 2,3-dichlorophenol whilst in hexane the order is reversed. For sparingly soluble compounds, the interlamellar spacing of the clays provides a hydrophobic environment, hence the adsorption of the phenols into the interlamellar space is favoured. Conversely, for the more soluble molecules, the equilibrium is displaced in favour of the solvent.

Table 3.8 shows the adsorption of 3-chlorophenol, chlorobenzene and 1-chloronaphthalene by the hydroxy and ethoxy substituted QAS-exchanged clays. The presence of the hydroxy and ethoxy groups on the aliphatic chain of the QAS did not increase the adsorption of the organics compared to BODDMAM.

Table 3.7: Adsorption of a Range of Organic Compounds by 1 g BODDMAM from a 10 mM Solution in Hexane.

Organic Compound		
Compound	Formula	Percentage Organic Adsorbed (%)
Benzene	C_6H_6	0
Chlorobenzene	C_6H_5Cl	0
Phenol	C_6H_5OH	88
3-Chlorophenol	ClC_6H_4OH	72
2,3-Dichlorophenol	$Cl_2C_6H_3OH$	64
Naphthalene	$C_{10}H_8$	3
1-Chloronaphthalene	$ClC_{10}H_7$	0
Naphthol	$C_{10}H_7OH$	91
4-Chloro-1-naphthol	$ClC_{10}H_6OH$	94
2,4-Dichloro-1-naphthol	$Cl_2C_{10}H_5OH$	53
Biphenyl	$C_6H_5C_6H_5$	0
4-Chlorobiphenyl	$ClC_6H_4C_6H_5$	0
4-Hydroxybiphenyl	$ClC_6H_4C_6H_4OH$	64

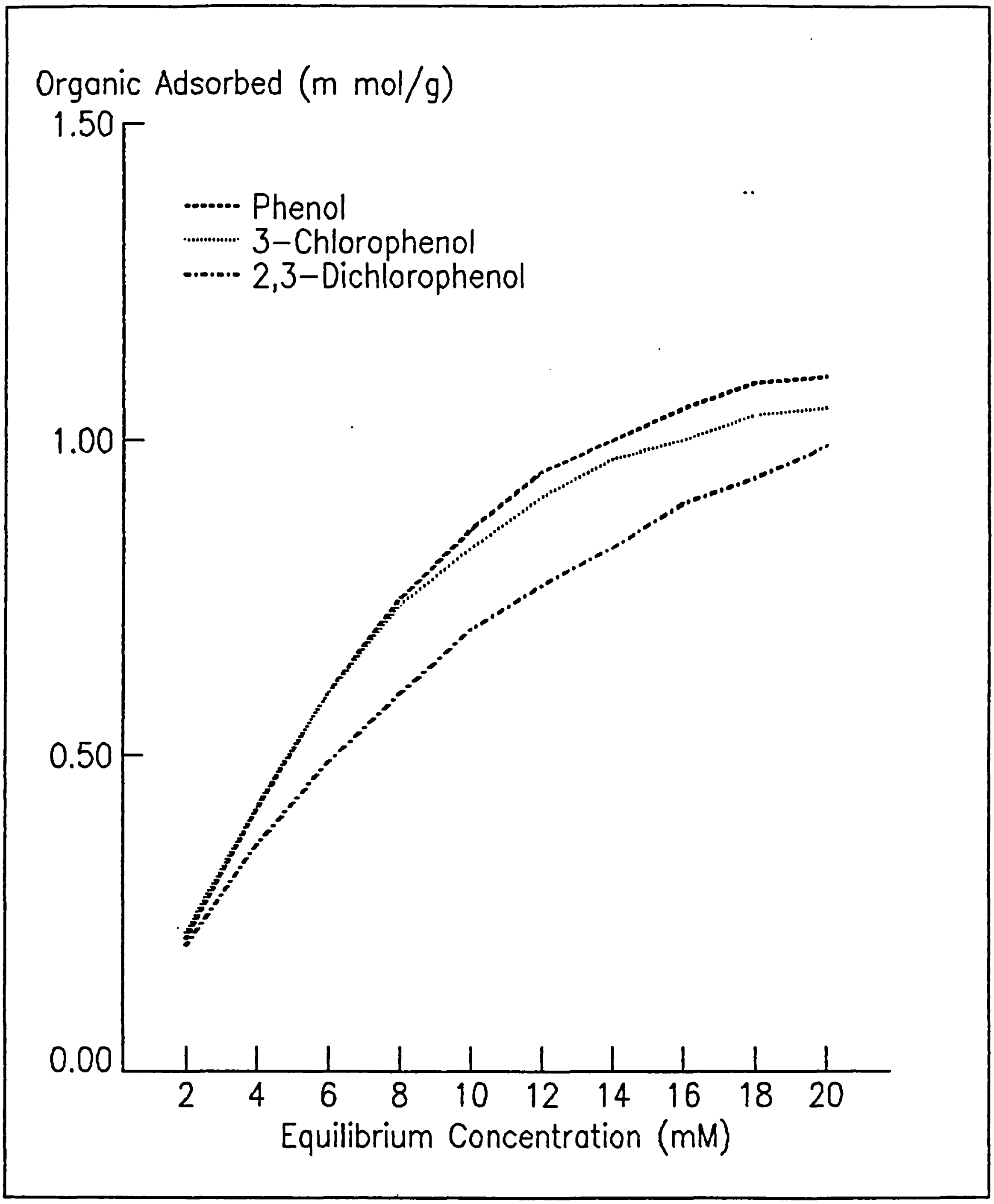


Figure 3.16: Adsorption of Phenol by BODDMAM from Hexane.

Table 3.8: Adsorption of Three Organic Compounds (10 mM) from Hexane by the Ethoxy and Hydroxy Substituted QAS-Exchanged Clays.

Organic Compounds	Percentage of Organic Adsorbed by Exchanged Clay (%)			
	C/12	C/25	O/12	HT/25
3-Chlorophenol	72	55	61	60
Chlorobenzene	0	0	0	0
1-Chloro -naphthalene	0	0	0	0

3.4 SUMMARY

In this work a range of exchanged clays were prepared using Wyoming bentonite and a series of quaternary ammonium salts. The exchanged clays were assessed for their ability to adsorb organic compounds (in particular phenol, 3-chlorophenol and 2,3-dichlorophenol) and the adsorption isotherms determined. The results showed that the major factors controlling the adsorption of the organics were:-

(i) The nature of the QAS, especially its size.
(ii) The interactions of the organic molecules with the interlamellar alkylammonium cation.
(iii) The interaction of the organic molecules with the solvent.

The adsorption of phenol, 3-chlorophenol and 2,3-dichlorophenol from 20.0 mM aqueous solutions were less than 15% for the unexchanged

Wyoming bentonite, however for BODDMAM adsorption exceeded 40%, 70% and 90% respectively. From hexane the order of magnitude of adsorption of the phenols was reversed being 88%, 72% and 64% respectively, illustrating the contrast in adsorbate-adsorbent interactions from those in aqueous solution. These results compared favourably with the adsorption of the phenols by a range of activated carbons commonly used in wastewater treatment.

The phenols remained adsorbed on the exchanged clay over extended leaching periods. pH had little effect upon the adsorption of the chloronated phenols, maximum adsorption occuring between 4 and 9. Phenol, on the other hand, showed a sharp maximum in adsorption at pH 10. Co-adsorption studies of organics and metalsusing BODDMAM inducated that zinc, cadmium and mercury could reduce 3-chlorophenol adsorption by either partial displacement of the QAS-cation or of the 3-chlorophenol itself.

Adsorption of a range of common organic pollutants showed that the exchanged clay adsorbed different compounds in differing amounts. Factors that affect the adsorption include the adsorbent/adsorbate interaction, the size of the adsorptive and the adsorptive/solvent interaction.

4. STABILISATION/SOLIDIFICATION

4.1 INTRODUCTION

The previous chapter has shown that QAS-exchanged clays adsorb a wide range of organic compounds from aqueous and non-aqueous solutions. The exchanged clays with the optimum adsorption capacity for the organics were found to be either trimethylated compounds or dimethyl benzyl compounds with single long aliphatic chains (C_{18}). Adsorption occurred over a range of pH values, ionic concentrations and time periods.

This work examined the potential of the exchanged clays as stabilising agents for organic contaminated wastes prior to cement-based solidification. The work uses model organic wastes in aqueous solution, in the presence of metal ions and as pure organic compounds. The macrostructural behaviour of the exchanged clays in the cement matrix, their ability to retain adsorbed organics and the structural effect of the clays on the cement matrix were investigated.

4.2 MATERIALS AND METHODS

4.2.1 Materials

Ordinary Portland Cement (OPC) was supplied by Blue Circle, UK. The chemical composition of a typical sample of the cement is shown in Table 4.1. The Wyoming bentonite was supplied by Laporte Industries, Widnes, UK.

The samples of exchanged clays were supplied by Steetly Berk Limited, Worksop, UK, (Bentone) and Akzo Chemie, Littleborough, Lancs., UK, (Perchem). The structure of the commercial organophilic clays, where known, are shown in Table 4.2. The clays used for all of the experiments were as supplied ex-works unless otherwise stated. The particle size was less than 200 µm.

All other reagents were AnalaR grade obtained from BDH Limited, Poole, UK, or Sigma Chemical Company, Poole, UK.

Table 4.1: Chemical Analysis of Ordinary Portland Cement

Oxide	Percent by Weight of sample dried at 105°C
Silicon dioxide (SiO_2)	20.10
Alumina (Al_2O_3)	5.30
Tellurium oxide (Te_2O_3)	3.50
Calcium oxide (CaO)	64.60
Magnesium oxide (MgO)	1.30
Sulphate (SO_3)	2.80
Sodium oxide (Na_2O)	0.13
Potassium oxide (K_2O)	0.77
Loss on ignition	0.80

Table 4.2: Structure of Commercial Exchanged Clays

Product Name	Composition of Exchanged Clay
Bentone 27	Organophilic magnesium montmorillonite
Bentone 34	Dioctadecyldimethyl ammonium bentonite $Al_5MgSi_{12}O_{30}(OH)_6.(CH_3)_2N(C_{18}H_{39})_2$
Bentone 38	Dioctadecyldimethyl ammonium bentonite $Mg_8LiSi_{12}O_{30}(OH)_6.(CH_3)_2N(C_{18}H_{39})_2$
Bentone SD1	Organophilic bentonite
Bentone SD2	Organophilic hectorite
Bentone EW	Smectite
Perchem 44	QAS/sodium montmorillonite QAS= $(CH_3)_2N(C_nH_{2n+1})_2$*
Perchem 97	QAS/sodium montmorillonite QAS= $(CH_3)_2.C_6H_5CH_2N(C_nH_{2n+1})$*
Perchem 462	QAS/sodium montmorillonite QAS= $(CH_3)_3N(C_nH_{2n+1})$*

* n = 1% C_{12}, 4% C_{14}, 31% C_{16}, 64% C_{18}, Trace C_{20}

4.2.2 Adsorption Experiments

The protocol for the adsorption experiments was described in Section 3.2.3. The commercially produced exchanged clays were screened for their ability to adsorb phenol, 3-chlorophenol and 2,3-dichlorophenol from 10 mM aqueous solutions. The amounts of the phenols adsorbed by each exchanged clay were determined in three separate experiments and the results presented as a mean of the three sets of adsorption data. Isotherms for the adsorption of phenol, 3-chlorophenol and 2,3-dichlorophenol by Perchem 462 and Perchem 97 from water were determined using the method described in Section 3.2.3.

All further experiments were carried out using Perchem 462, the exchanged clay that gave the best results from the screening tests and, for the initial leach test work, Perchem 97 was also used as it most closely corresponded to BODDMAM.

4.2.3 Sample Preparation

(a) Solidification of Samples for Physical Testing

The samples were prepared using either Perchem 462 or Wyoming bentonite, OPC and water. The exchanged clay was initially mixed with water in the water/clay ratio of 0.67 to prevent the clay from adsorbing the water of hydration from the cement. The water/clay ratio was determined qualitatively by measuring the amount of water retained by the clay filter cake, after having been suspended in excess water for 3 hours (100 g clay: 1 l water) and then filtered. The water retained in the filter cake was assumed to be adsorbed by the clay. To the clay paste was added cement and extra water, for the hydration of the cement, in the ratios shown in Table 4.3. In Mixes 3 and 4 (Table 4.3) the water contained 100 mg/l antifoam. Antifoam acts to reduce the amount of foam in a liquid system by reducing the surface area, so preventing the formation of bubbles. Mix 6 contained exchanged clay that had been washed in 2 x 2 l of distilled water to remove the excess QAS adhering to the outside of the clay. The prewashed clay samples were prepared by suspending 100 g of Perchem 462 in 2 l of water and stirring on a

Table 4.3: Ratios of Ordinary Portland Cement (OPC), Exchanged Clay and Water used in Physical Testing Specimens

Mix	Clay*/OPC Ratio	Water/OPC Ratio	Water/Clay* Ratio	Comments
1(a)	0.00	0.35	----	
(b)	0.00	0.60	----	
2(a)	0.50	0.35	0.67	
(b)	0.50	0.60	0.67	
3(a)	0.00	0.35	----	100 mg/l antifoam in water
(b)	0.00	0.60	----	100 mg/l antifoam in water
4(a)	0.50	0.35	0.67	100 mg/l antifoam in water
(b)	0.50	0.60	0.67	100 mg/l antifoam in water
5(a)	1.00	0.35	0.67	
6(a)	0.50	0.35	0.67	Clay washed with 2 x 2 l water before mixing
(b)	0.50	0.60	0.67	Clay washed with 2 x 2 l water before mixing

* Clay used was Perchem 462

magnetic stirrer for 3 hours, after which the clays were allowed to settle. The foam and supernatant were removed and a further 1.5 l of water added. The clay was again stirred for 3 hours and then allowed to settle. After removal of the supernate the clay was vacuum filtered through Whatman No. 1 paper to dryness. The weight of the clay was measured and the amount of water adsorbed onto the clay calculated. Extra water was added to the filter cake to give the same water/clay ratio as that used in Mixes 2, 4 and 5. The filter cake was then mixed with the cement and water as described above.

The cement/clay mixes were mixed for at least 5 minutes, until the pastes were homogeneous, then transferred into cylindrical moulds. The moulds were shaken intermittently for a total of 15 minutes to remove any trapped air and then allowed to cure for 24 hours. After 24 hours the samples were demoulded and allowed to cure for 24 days for the water adsorption experiments (Section 4.2.4(b))and 28 days for the compressive strength tests (Section 4.2.4(c)) in sealed polyethene bags (100% relative humidity) and at 20 ± 2°C.

(b) Solidification of Phenols from Dilute Aqueous Solutions

The maximum weight of each of the phenols that was adsorbed by 1.0 g of the exchanged clays was determined in the adsorption experiments (Section 4.2.2). Samples of 100 g of each exchanged clay were required for the preparation of sufficient quantities of the solidified samples for the dynamic and the equilibrium leach testing. Aqueous solutions (1 l) of phenol and 3-chlorophenol were made containing 90% of the maximum weight of the phenol which could be adsorbed by the clay (high loading). A second set of aqueous solutions were prepared containing one-tenth of the weight of phenol and 3-chlorophenol used above (medium loading). For 2,3-dichlorophenol the maximum weight that was adsorbed by 1.0 g of Perchem 462, for instance, was found to be 1500 mg/g. The solubility of 2,3-dichlorophenol in water at 20°C is 4.5 x 10^3 mg/lso the maximum weight of dichlorophenol soluble in 1 l of water was 4500 mg.

A 2 l aqueous solution containing 8200 mg of 2,3-dichlorophenol was prepared and 100 g of clay added to adsorb the phenol (high loading). Solutions containing one-tenth and one-hundredth of this concentration was also used (medium and low loading respectively).

For preparation of the control samples, the low aqueous solubility of the dichlorophenol resulted in only very low concentrations of dichlorophenol being present in the OPC-only mixes, hence the low loaded clay samples which corresponded to these concentrations were also tested in the leach tests. The concentrations of the solutions used and the weight of the the phenol adsorbed by the 100 g of exchanged clay are shown in Table 4.4.

To maximise the adsorption of the phenols from the aqueous solutions, they were rapidly stirred, on magnetic stirrers, and the clay added slowly in order to obtain a homogeneous suspension. The clays were stirred for 24 hours to ensure complete adsorption of the phenols. After 24 hours the suspensions were filtered through Whatman No. 1 paper under vacuum. The filtrates were analysed colourimetrically (APHA-AWWA-WPCF, 1980) to determine the weight of phenol adsorbed by the clays. The filter cake was weighed, the amount of water absorbed by the clays determined and, if necessary, additional water added to make the total water/clay ratio equal to 0.67. Samples of OPC (200 g) were mixed into the clay pastes, and water to hydrate the cement added (water/cement (w/c) = 0.35). The weights of each of the constituents used are shown in Table 4.5.

Table 4.4: Weight of Phenols in Leach Test Mixes

Loading of phenol onto clay	Phenol		3-Chlorophenol		2,3-Dichlorophenol	
	Concentration of Solution (mg/l)	Weight Adsorbed by Clay✱ (mg)	Concentration of Solution (mg/l)	Weight Adsorbed by Clay✱ (mg)	Concentration of Solution (mg/l)	Weight Adsorbed by Clay✱ (mg)
Perchem 462						
High Load	4700	4698	9000	8992	8900	8746
Medium	470	433	900	599	1330	1272
Low Load	ND	----	ND	----	132	130
Perchem 97						
High Load	4700	3137	9000	8621	8900	8760
Medium	470	421	900	887	1330	1328
Low Load	ND	----	ND	----	132	130
Wyoming Bentonite/OPC						
High Load	4700	1680	9000	3611	NS	----
Medium	470	133	900	346	1330	435
Low	ND	----	ND	----	132	50
OPC Control						
High	----	3080*	----	NS	----	NS
Medium	----	ND	----	602*	----	NS
Low	----	ND	----	ND	----	50*

ND = Not determined
NS = Required weight of phenol not soluble in water.
* = No adsorption stage, complete solution solidified.
✱ = 100 g of clay in all cases.

Table 4.5: Composition of Leach Test Mixes.

Loading of phenol onto Clay	Clay (g)	Ordinary Portland Cement (g)	Water (ml)	Total Inorganic Solids (%)
Perchem 462				
High	100	200	137	68.5
Medium	100	200	137	68.5
Low	100	200	137	68.5
Perchem 97				
High	100	200	137	68.5
Medium	100	200	137	68.5
Low	100	200	137	68.5
Wyoming Bentonite/OPC				
High	100	200	170*	64.0
Medium	100	200	170*	64.0
Low	100	200	170*	64.0
OPC Control				
High	0	400	140	74.0
Medium	0	400	140	74.0
Low	0	400	140	74.0

* Extra water required due to adsorbtive properties of unexchanged Wyoming Bentonite.

When the mixes were homogeneous (minimum mixing time 5 minutes) cylindrical dynamic leach test moulds (60 mm by 60 mm) were filled. The moulds were compacted by vigorous intermittent vibration over a period of 15 minutes and then left to cure for 24 hours. The remainder of each of the mixes were placed in 100 ml polyproplene beakers, compacted and stored for 28 days to cure. After 24 hours the dynamic leach test samples were demoulded and left to cure for a further 27 days. Special temperature controls were not applied during the curing period since the ambient temperature was in the range 20 ± 2°C. Samples were stored in sealed containers to maintain the humidity and in the absence of light to prevent any photochemical reactions.

Two separate sets of control experiments were run in conjunction with the phenol/exchanged clay samples. The first set of control samples contained only OPC and aqueous solutions of the phenols. The required concentration of the phenols were dissolved in the water for hydration of the OPC. Only phenol could be prepared at high loadings due to the low solubility of the other phenols in water. The second set of controls contained unexchanged Wyoming bentonite, OPC (OPC/WB ratio 0.5), and aqueous phenolic solution equal in volume to the amount of water required for the clay and for hydration of the OPC. The Wyoming bentonite was mixed with the phenolic solution and left for 24 hours to allow any adsorption to take place. The clay paste was then solidified with OPC. The Wyoming bentonite/OPC mix was placed in the moulds and left to cure under the same conditions as the exchanged clay samples. The concentrations of phenol in the final dynamic leach test moulds and in the control samples are shown in Table 4.5.

(c) Long Term Stability of Exchanged Clays in a Cement Matrix

The stability of the QAS in the solidified exchanged clay was determined over an 165 day dynamic leach test. Excess QAS was removed from the clay by suspending 100 g of exchanged clay in 1 l water, stirring for 24 hours and the resulting suspension was then filtered under vacuum. The filter cake was solidified with 200 g OPC and distilled water (water/clay ratio 0.67 and w/c ratio 0.35). The moulds were prepared and the samples stored as described above.

(d) Solidification of Aqueous Zinc and 3-Chlorophenol Solutions

Aqueous solutions (200 ml) of 3-chlorophenol. zinc nitrate and mixtures of both compounds were prepared to give the range of concentrations shown in Table 4.6. To each solution 100 g of Perchem 462 exchanged clay was added and the suspensions stirred on magnetic stirrers for 24 hours to allow adsorption of the zinc and 3-chlorophenol. After 24 hours 200 g of OPC was added to each complete aqueous suspension, and the paste well mixed to ensure homogeneity. Each mix was cast in cylindrical moulds (60 mm x 60 mm), for dynamic leach testing, the paste being compacted by manual vibration. The remainder of each of the mixes were placed in 100 ml polypropylene beakers for use in the equilibrium leach tests. All of the samples were cured for 28 days at 20 ± 2°C in 100% relative humidity.

Table 4.6: Weight of Zinc and 3-Chlorophenol Solidified for Leach Testing.

Loading	Mix Number	Weight of 3-Chlorophenol (mg)	Weight of Zinc (mg)
High/High	1.	3358.0	2601.0
High/Medium	2.	3360.0	261.9
Medium/Medium	3.	387.5	259.9
Low/Low	4.	43.6	25.8
Control High	5.	6020.0	0.0
Control Medium	6.	401.0	0.0
Control High	7.	0.0	2600.0
Control Medium	8.	0.0	260.5
Blank	9.	0.0	0.0

(e) Solidification of Pure Organic Compounds

Previous work (Section 3.0) has investigated the adsorption of the organic compounds by the clays in solution, for example the adsorption of phenol from water. Competition between the solvent and the clay for the solvation/adsorption of the organic compounds has a significant effect upon the concentration of the organic compound adsorbed. This work investigated the stabilisation of small concentrations of pure organic liquids, chloronaphthalene and chlorobenzene, using two different methods of adsorbing the organics and QAS onto the clay prior to cement-based solidification.

For the first method, 20 g samples of prewashed Perchem 462, or the equivil~~a~~ent weight of prewashed filter cake, were mixed with between 10 m mol and 100 m mol of either chloronaphthalene or chlorobenzene. To each sample was added 20 g OPC and 37 ml of water (w/c = 0.35, w/clay = 0.67). The OPC was well mixed with the clay until a homogeneous paste was obtained. Each sample was placed in a 100 ml polypropylene beaker and left to cure for 28 days at room temperature and 100% relative humidity. Control samples were prepared containing the organic compounds and OPC only or Wyoming bentonite and OPC mix. The OPC-only controls were prepared by mixing the dry OPC and the organic compound and water added to hydrate the cement. The mixture was worked to form a paste and allowed to cure for 28 days. The organics were found not to mix with the OPC paste and formed a layer on the surface of the sample. The WB/OPC samples were prepared by mixing the organic compounds with the clay and adding the OPC and water. The clay adsorbed the organic compounds well and combined with the OPC to form a homogeneous mix.

The second method required the organic to be dissolved into the QAS prior to adsorption onto the montmorillonite. Pure QAS (0.1 mol), either crystalline (BODDMA-Cl) or in a 50% alcoholic solution (ODTMA-Cl), were mixed with the organic compound. To each mix was added 52 g Wyoming bentonite and 200 ml water. The suspension was stirred for three hours to allow any exchange onto the clay. The clay suspensions were filtered, weighed and solidified with 52 g OPC and water to give the correct w/c ratio, and cured under the standard conditions. Control samples were made using the OPC paste plus the QAS and the organic compound to determine if the QAS alone was able to enhance the stabilisation on the organic. The compositions of all of the mixes and the concentrations of organic compounds adsorbed are shown in Table 4.7.

Table 4.7: Composition of Pure Organic Stabilisation Mixes

	Weight						
Sample	Organic* (m mol)	P. 462 (g)	W.B. (g)	BODDMAM (m mol)	ODTMAM (m mol)	OPC (g)	Water (ml)
1.	20	20	0	0	0	40	37
2.	100	20	0	0	0	40	37
3.**	20	20	0	0	0	40	37
4.**	100	20	0	0	0	40	37
5.	50	0	52	100	0	104	88
6.	10	0	52	100	0	104	88
7.	10	0	52	0	0	104	88
8.	10	0	0	0	100	40	14
9.	50	0	0	0	0	40	14

* = Chlorobenzene or 1-Chloronaphthalene

** = Using prewashed Perchem 462

4.2.4 Physical Tests

(a) Setting Rate

The setting rate of the samples was measured on the equilibrium leach test samples using a concrete pocket penetrometer (Wykeham Farrance Engineering ltd., UK). The measurements were taken from 3 hours after the initial mixing of the samples. Subsequent resistance measurements on the samples were made at regular intervals until the hardness exceeded 4.8 x 10^{-6}N m^{-2}. The setting rate was determined by calculating the rate of change of hardness of the samples with time.

(b) Unconfined Compressive Strengh Tests

Unconfined compressive strength (UCS) measurements were carried out on the 60 mm diameter cylinders (60 mm high) after 28 days curing. The cylindrical samples were prepared for testing by measuring the dimensions of each sample to see if any expansion or contraction of the samples had occurred during curing. The end surfaces were then ground to provide smooth parallel faces for testing using fine sand paper. The tests were performed in triplicate, and the means of the three results taken. The measurement was carried out using a Universal Test Machine - Amsler Grade Al Machine.

Compressive strength tests were also carried out on the blocks used in the dynamic leach tests to compare the effect of the organics and 28 days of leaching on the strength of the blocks. After the leach tests the blocks were dried, at room temperature, in a stream of air for 48 hours before being prepared and tested as described above.

(c) Water Absorption

The procedure adopted was that of the Concrete Society (1986). The samples were cured for 24 days after mixing and then placed in an oven at 105°C for 72 hours, until they reached constant weight. The samples were cooled in a vacuum desiccator for 24 hours. Each sample was weighed and then immediately immersed in a tank containing distilled water at 20°C, with the longitudinal axis of the sample core horizontal and covered by a depth of 25 mm of water. The samples were immersed for 30 minutes and then removed, shaken, the surface dried and reweighed. The samples were then replaced for 24 hours and the weighing procedure repeated.

(d) Oxygen Permeability

The permeation of a cement or an OPC solidified waste is of prime importance as it governs two interrelated properties, durability and leachability. The durability of a solidified sample reflects the long term stability of the treated material whilst the leachability indicates the mobility of contaminants in the solidified samples which may escape from the solidified material with time.

For solidified materials there are no standard methods for measuring permeability. The experimental measurement of water permeability in cementitious systems has several major drawbacks. Firstly, the time taken to achieve a steady flow regime is considerable (8 to 10 days) and the flow of water through the cementitious matrix during measurement may cause changes in the microstructure of the cement, for example, by causing further hydration. Thirdly for solidified waste samples the flow of water through the sample would cause leaching of the wastes and this would modify the flow regime of water through the matrix.

An alternative to using water to measure the permeability of cement samples is to measure the gas permeability. There is no established relationship between the gas and water permeabilities in solid samples but gas permeability can give reproducable results which can be compared with control samples. Gas permeability has several advantages over water it rapidly reaches equilibrium in a few hours and the passage of the gas through the sample has no effect upon the microstructural properties of the cement.

Oxygen was chosen to measure the permeability of the solidified OPC/clay samples in this work. The formulations of the mixes tested are given in Table 4.3, numbers 1, 2, 5 and 6. The mixes contain, respectively, OPC paste, OPC/Perchem 462 and OPC/prewashed Perchem 462 at two different water/cement ratios. The mixes, prepared as in Section 4.2.3(d), were cast in 45 x 100 mm diameter specially prepared cylindrical moulds, with polyethene film at the base to prevent mould oil from penetrating the paste. Compressive strength specimens were cast from the same paste at the same time. The mixes were allowed to cure at 20°C and 100% relative humidity for 24 hours before demoulding and curing for a further 27 days.

After 28 days the cylinders were placed in a sealed container with an atmosphere of 52% relative humidity maintained by saturated aqueous solutions of sodium dichromate for a further 84 days. All tests were performed on duplicate samples.

Oxygen permeability measurements were carried out using a gas permeability cell (Figure 4.1). The cell consists of a circular brass base cylinder and top plate. The sample was placed on the base plate and a soft PVC sleeve placed around it. The cylinder was located around the PVC sleeve and the top plate secured in place. The top plate was pneumatically pressed down onto the sleeve so squeezing the PVC tightly around the sample to obtain a good seal. The oxygen was allowed to flow through the sample until a steady state was reached, the flow being measured by a bubble flow meter for a series of inflow pressures. The permeability values were calculated using an equation derived from a combination of D'Arcy and Poiseuille's equations:-

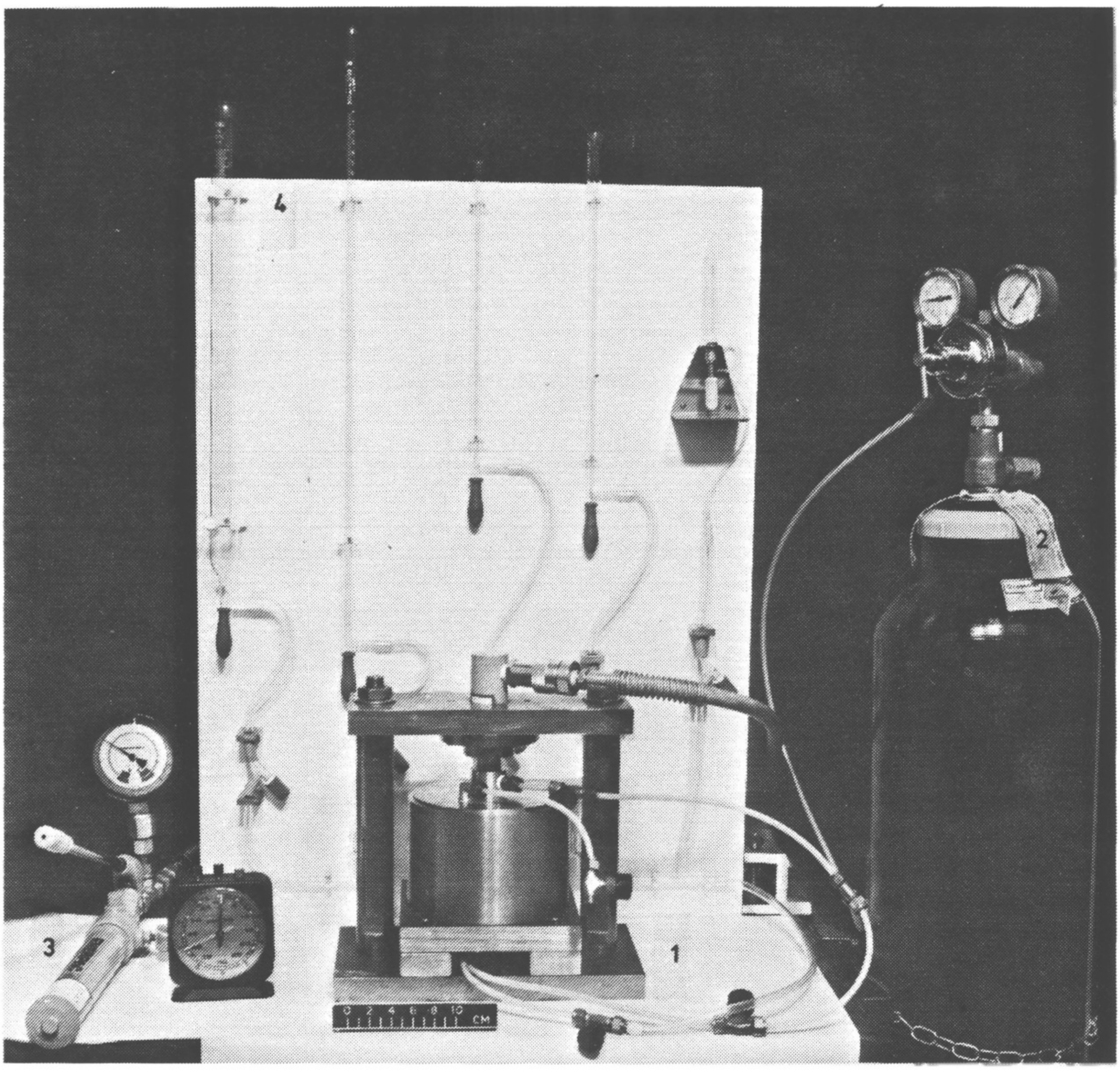


Figure 4.1: Photographic Plate of Oxygen Permeability Rig.

1. = Permeability Cell
2. = Oxygen Supply
3. = Pneumatic Pump
4. = Bubble Gas Flow Meter

$$k = \frac{2.Q.l.\eta.P_1}{(P^2_2 - P^2_1).A}$$

where k = intrinsic permeability (m^2), Q = flow rate (m^3/sec), l = thickness of sample (m), η = viscosity (Nsm^{-2}), P_1 = outlet pressure (Nm^{-2}), P_2 = inlet pressure and A = cross sectional area (m^2).

(e) Mercury Intrusion Porosimetry

The total porosity and pore size distributions of the mixes shown in Table 4.3 numbers 1, 2, 5 and 6 were determined on 28 day old samples. The instrument used in the determination was a Carlo-Erba Series 200 Mercury Intrusion Porosimeter (Carlo Erba, UK). The pore volume, as afunction of the pore radius, was calculated according to the equation for cylindrical pores devised by Winslow & Diamond (1970).

$$d = \frac{-4\gamma Cos\theta}{P}$$

where P = applied pressure (Nm^{-2}), d = pore diameter (mm), γ = surface tension (Nm^{-1}), θ = contact angle of mercury on pore wall.

4.2.5 Leach Tests

(a) Dynamic leach Tests

The procedures for both dynamic and equilibrium leach tests are adapted from those developed by Environment Canada et al. (1986).

For the dynamic leach tests the samples, in the form of 60 mm diameter cylinders, were rinsed briefly in distilled water to remove any dust adhering to the outside of the blocks. The samples were then suspended in 1 l of distilled water in nylon nets. The leachant in the bottles was stirred gently throughout the test, the temperature of the samples being kept at 20 ± 2°C. The leachate from the blocks was sampled after 1, 2, 4, 7, 10, 14, 18, 22 and 28 days. Before analysis of the leachate the sample blocks were removed from the containers, allowed to drip dry and 100 ml aliquots of the leachate retained. The remainder of the leachate was discarded and the blocks re-suspended in a fresh 1 litre aliquot of distilled water. Leachate analysis was carried out using the standard colourimetric method previously described (Section 4.2.3(b)). When low dilutions of the leachate were required for the colourimetric analysis N-2-hydroxyethyl-piperazine N'-3-propanesulphonic acid (HEPPS) buffer was used instead of the phosphate/ammonium buffer, in order to avoid precipitation of metal phosphate salts formed after leaching of metals from the cement.

(b) Equilibrium Leach Test

For the equilibrium leach tests the solidified samples were analysed after 28 and 56 days of curing. Prior to analysis the samples were crushed manually using a pestle and mortar and the particle size sieved to between 0.5 and 2.0 mm. Approximately 40 g of crushed samples were weighed into polypropylene screw capped containers and four times the weight of distilled water added. The containers were sealed and shaken on a rotary shaker for a 7 day period. After 7 days the samples were settled for 1 hour to allow the solids to separate and the supernate was then filtered through 0.45 μm membrane filters. After suitable dilution analysis was performed colourimetrically.

(c) Equilibrium Leach Test on Pure Organic Solidified Samples

The solidified samples were analysed after 28 days of curing. The samples were crushed manually using a pestle and mortar and the particle size sieved to between 0.5 and 2.0 mm. Approximately 30 g of the crushed samples were weighed into containers and a equal weight added to a second container. To the first container four times the weight of water was added and to the second four times the sample weight of methanol. The containers were shaken end-over-end for 7 days. After 7 days the samples were filtered through 0.45 µm membrane filters. The methanol-extracted filter cake was resuspended in the original volume of fresh methanol and shaken for a further 24 hours and re-filtered. This procedure was repeated on 7 successive days to remove all of the organic compounds present in the sample.

The aqueous filtrate was extracted with hexane to remove and concentrate the organic compounds, then analysed by UV spectrophotometry to determine the concentrations present. The methanol filtrates were combined after the 7 day period and the chlorinated organic compounds extracted into hexane to concentrate the samples prior to analysis. To determine the partition coefficient between hexane and methanol, a series of standard solutions of chlorobenzene and chloronaphthalene were prepared in methanol, extracted with hexane and the concentration of the chlorinated organic determined. The hexane extracts were analysed by UV spectrophotometry.

(d) Long Term Stability of QAS on Clay in the Cement Matrix

To determine the long term stability of the QAS on the clay in the cement matrix exchanged clay samples were solidified in OPC and, after 28 days curing, subjected to leaching tests for a total of 23 weeks. Dynamic leach tests (Section 4.2.5(a)) were carried out inorder to monitor the amount of quaternary ammonium compound leached into the water. Unlike previous dynamic leach tests, the leachate, at regular time intervals of either 3 or 7 days, was analysed by removing 5 ml aliquots and replacing them with 5 ml of distilled water. Analysis of the leachate was carried out by TOC analysis of three 0.40 µl subsamples. The test was carried out over a 161 day period.

4.3 RESULTS

4.3.1 Selection of Exchanged Clays

A series of exchanged clays were prepared in the laboratory and tested for their ability to adsorb phenol, 3-chlorophenol and 2,3-dichlorophenol. The results of these experiments (Section 3.3.1) showed that the QAS with chain lengths of C_{14} to C_{18} adsorbed the highest concentration of all of these phenols. With a view to the ultimate use of exchanged clays on a large-scale commercial basis, and because of the large quantities of exchanged clays required for subsequent experiments, a survey of commercially available exchanged clays was carried out. Commercially prepared exchanged clays were selected for adsorption studies on the basis of their similarity of structure and chain length to the laboratory-prepared samples. The clays shown in Table 4.8 were tested to determine the amount of phenol, 3-chlorophenol and 2,3-dichlorophenol adsorbed by 1.0 g of the exchanged clay from 10.0 mM of aqueous phenol solution.

The results show that, under these conditions, Perchem 462 showed the greatest adsorption of the phenols. The weight of the phenols adsorbed by the Perchem 462 clay compared favourably to BODDMAM which adsorbed 44%, 91% and 98% of the phenol, 3-chlorophenol and 2,3-dichlorophenol respectively from 10 mM solutions in 3 hours. Subsequent tests were carried out on Perchem 462, a trimethylalkylammonium exchanged montmorillonite, and Perchem 97 which corresponded to the benzyl substituted alkylammonium salt exchanged onto the montmorillonite (BODDMAM). Adsorption profiles of a range of phenolic concentrations by Perchem 462 and Perchem 97 are shown in Figure 4.2.

Table 4.8: Percentage of Phenol adsorbed by Commercial Exchanged Clays

Product Name	Percentage Adsorbed* (%)		
	Phenol	3-Chlorophenol	2,3-Dichlorophenol
Bentone 27	40	68	75
Bentone 34	55	76	83
Bentone 38	42	75	81
Bentone SD1	31	79	88
Bentone SD2	36	79	89
Bentone EW	4	28	10
Perchem 44	31	65	82
Perchem 97	42	82	83
Perchem 462	64	92	96
BODDMAM	44	91	98

* Adsorption by 1.0 g of exchanged clay from 100 ml of 10 mM aqueous phenol solution.

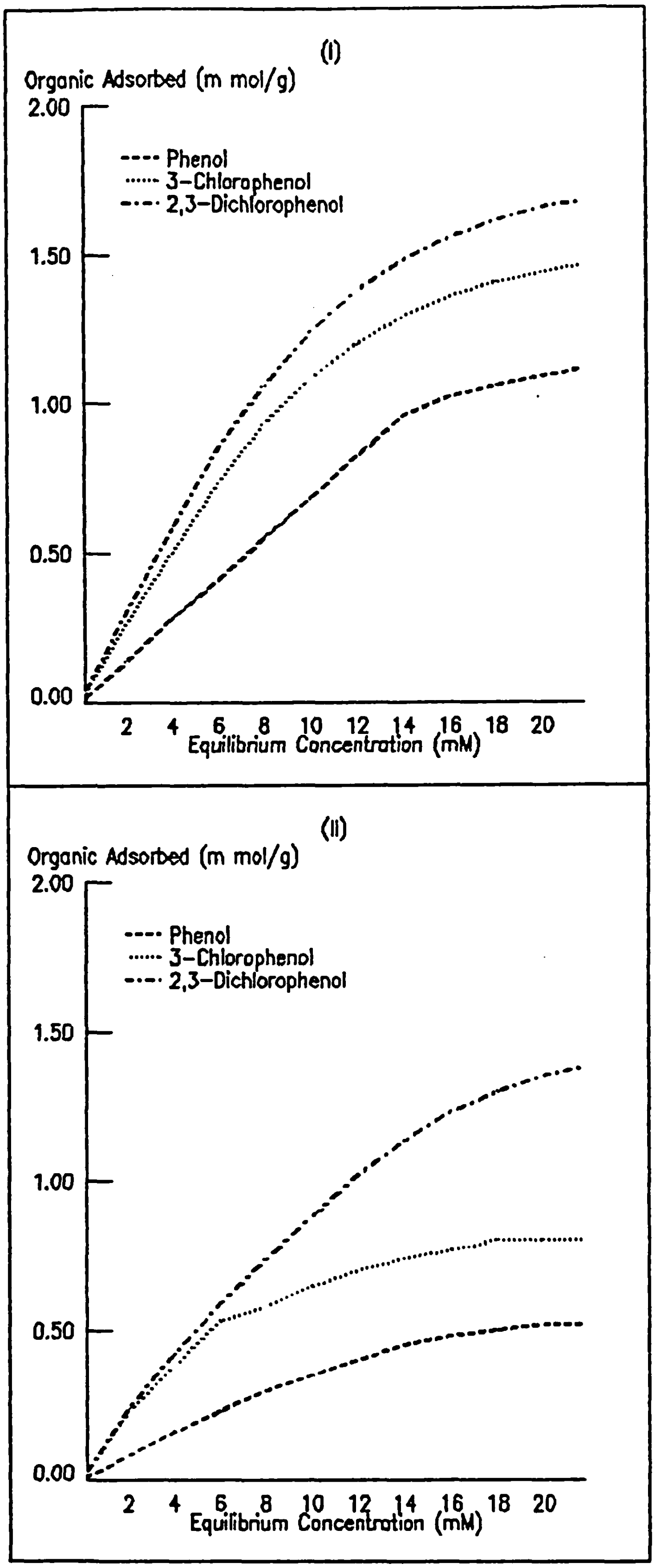


Figure 4.2: Adsorption of Phenols from Aqueous Solution by (I) Perchem 462 and (II) Perchem 97.

4.3.2 Physical Tests

To determine the optimum mix and to characterise the performance of the exchanged clay in a cement matrix, a series of physical tests were performed on different exchanged clay/cement mixes.

(a) Unconfined Compressive Strength Tests

The effect of the exchanged clays at the two water/cement ratios upon the strength of the solidified samples was examined by measuring the UCS of a range of different mixes (the compositions of which are shown in Section 4.2.3(a) Table 4.3). The results of the compressive strength tests are shown in Figure 4.3. The results showed that the lower water/cement ratio (0.35) produced stronger mixes in all cases. The addition of the exchanged clay greatly reduced the strength of the mixes (Mix 2) compared with the OPC only mixes (Mix 1), and increasing the exchanged clay/cement ratio further weakened the matrix (Mix 5). In the case of the higher water/cement ratio, and to a lesser extent for the lower w/c ratio, the exchanged clay/OPC mixes were highly aerated, the matrix resembling a "honeycomb" of air bubbles. The UCS of these mixes was much lower than expected. The bubbles were caused by the mix water washing the excess QAS from the clay's outer surface and, due to the surfactant properties of the QAS, producing foam which remained trapped in the matrix. The addition of antifoam had no effect upon the strength of either the lower w/c ratio clay/cement samples or the cement-only controls (Mix 4 and 3 respectively). The presence of antifoam slightly reduced the foaming effect in the high w/c ratio mixes (Mix 4) compared to Mix 2, and a corresponding increase in the strength was observed. The most effective method of reducing the foaming of the mixes and improving the strength of the matrix was found to be washing the exchanged clay to remove the excess QAS. The compressive strength of Mix 6 shows the dramatic effect of strength increase when using washed exchanged clay.

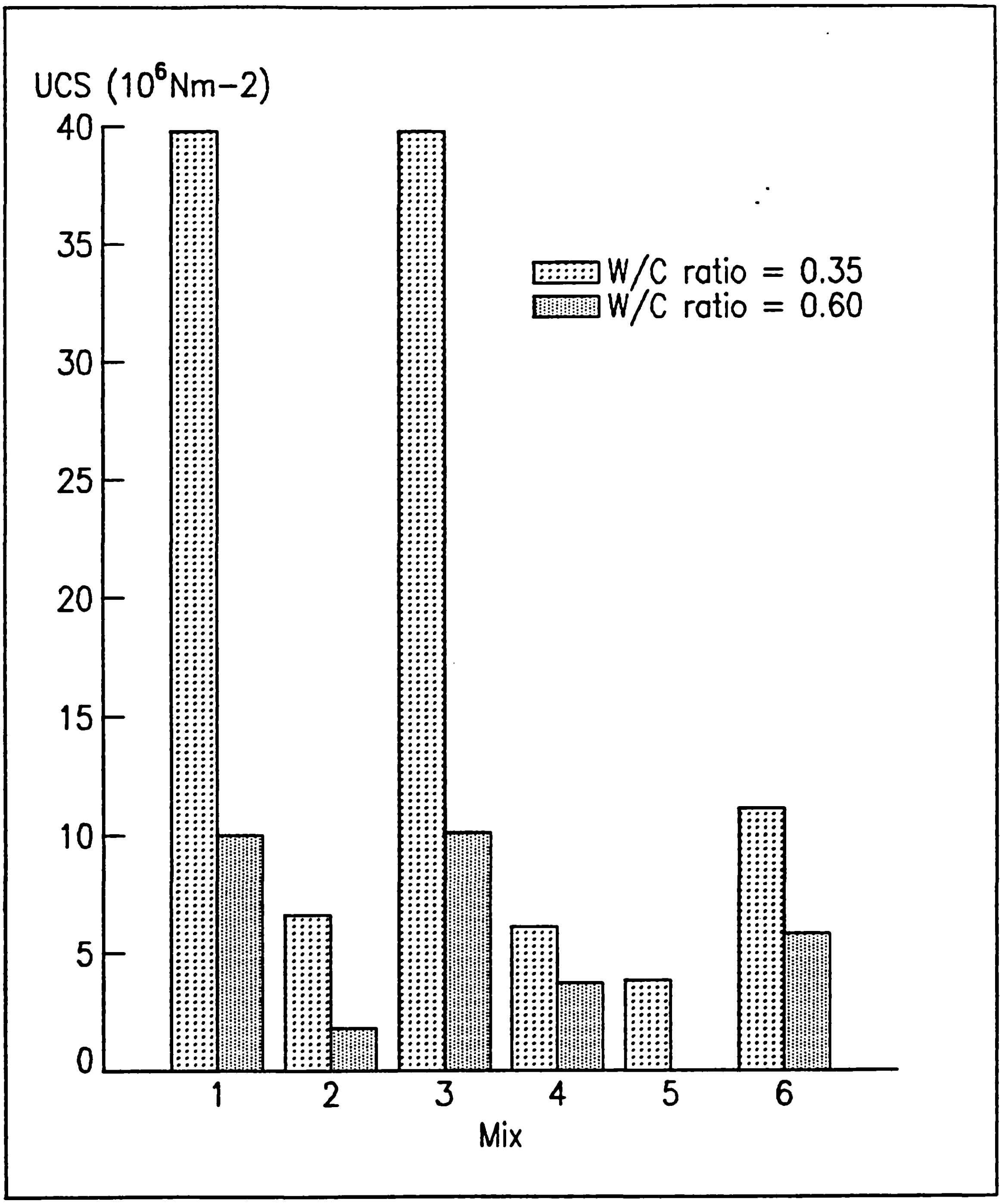


Figure 4.3: Unconfined Compressive Strengths of Solidified Samples.

Mix 1 = OPC only; Mix 2 = Perchem 462/OPC; Mix 3 = OPC + Antifoam; Mix 4 = Perchem 462/OPC + Antifoam; Mix 5 = Perchem 462/OPC (1:1) and Mix 6 = Perchem 462(washed)/OPC.

The effects of the phenolic compounds on the 28 day UCS of the solidified samples are shown in Figure 4.4. The difference in the UCS between the aqueous phenolic compounds and pure water in the exchanged clay/OPC mix was small, the maximum difference, for 3-chlorophenol, being less than 20%. The UCS of the OPC-only mixes showed a greater difference in strength between the different mixes, although the pattern of hardness for the three phenols is the same. The major difference between the two sets of samples was, once again, caused by the presence of the exchanged clay which had a detrimental effect upon the OPC strength.

The effect of the phenolic compounds and the exchanged clay on the setting rate of the mixes is shown in Table 4.9. Also shown are the UCS of the dynamic leach test samples (Section 4.3.3(a)) after 56 days (28 days curing and 28 days leaching). The phenol dosed cement-only samples showed a slight increase in strength (compared with Mix 1 in Figure 4.3) and a high setting rate. The clay/cement samples showed very little increased strength due to the presence of the phenolic compounds compared with Mix 2 in Figure 4.3. However, Perchem 97 seemed to give a weaker matrix than Perchem 462. The Wyoming bentonite/cement samples were very low in strength and had a low setting rate. The compressive strengths of the leach tested samples showed an overall decrease in strength for those samples containing the exchanged clay, and a slight increase in strength for the OPC-only samples compared with the comparable non-leach tested samples.

The presence of zinc in the Perchem 462/OPC solidified samples (Figure 4.5) seems to have little effect on the compressive strength of the matrix.

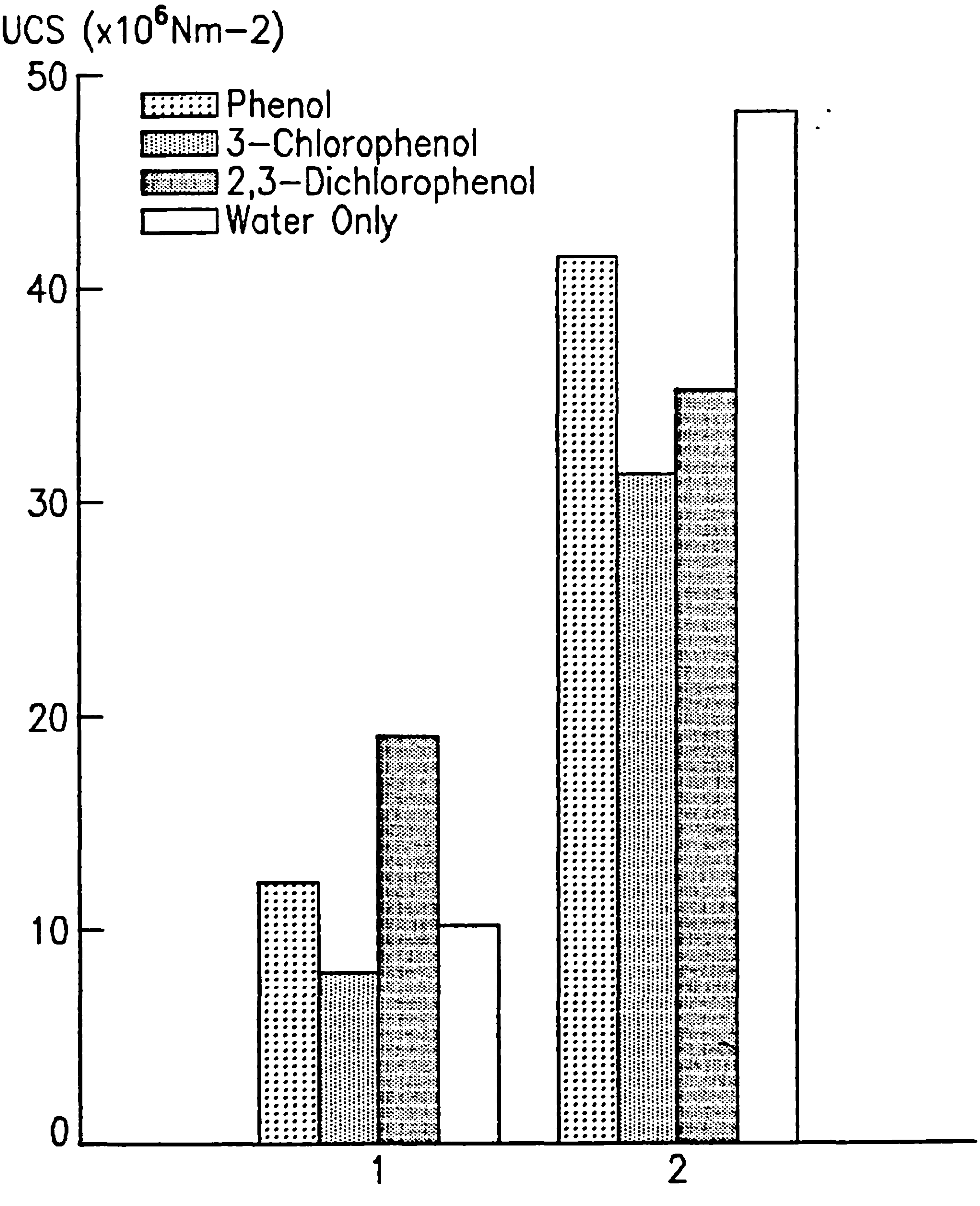


Figure 4.4: Effect of Phenols on Unconfined Compressive Strength of Solidified Samples.

Mix 1 = Perchem 462/OPC and Mix 2 = OPC Only

Table 4.9: Setting Rates of QAS-Exchanged Clay/OPC Samples dosed with Phenolic Compounds and Compressive Strengths*.

Sample	Loading of phenols	Setting Rate ($\times 10^6$ Nm^{-2})					Compressive Strength ($\times 10^6$ Nm^{-2})
		3 Hours	5 Hours	7 Hours	24 Hours	48 Hours	
PHENOL							
Clay 462/OPC	High	0.3	0.4	ND	>4.8	>4.8	9.2
Clay 97/OPC	High	0.1	0.9	3.4	>4.8	>4.8	5.8
WB/OPC	High	0.3	0.4	0.4	2.2	3.1	0.9
OPC	High	0.3	2.7	>4.8	>4.8	>4.8	48.7
Clay 462/OPC	Medium	0.0	0.1	0.4	>4.8	>4.8	7.4
Clay 97/OPC	Medium	0.3	0.5	2.5	>4.8	>4.8	10.6
WB/OPC	Medium	0.3	0.4	0.5	0.6	1.2	0.6
OPC	Medium	0.3	2.7	>4.8	>4.8	>4.8	50.4
3-CHLOROPHENOL							
Clay 462/OPC	High	0.3	0.5	ND	>4.8	>4.8	7.5
Clay 97/OPC	High	0.3	0.3	>4.8	>4.8	>4.8	4.4
WB/OPC	High	0.2	0.3	0.5	2.4	2.5	0.9
Clay 462/OPC	Medium	0.1	0.3	0.5	>4.8	>4.8	8.4
Clay 97/OPC	Medium	0.5	0.9	ND	>4.8	>4.8	10.9
WB/OPC	Medium	0.3	0.7	0.7	0.8	0.8	0.8
OPC	Medium	0.3	ND	>4.8	>4.8	>4.8	41.6
2,3-DICHLOROPHENOL							
Clay 462/OPC	High	0.3	0.5	0.8	>4.8	>4.8	4.0
Clay 97/OPC	High	0.3	1.5	ND	>4.8	>4.8	9.0
Clay 462/OPC	Medium	0.1	0.1	0.3	>4.8	>4.8	6.9
Clay 97/OPC	Medium	0.5	1.0	2.3	>4.8	>4.8	11.0
WB/OPC	Medium	0.2	0.2	0.5	1.5	2.3	0.5
Clay 462/OPC	Low	0.1	0.3	0.3	>4.8	>4.8	12.6
Clay 97/OPC	Low	0.4	1.0	3.1	>4.8	>4.8	7.7
WB/OPC	Low	0.2	0.5	0.6	1.6	1.6	0.3
OPC	Low	1.8	ND	>4.8	>4.8	>4.8	65.9
CONTROL							
Clay 462/OPC	None	0.0	0.1	0.2	>4.8	>4.8	11.1
Clay 97/OPC	None	0.1	0.5	0.9	>4.8	>4.8	6.2
WB/OPC	None	0.3	0.7	0.9	2.7	2.8	0.7
OPC	None	0.3	1.8	3.9	>4.8	>4.8	48.2

ND = Not Determined
*after 28 days leach testing

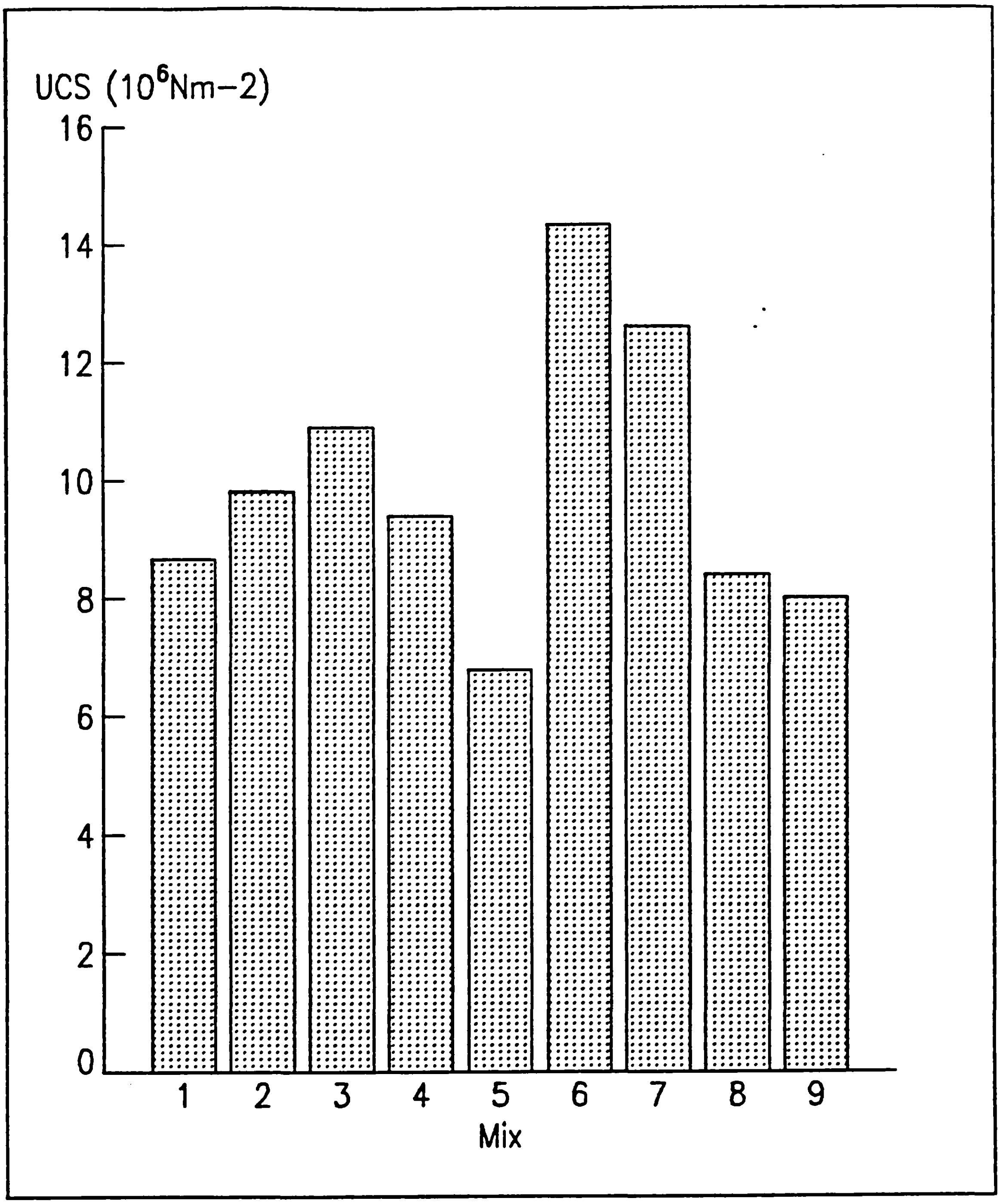


Figure 4.5: Effect of Zinc and 3-Chlorophenol on the Unconfined Compressive Strength of Solidified Samples.

Loading	Mix Number	Weight of 3-Chlorophenol (mg)	Weight of Zinc (mg)
High/High	1.	3358.0	2601.0
High/Medium	2.	3360.0	261.9
Medium/Medium	3.	387.5	259.9
Low/Low	4.	43.6	25.8
Control High	5.	6020.0	0.0
Control Medium	6.	401.0	0.0
Control High	7.	0.0	2600.0
Control Medium	8.	0.0	260.5
Blank	9.	0.0	0.0

(b) Water Absorption

Results of the water absorption experiments are shown in Figure 4.6. The 30 minute immersion results give an indication of the different permeabilities of the mixes (The Concrete Society, 1985). The 24 hour absorption experiment highlights these differences. The ability to measure water absorption by the cement mixes is of prime importance, particularly in understanding some features of the dynamic leach test and, indeed, important when considering the final use for the stabilised mixes.

From Figure 4.6 several points can be observed. Increasing the water/cement ratio increased the absorption of water by over 50% (Mixes a compared to b, Table 4.3). The addition of the exchanged clay also increased the water absorption and higher clay-to-cement ratios magnified the effect (Mixes 2 and 5 respectively). The higher w/c ratio in the clay/cement mixes increased the foaming caused by the excess QAS adsorbed onto the outside of the clay (Mix 2(b)). Washing the clay before preparation of the mix produced a sample which absorbed only slightly more water during the absorption tests than the cement-only controls (Mixes 1 and 6). The addition of antifoam to the clay/cement mix in order to reduce the foaming, caused by the excess QAS, seemed to have little effect upon the water absorption test results (Mix 4). After 30 minutes the difference in water absorbed by the cement-only samples and the cement/clay samples was small, but after 24 hours the cement-only samples had absorbed very little additional water whereas the cement/clay samples had absorbed more than twice the percentage of water absorbed in 30 minutes.

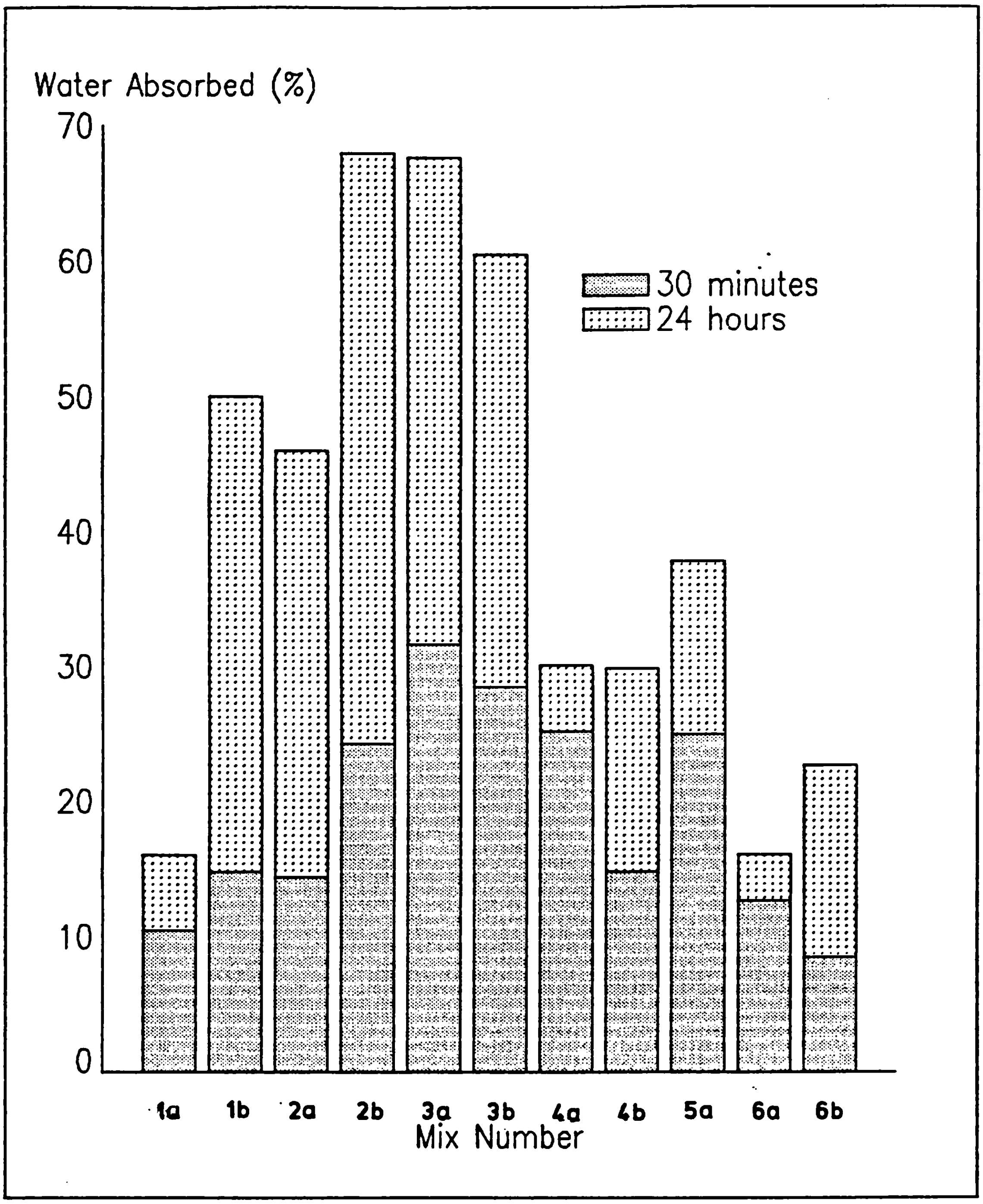


Figure 4.6: Water Absorption Test.

Mix 1 = OPC only; Mix 2 = Perchem 462/OPC; Mix 3 = OPC + Antifoam; Mix 4 = Perchem 462/OPC + Antifoam; Mix 5 = Perchem 462/OPC (1:1) and Mix 6 = Perchem 462(washed)/OPC.

(c) Oxygen Permeability

Permeability data are shown in Figure 4.7(I) with the densities of each mix after 28 days curing shown in Figure 4.7(II). The 0.35 water/cement ratio mixes show surprisingly little difference in permeability between the OPC-only mix and the samples containing the exchanged clay. Similarly, the difference between the washed and unwashed clays was minimal. For the 0.6 water/cement ratio, however, the difference between the three mixes was considerable. The OPC-only mix had a very low permeability, while the sample containing unwashed clay was extremely permeable. The difference in permeability between the washed and unwashed mixes was appreciable but not as large as might have been expected. The probable reason for this is that although the samples were very porous, the bubbles being visible to the eye, the cells were not connected and so the permeability of the samples is not great. This effect is illustrated in Figure 4.8.

(d) Mercury Intrusion Porosimetry

The porosity of the mixes was measured by MIP and the results are shown in Figure 4.9. Figure 4.9(I) shows the total cumulative pore volume of the mixes and Figure 4.9(II) shows the percentage of pores with a radius greater then 1000 nm. Pores greater than 1000 nm were considered to be voids due to the entrapped air. The total cumulative pore volume for both the w/c ratio mixes demonstrates the expected maximum value for the mixes containing the unwashed clay. The high percentages of pores with a radius greater than 1000 nm for the clay mixes (particularly the unwashed clay mixes) was due to the foaming effect of the QAS.

From the results of the physical tests, the optimum mix of cement and clay to give the highest strength and lowest permeability was found to be Mmix 6(a), Table 4.3. Mix 6(a) was made with the washed exchanged clay at the low water/cement ratio. Mix 11, which had a higher water/cement ratio, also had good physical

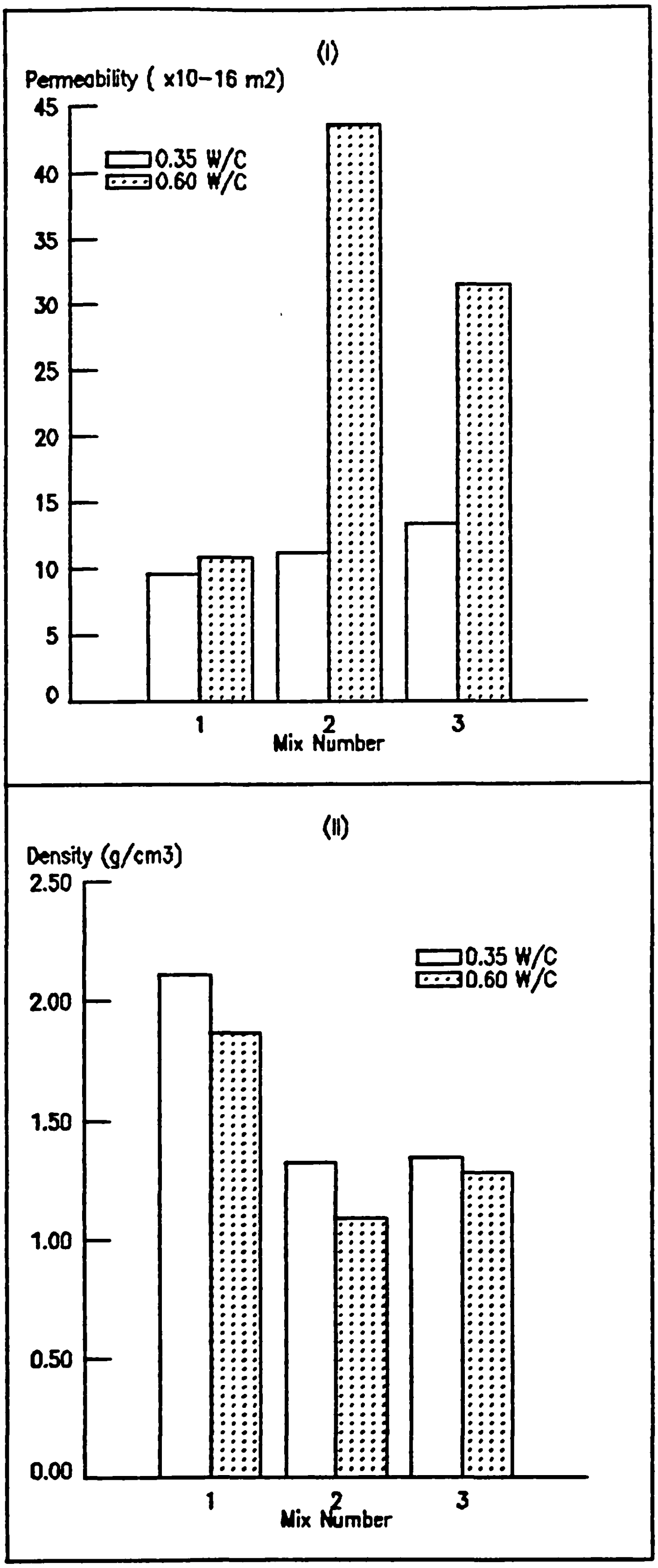
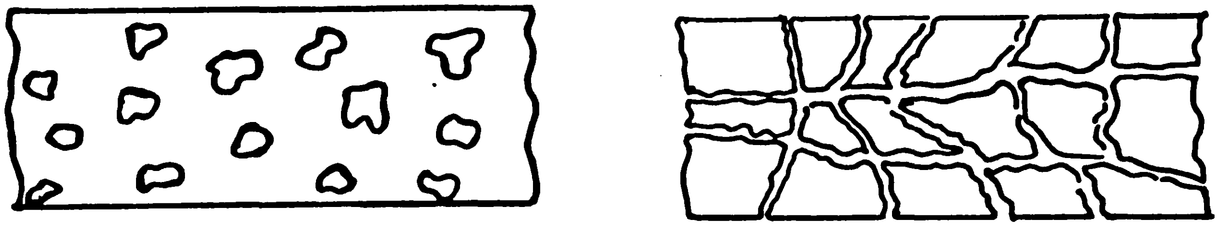


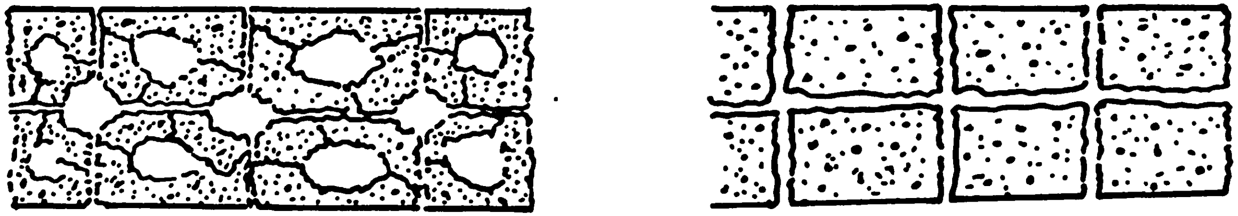
Figure 4.7: Oxygen Permeability Samples Showing (I) Permeability Results and (II) the Density of the Permeability Samples.

Mix 1 = OPC only; Mix 2 = Perchem 462/OPC; Mix 6 = Perchem 462(washed/OPC).



(I) Porous, impermeable material.

(II) Porous, permeable material.



(III) Highly porous, low permeability material.

(IV) Low porosity, high permeability material.

Figure 4.8: Schematic Diagram to show the Effect of Porosity and Permeability in a Solid Matrix (after Bakker, 1983).

characteristics, although the higher w/c ratio reduced the strength and increased the permeability.

The samples for the dynamic leach test were "washed" once as part of the procedure for adsorbing phenolic compounds which greatly reduced the foaming problem in these mixes. The physical characteristics of the phenolic mixes would be expected to be similar to that seen in Mixes 6(a), Table 4.3.

4.3.3 Solidification of Phenols From Dilute Aqueous Solution

The physical tests showed that the optimum w/c ratio is 0.35, for solidification of the exchanged clays, hence this ratio was used for the leach tests. The physical tests showed that a washing stage was required for the clays, prior to use, but this stage was combined with the adsorption stage, so no formal prewashing was required.

Two types of leach test were performed on the samples. Dynamic leach tests used whole cylindrical samples (60 mm x 60 mm) suspended in gently stirred leachant. This test was performed on 28 day old samples and usually lasted a total of 28 days. The equilibrium leach test was performed on ground samples after 28 and 56 days of curing to give the maximum possible release (Sollars & Perry, 1989). The different leach test results were compared to ascertain the overall leaching performance of the samples.

(a) Dynamic Leach Test

The results of the dynamic leach test are shown in Figure 4.10. The results show the total weight of each phenol released over the 28 day period as a percentage of the total weight of phenol originally present in the sample. It should be emphasised that the actual concentration of phenol in the leachate varied considerably between days 1 and 28 of the test, the maximum release occurring within the first few days of the test. Although similar percentages of phenol

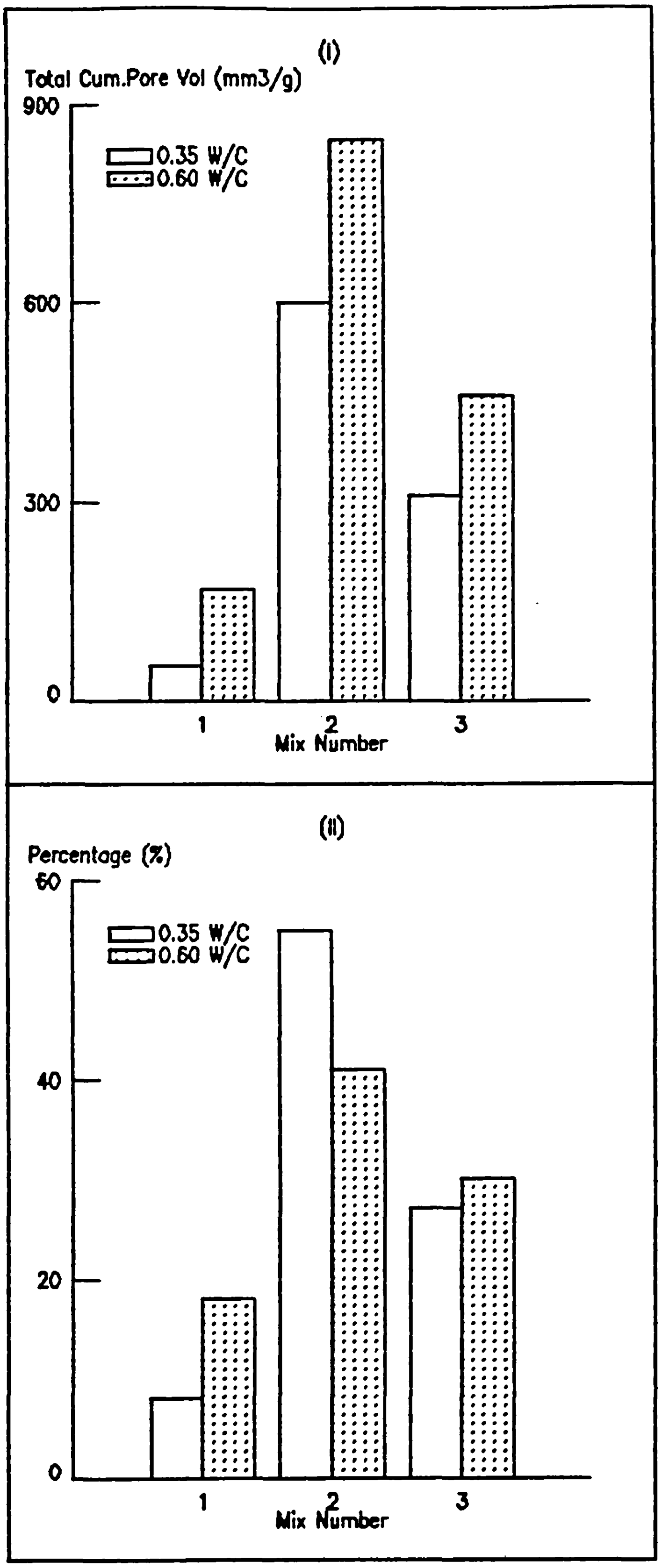


Figure 4.9: Mercury Intrusion Porosimetry to Show (I) Total Cumulative Pore Volume and (II) Percentage of Pores with Radii above 1000 nm.

Mix 1 = OPC only; Mix 2 = Perchem 462/OPC; Mix 6 = Perchem 462(washed/OPC).

were released from clays loaded with different concentrations of the phenols, the leachate concentrations were several orders of magnitude different. The general trends demonstrated at all three phenol concentrations (Figure 4.10(I), (II) and (III)) were that the unexchanged Wyoming bentonite/OPC mix did not stabilise any of the phenols, and, moreover, the clay caused large increases in leaching compared to the other mixes. The exchanged clays stabilised the phenols well, particularly as the degree of chlorination in the phenols increased. This effect had previously been demonstrated in the adsorption studies. The OPC/water mix appeared able to stabilise phenols as effectively as the exchanged clay mix, particularly the phenol-dosed samples at high concentrations (Figure 4.10(I)). This effect was probably due to the nature of the leach test which was strongly dependent upon the rate of penetration of the aqueous leachate into the sample and its diffusion through it, so the low permeability of the cement-only mix ensured good retention of the phenol.

Figure 4.10(I) shows the release from samples loaded with high concentrations of phenol, approximately equal to the maximum adsorption capacity of the clay determined by the adsorption studies. Perchem 462 (Mix 1) released approximately 15% of each phenolic compound, whereas Perchem 97 showed a greater release of phenol and 3-chlorophenol. The OPC mix (Mix 4) released much less phenol than expected (the only organic sufficiently soluble in water to allow the high loading concentration to be reached).

The medium loading samples (Figure 4.10(II)) showed a similar pattern of release to the high loading samples, except that the percentage of organic released by the exchanged clay samples (Mixes 1 and 2) was considerably reduced. The samples loaded with low concentrations of 2,3-dichlorophenol (Figure 4.10 (III)) also showed a low release for the exchanged-clay samples.

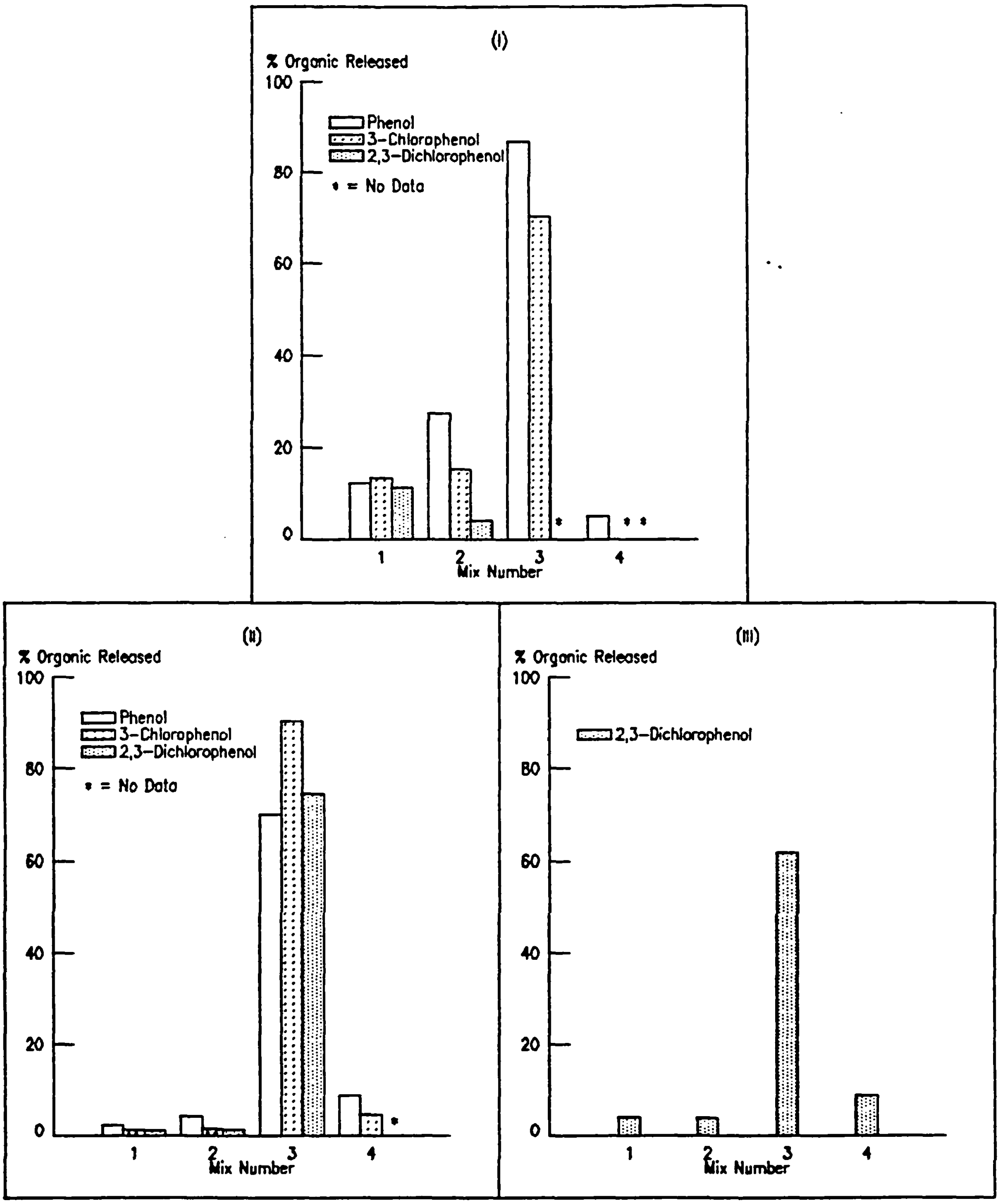


Figure 4.10: Dynamic Leach Test Results for Solidified Samples, (I) High, (II) Medium and (III) Low Phenol Loadings.

Mix 1 = Perchem 462/OPC; Mix 2 = Perchem 97/OPC;
Mix 3 = Wyoming Bentonite/OPC and Mix 4 = OPC Only.

(b) Equilibrium Leach Test

The results of the equilibrium leach test on 28 day old crushed samples are shown in Figure 4.11. They are represented in a similar form to the dynamic leach test results in Figure 4.10 so may be compared directly. In general it would be expected that the equilibrium leach test would release higher concentrations of the phenols compared with the dynamic leach test results, as the samples are ground and subjected to severe leaching conditions. However, if the phenols are well bound in the matrix the release would still be small, and only the unbound molecules would be released. From Figure 4.11(I) it can be seen that almost 100% of the phenols are released from the unexchanged Wyoming bentonite mix (mix 3), and that the OPC-only sample released about 40% of the phenol present, suggesting that the stabilising effect seen in Figure 4.11(I) was due to the inability of the leachate to penetrate the sample. The Perchem 462 mix (mix 1) released less than 24% of the phenol present in the sample, and similarly low percentages for the other phenols. The medium and low loading of the samples clearly demonstrated the ability of the exchanged clay mixes to stabilise the phenols present compared to the OPC-only mix.

When the samples are allowed to cure for a longer period a gradual hardening of the matrix would be expected, with a corresponding reduction in phenols released. Figure 4.12 shows the results of the equilibrium leach tests carried out on samples, identical to those used in the previous test, after 56 days. In general, it can be seen that the additional curing time has caused a reduction in the release of the phenols from all of the mixes, both samples and controls, particularly in the presence of high concentrations of the phenols.

(c) Long-term Stability of QAS in Exchanged-Clays in a Cement Matrix

The release of QAS by the cement-solidified exchanged clay over a long period of leaching is of great importance in predicting the

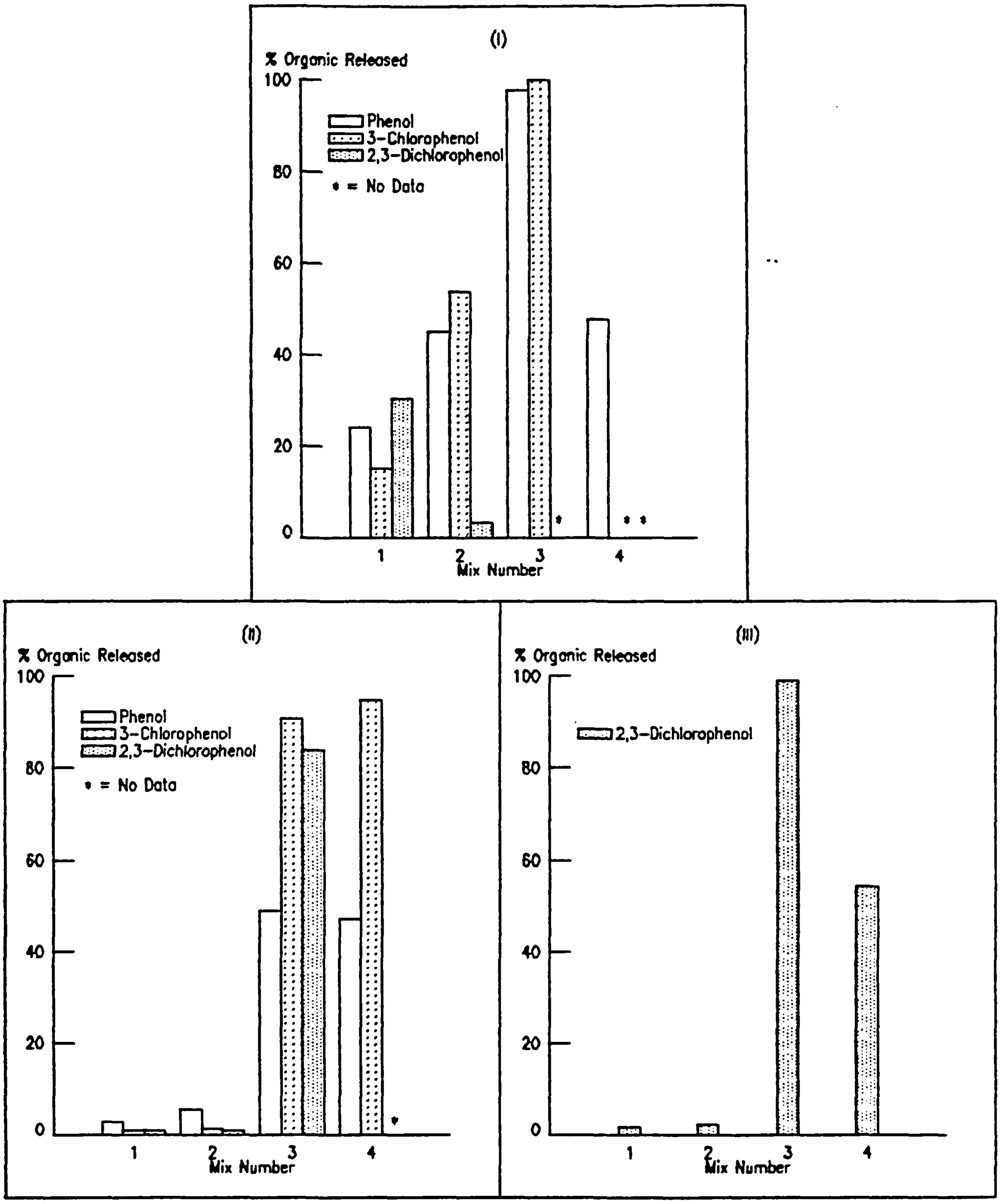


Figure 4.11: Equilibrium Leach Test Results After 28 Days Curing for Solidified Samples at (I) High, (II) Medium and (III) Low Phenol Loadings.

Mix 1 = Perchem 462/OPC; Mix 2 = Perchem 97/OPC; Mix 3 = Wyoming Bentonite/OPC and Mix 4 = OPC Only.

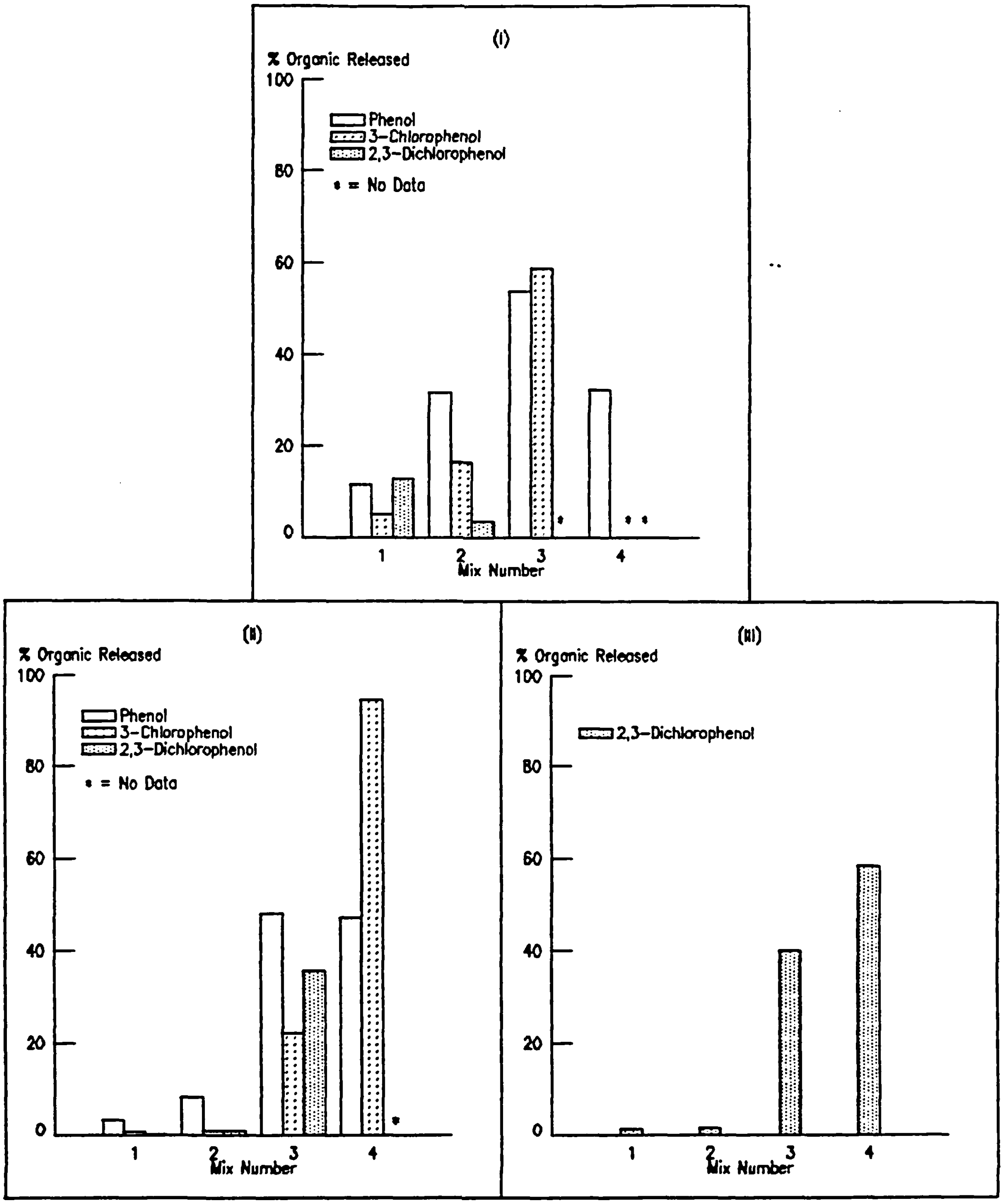


Figure 4.12: Equilibrium Leach Test Results After 56 Days Curing for Solidified Samples at (I) High, (II) Medium and (III) Low Phenol Loadings.

Mix 1 = Perchem 462/OPC; Mix 2 = Perchem 97/OPC; Mix 3 = Wyoming Bentonite/OPC and Mix 4 = OPC Only.

long-term stability of the samples. Figure 4.13 shows the results of dynamic leach tests on the Perchem 462/OPC mix over a 23 week period. The release of TOC was measured and the concentration of QAS caluculated from that value. The results show that there was a small reduction in the TOC in the leachate of 32 mg/l over the entire 22 week period. It was anitcipated, however that the TOC concentration would remain constant, which would have suggested that the exchanged clay was unaffected by leaching, or that the TOC would increase over the period, which would have suggested that the QAS was being leached from the matrix. The reduction in TOC may suggest that the excess QAS, originally released by the clay, was re-adsorbed into the clay as an equilibrium between the leachate and the clay was established. Other reasons for the reduction in TOC could be due to the decay of the organic compounds in the leachate responsible for the TOC levels or due to bacterial degradation of the organic species present. The peak at 17 weeks may indicate the point at which the cement became saturated, and the subsequent decline may be due to readsorption of TOC by the clay.

4.3.4 Solidification of Zinc and 3-Chlorophenol From Aqueous Solution

The concentrations of 3-chlorophenol used throughout the leaching tests were chosen with reference to the earlier leach test studies performed with 3-chlorophenol alone. Zinc was the metal chosen because, in the adsorption studies (Section 3.3.5), it was shown to displace the QAS from the clay. Poon (1985) showed that zinc retarded the hydration of the OPC matrix by forming a coating on the cement particles. The degree of retardation depended on the thickness of the coating. The retardation resulted in a reduction in strength and impermeability of the solid product.

Three different concentrations of 3-chlorophenol and zinc were solidified and these concentrations were designated, high, medium and low (see Table 4.6). The concentrations chosen represent, in the case of 3-chlorophenol, the maximum concentration which was adsorbed

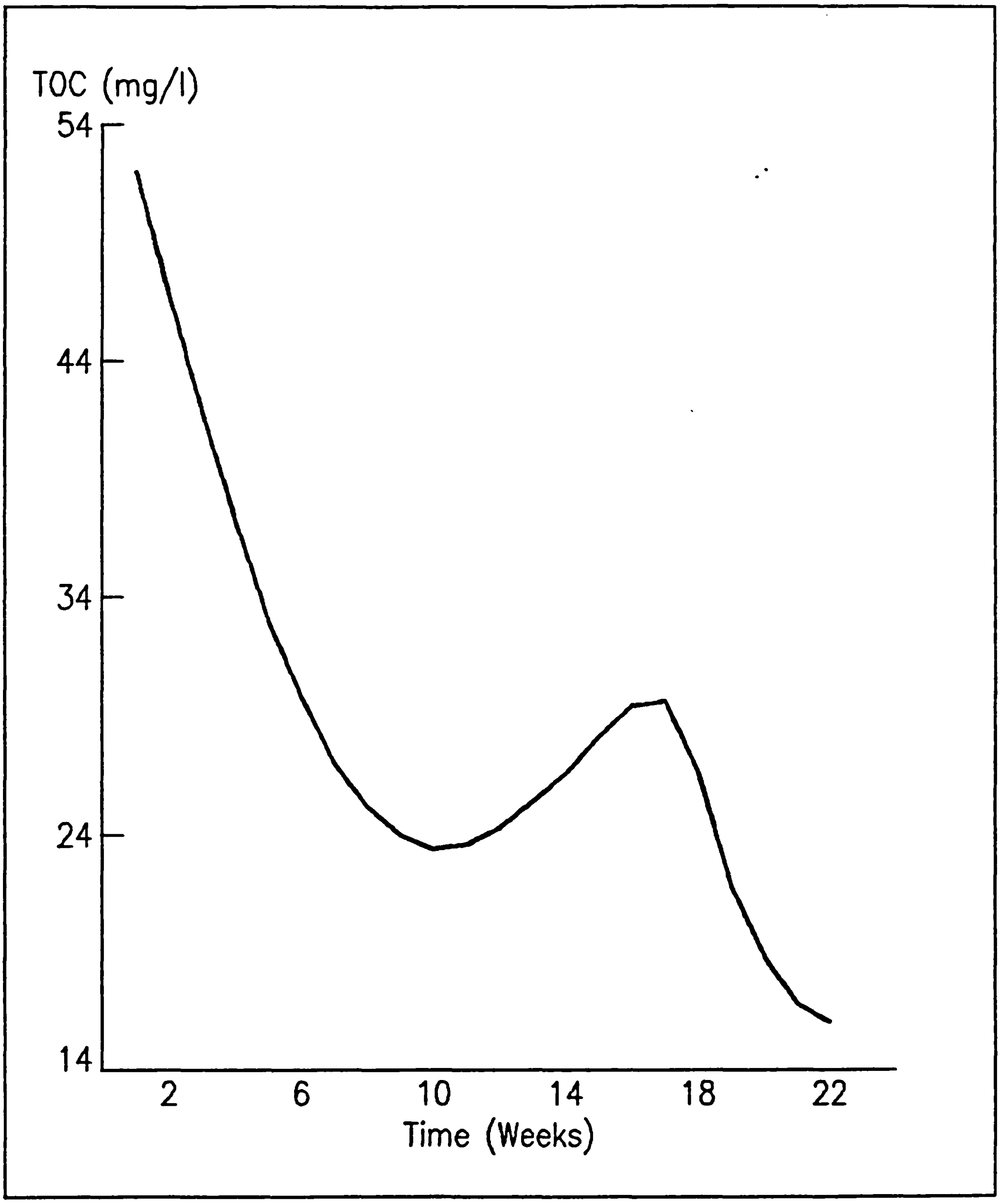


Figure 4.13: Long Term Stability of QAS on Exchanged Clays in the Cement Matrix.

by the clay from a dilute aqueous solution (high loading), one tenth of the high concentration (medium loading) and one hundredth of the high loading in the case of the low loading samples. For zinc, the high concentration was approximately the maximum concentration of zinc which did not show significant release from an OPC matrix after solidification. The medium and low concentrations are one-tenth and one-hundredth of the high concentration respectively.

(a) Dynamic Leach Tests

The results of the dynamic leach test are shown in Figure 4.14. The percentage of 3-chlorophenol and zinc released from the samples are shown in Figures 4.14(I) and 4.14(II) respectively. The highest percentage of 3-chlorophenol released was from the sample with high concentrations of zinc and 3-chlorophenol, conversely zinc shows a maximum release in the low loaded samples. The samples that contained only medium concentrations of zinc but high and medium concentrations of 3-chlorophenol gave a percentage release very similar to the control (Mix 5, Figure 4.14(I)).

Figure 4.14(III) shows the concentration of QAS released from the clay into the leachate during the leach tests. The concentration of QAS was measured by determining the TOC of the leachate and subtracting from this the concentration of 3-chlorophenol and any organic matter, other than QAS, released from the clay itself present in the leachate. The highest concentration of QAS was found in the leachate of the high loading zinc control. This result, together with the high release of the 3-chlorophenol in the presence of high concentrations of zinc, suggests that the zinc was displacing the QAS from the clay.

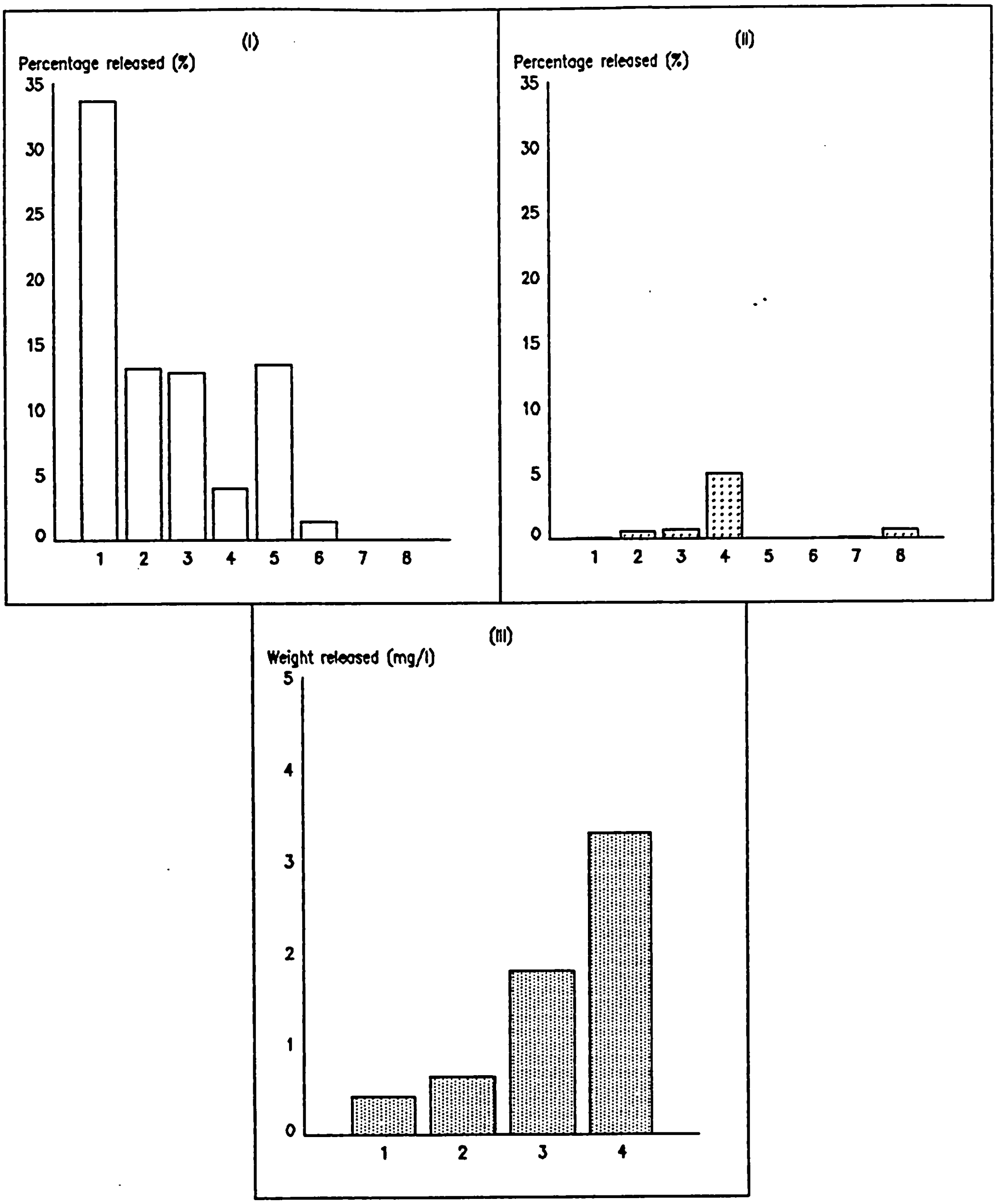


Figure 4.14: Dynamic Leach Test Results Showing the Percentage of (I) 3-Chlorophenol, (II) Zinc and (III) the Weight of QAS Released.

Loading	Mix Number	Weight of 3-Chlorophenol (mg)	Weight of Zinc (mg)
High/High	1.	3358.0	2601.0
High/Medium	2.	3360.0	261.9
Medium/Medium	3.	387.5	259.9
Low/Low	4.	43.6	25.8
Control High	5.	6020.0	0.0
Control Medium	6.	401.0	0.0
Control High	7.	0.0	2600.0
Control Medium	8.	0.0	260.5
Blank	9.	0.0	0.0

(b) Equilibrium Leach Tests

The results of the equilibrium leach tests after 28 and 56 days curing are shown in Figures 4.15 and 4.16 respectively. In general, the 28 day leach test results showed higher releases than the 56 day results as the matrix had cured further and was more durable after the extra curing time. The release of 3-chlorophenol and zinc from the samples after 56 days curing had a very similar pattern (though lower percentage releases) to the results obtained from the dynamic leach test. After 28 days curing, the release of 3-chlorophenol from the samples differed significantly from the dynamic leach test results, the 3-chlorophenol only sample giving a similar release to the dynamic leach test results, but a far greater release than any of the zinc/3-chlorophenol samples. By 56 days the 3-chlorophenol release from Mix 5 had been reduced to below that of Mix 1, in a similar way to the dynamic leach test results. The concentration of QAS released from all of the samples was very similar. Unlike the dynamic leach test, no increase in QAS concentration was seen for the high load zinc sample.

4.3.5 Solidification of Pure Organic Compounds

(a) Equilibrium Leach Tests

Figure 4.17 shows the organic released from the stabilised samples expressed as a percentage of the concentration of organic in the aqueous leachate compared to the concentration in the methanol. The concentration of the organic in the methanol was considered to be close to the concentration of the organic in the sample after losses by evaporation and in handling had been accounted for. Chlorobenzene concentrations in the leach test samples were found to be significantly lower than in the original samples due to evaporation during curing. The concentration of chlorobenzene and chloronaphthalene in the aqueous leachate was limited by their solubility in water.

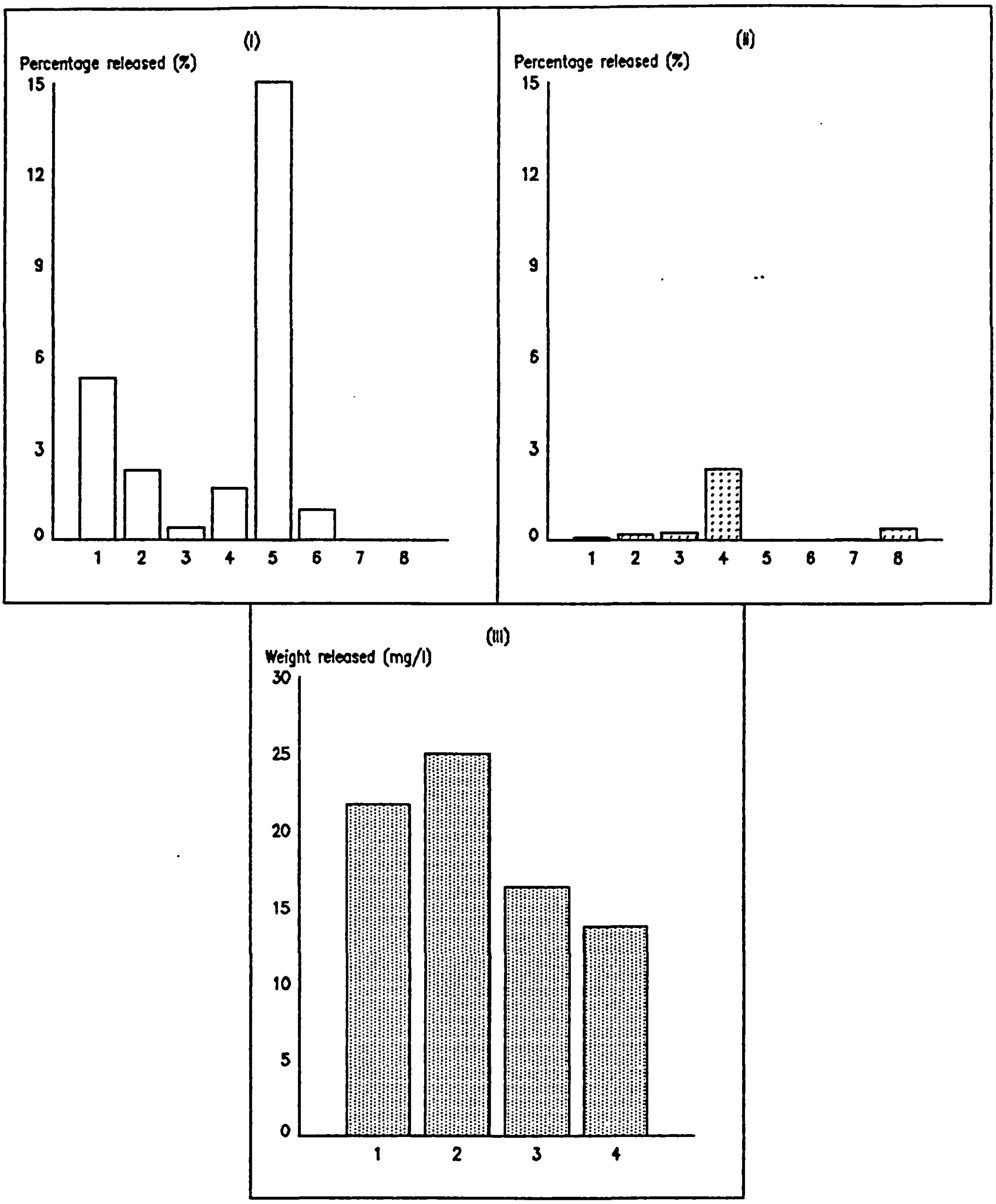


Figure 4.15: Equilibrium Leach Test Results After 28 Days Curing Showing the Percentage of (I) 3-Chlorophenol, (II) Zinc and (III) the Weight of QAS Released.

Loading	Mix Number	Weight of 3-Chlorophenol (mg)	Weight of Zinc (mg)
High/High	1.	3358.0	2601.0
High/Medium	2.	3360.0	261.9
Medium/Medium	3.	387.5	259.9
Low/Low	4.	43.6	25.8
Control High	5.	6020.0	0.0
Control Medium	6.	401.0	0.0
Control High	7.	0.0	2600.0
Control Medium	8.	0.0	260.5
Blank	9.	0.0	0.0

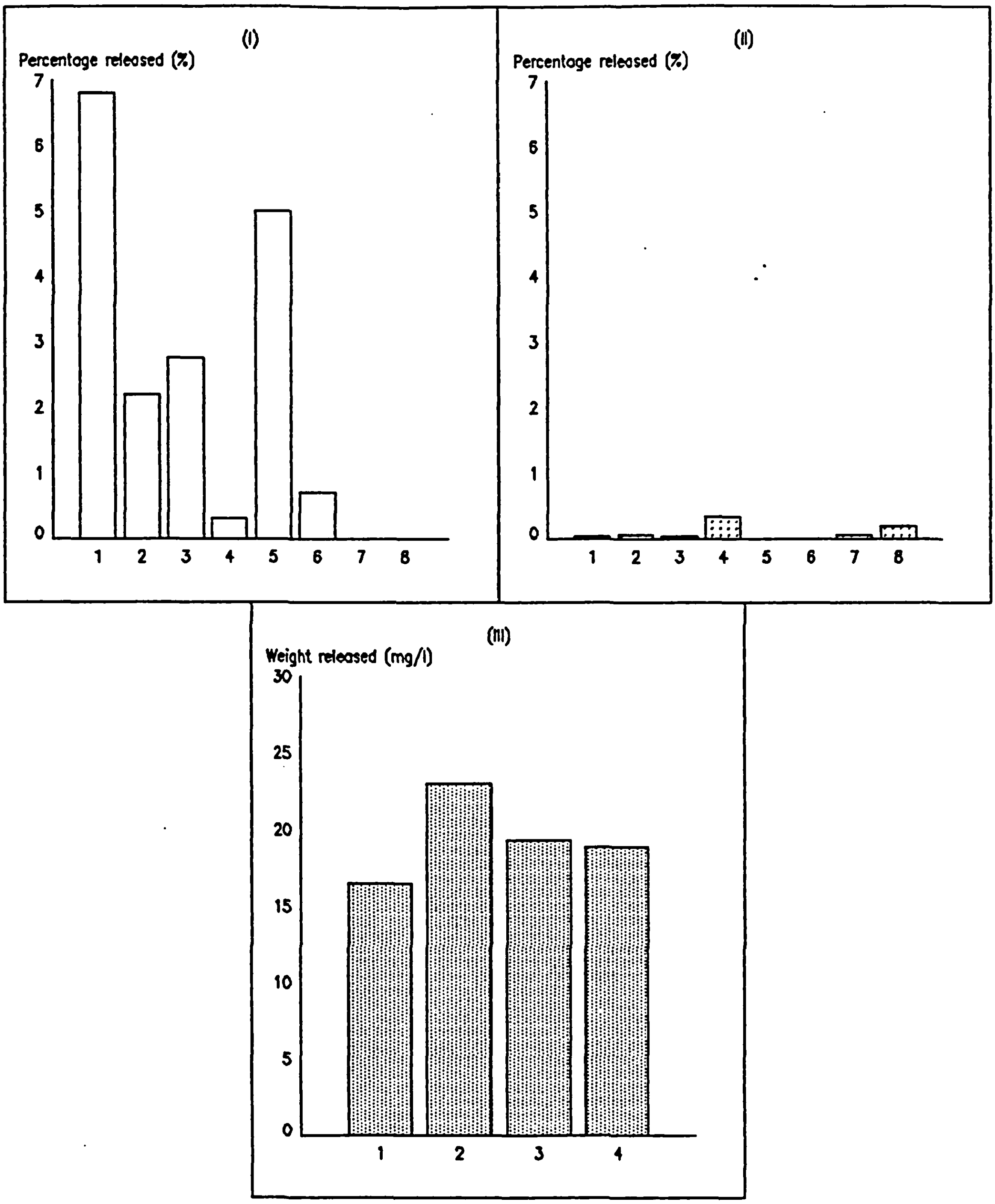


Figure 4.16: Equilibrium Leach Test Results After 56 Days Curing Showing the Percentage of (I) 3-Chlorophenol, (II) Zinc and (III) the Weight of QAS Released.

Loading	Mix Number	Weight of 3-Chlorophenol (mg)	Weight of Zinc (mg)
High/High	1.	3358.0	2601.0
High/Medium	2.	3360.0	261.9
Medium/Medium	3.	387.5	259.9
Low/Low	4.	43.6	25.8
Control High	5.	6020.0	0.0
Control Medium	6.	401.0	0.0
Control High	7.	0.0	2600.0
Control Medium	8.	0.0	260.5
Blank	9.	0.0	0.0

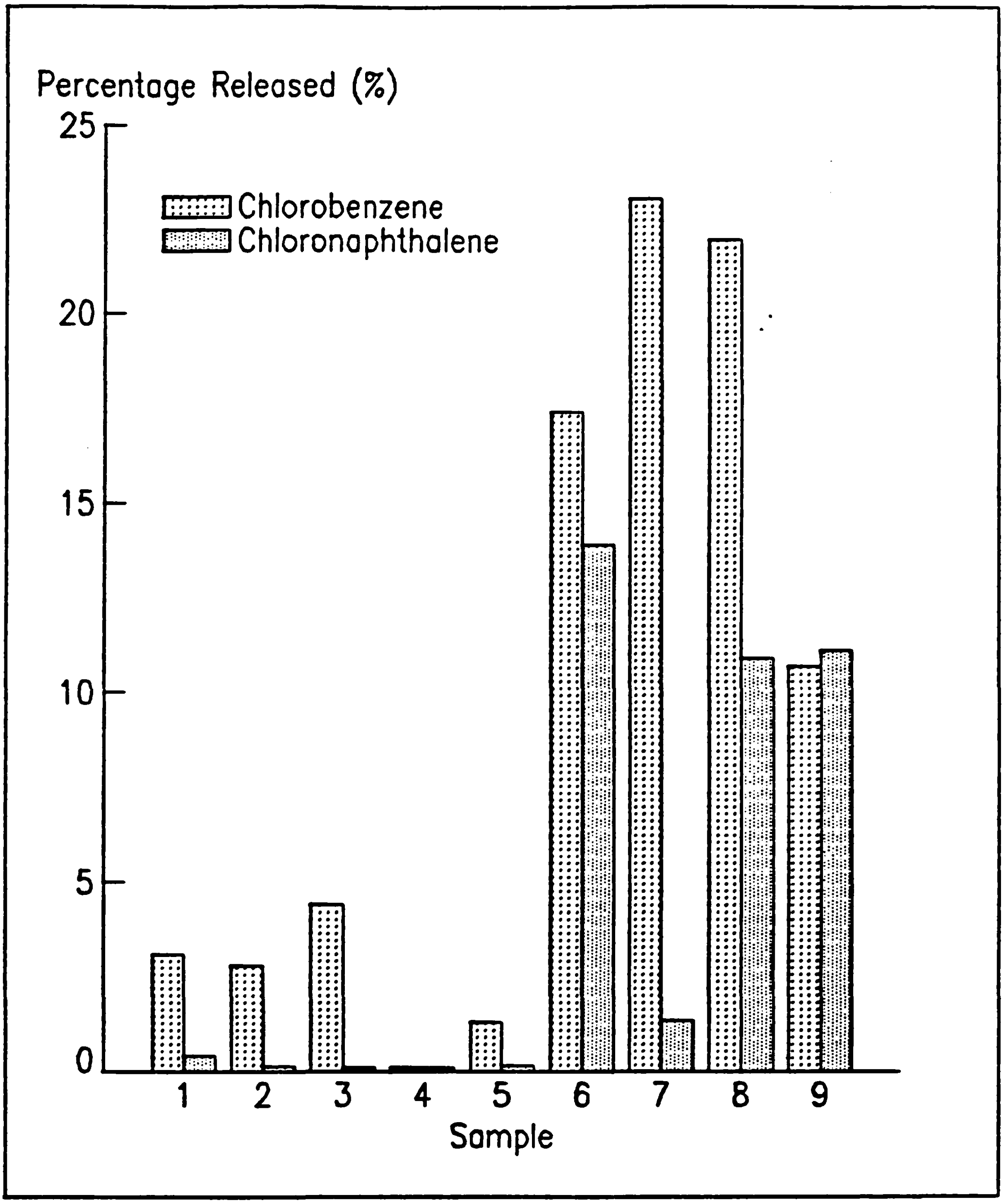


Figure 4.17: Release of Organic Compounds from Solidified Samples.

Sample	Weight Organic* (m mol)	P. 462 (g)	W.B. (g)	BODDMAM (m mol)	ODTMAM (m mol)	OPC (g)	Water (ml)
1.	20	20	0	0	0	40	37
2.	100	20	0	0	0	40	37
3.*	20	20	0	0	0	40	37
4.*	100	20	0	0	0	40	37
5.	50	0	52	100	0	104	88
6.	10	0	52	100	0	104	88
7.	10	0	52	0	0	104	88
8.	10	0	0	0	100	40	14
9.	50	0	0	0	0	40	14

* = Chlorobenzene or 1-Chloronaphthalene

* = Using prewashed Perchem 462

Solidification of chlorobenzene and chloronaphthalene by the exchanged clay/OPC mix was very effective, because the exchanged clay provided an interface between the organic compounds and the inorganic OPC matrix. The clay interface allowed high concentrations of the organics to be incorporated into the matrix, far higher than could be adsorbed by the OPC alone or by the WB/OPC mix. Leaching of the organics from the stabilised samples was low (Figure 4.17), and significantly lower than from the control samples. These results show that the organophilic clay was able to adsorb organic compounds and bind them more firmly than clay alone which, although known to adsorb organic molecules readily, was unable to stabilise them under the conditions of the test.

Solidification of the organic compounds by mixing the organics with the QAS prior to exchange onto the clay did not give very encouraging results (Figure 4.17). The unexchanged clay was able to adsorb some of the organic liquids, however the organics were readily released from the samples during leach testing. The presence of the QAS in the mix did not enhance the adsorption onto the clay or stabilisation of the organics and, due to of its surfactant properties, increased the solubility of the organic in the aqueous leachate. This effect was also seen in the QAS/OPC controls which not only had the high release of both the chlorinated organics but also a high concentration of QAS in the leachate.

4.4 Summary

Commercially prepared exchanged clays were selected for initial adsorption studies on the basis of their similar structures and chain lengths to the most successful laboratory-prepared samples. Perchem 462 was found to be the best adsorbent and so was used in the S/S experiments.

The physical tests showed that the presence of the clay reduced the strength and increased the permeability of the cement matrix.

Higher w/c ratios caused foaming problems due to the excess QAS on the clay. This effect could be reduced by washing the clay prior to incorporation into the cement matrix. The introduction of phenols into the cement matrix reduced the strength of the cement only samples, but had no effect upon the clay/cement mix.

Phenolic compounds in aqueous solution could be solidified, in low concentrations, by the cement paste without the use of exchanged clay. Equilibrium leach tests, which involved crushed samples shaken in aqueous leachate for 7 days, showed however, that the phenols were not stabilised as they were readily released during testing. In contrast, phenols could be solidified with the exchanged clay at weights up to one hundred times that in the cement-only controls. Even at the highest loading, the clay/cement mix retained the phenols well under equilibrium leaching conditions. Dynamic leach tests, using monolithic samples in stirred aqueous leachate, indicated that phenol retention by the cement-only control matrix was comparable with that of the exchanged clay/cement matrix, over the duration of the test, for samples containing low concentrations of the phenols. For higher concentrations, however, fully analogous cement-only controls could not be prepared due to the phenols' solubility limitations. At low phenol concentrations the comparable results of the cement-only controls and the cement/clay mixes in the dynamic leach test were due to the nature of the test in which the permeability of the sample was an important factor in governing the amount released. The low permeability of the cement matrix reduced the contact time between the aqueous leachate with phenol entrapped in the cement matrix.

Solidification of zinc and chlorophenol by cement and clay had higher releases from the leach tests than the solidification of either compound alone, suggesting competition for the same adsorption sites in the clay. Pure chlorobenzene and chloronaphthalene, which could not be solidified by cement alone were successfully solidified by the clay/OPC mix. The solidified sample had a good strength and leaching of the organic compounds was low.

5. MICROSTRUCTURAL ANALYSIS

5.1 INTRODUCTION

Since the chemical reactions of ordinary Portland cement with water are responsible for the macrostructural properties of the paste, the effect of additives on the hydration reactions are of prime importance (Jawed et al., 1983). Investigations of cement chemistry and the effect of additives are, however, difficult as cement is a complex mixture of numerous compounds (Section 1.5.1), the hydration mechanisms of which are still under debate (Double, 1983).

The effect of organic compounds on cement paste has only recently received attention (Skipper et al., 1987 and Eaton et al., 1987). Eaton et al. have investigated the effect of two organic compounds on cement paste, but few attempts have been made to recognise how the individual phases are affected. This study looks at the effect of two organic compounds (3-chlorophenol, a polar hydrophilic compound and chloronaphthalene, a non polar compound) on cement hydration and shows how the hydration phases are affected.

The presence of clay in cement paste has long been known to adversely affect the strength of cement paste (Haque, 1981) and consequently the amount of clay in concreting aggregates is carefully controlled. The mechanism by which clays affect strength is unknown. This study looks at how clay influences cement hydration, and how the cement affects the clay.

The final part of this work shows how the clays are able to adsorb the organic compounds and reduce the detrimental effect of the organic compounds on cement hydration.

5.2 MATERIALS AND METHODS

5.2.1 Sample Preparation

The samples examined in this work were prepared using the materials and methods described in Section 3.2, for the clays and Section 4.2, for the solidified samples.

In addition, for x-ray diffraction (XRD) analysis exchanged clay (20 g) was treated with 100 ml aliquots of 0.1 M potassium hydroxide solution. The clay suspensions were mixed in stoppered flasks and allowed to stand for 1 to 28 days, the flasks being shaken at daily intervals. The clays were filtered and dried at 105°C for 24 hours and ground to <100 µm. Calcium hydroxide treated clays were prepared in a similar way using 100 ml of saturated calcium hydroxide solution and 20 g of exchanged clay.

5.2.2 Scanning Electron Microscopy

Analysis was performed by a Jeol 35CF (London, UK) Scanning Electron Microscope (SEM) fitted with energy dispersive spectroscopy (EDS), (Links, High Wycombe, UK).

Samples for SEM analysis were cured for the required time period and then dried over silica gel in a vacuum desiccator for 24 hours. The dried solid samples were carefully fractured and representative sections mounted on examination stubs using epoxy resin. The samples were replaced in the vacuum desiccator for a further 24 hours. Powdered samples were mounted on the examination stubs using double-sided adhesive tape. All of the samples were earthed by judicious application of silver dag, from the edge of the sample to the stub, prior to coating with gold (Emscope "sputter coater", UK) to make them electrically conductive.

5.2.3 X-ray Diffraction Analysis

X-ray diffraction analysis was performed by a Siemens x-ray powder diffractometer (Siemens, Sunbury-on-Thames, UK) with a CuK_α radiation source. Specimens for XRD analysis were prepared by crushing to <100 µm and drying over silica gel in a vacuum desiccator for 24 hours. Just prior to analysis the samples were sieved through a 75 µm sieve onto silicon discs, which had previously been coated with a thin layer of silicon grease to help the samples adhere. Analysis was carried out on rotating samples using divergence and anti-scatter slits of 0.3°, 0.05° between 2 θ angles of 2° to 10° and 1°, 0.15° between 2θ angles of 4° to 60° with collection rates between 1 and 5°/second.

5.3 RESULTS

5.3.1 Exchanging Quaternary Ammonium Cations onto Wyoming Bentonite

The XRD pattern of Wyoming bentonite at low diffraction angles was compared with that of BODDMAM (Figure 5.1), to show the effect of introducing the QAS into the interlamellar space of the clay. The interlamellar space increased from 0.994 nm for the unexchanged clay to 1.996 nm for BODDMAM; this change was due to the QAS pushing the clay's silicate layers apart. Figure 5.1 also shows the effect of adsorbing 3-chlorophenol onto the exchanged clay. The chlorophenol did not greatly affect the XRD pattern of the clay, but a slight decrease in the interlamellar space to 1.914 nm was observed. This reduction may be due to the adsorbed chlorophenol interacting with the QAS and effectively "pulling" the QAS chains together so slightly reducing the spacing of the clay layers.

Figure 5.2 shows the XRD pattern of prewashed Perchem 462 compared to Wyoming bentonite. Once again the interlamellar spacing

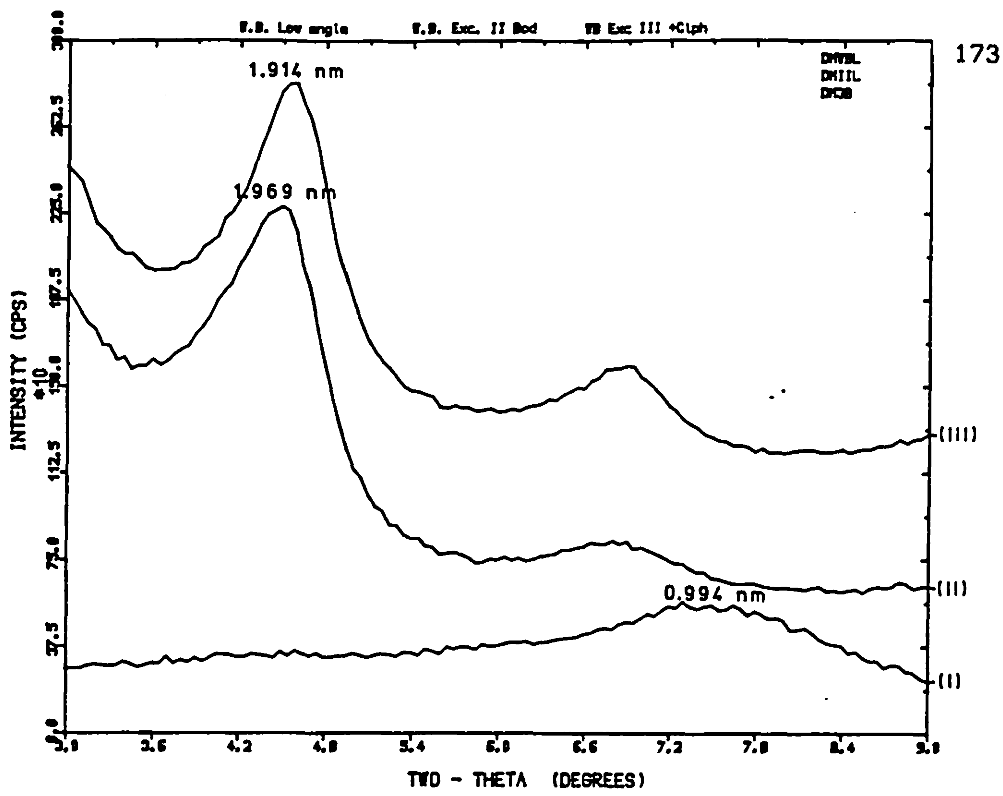


Figure 5.1: XRD Pattern of (I) Wyoming Bentonite, (II) BODDMAM and (III) BODDMAM with Adsorbed 3-Chlorophenol.

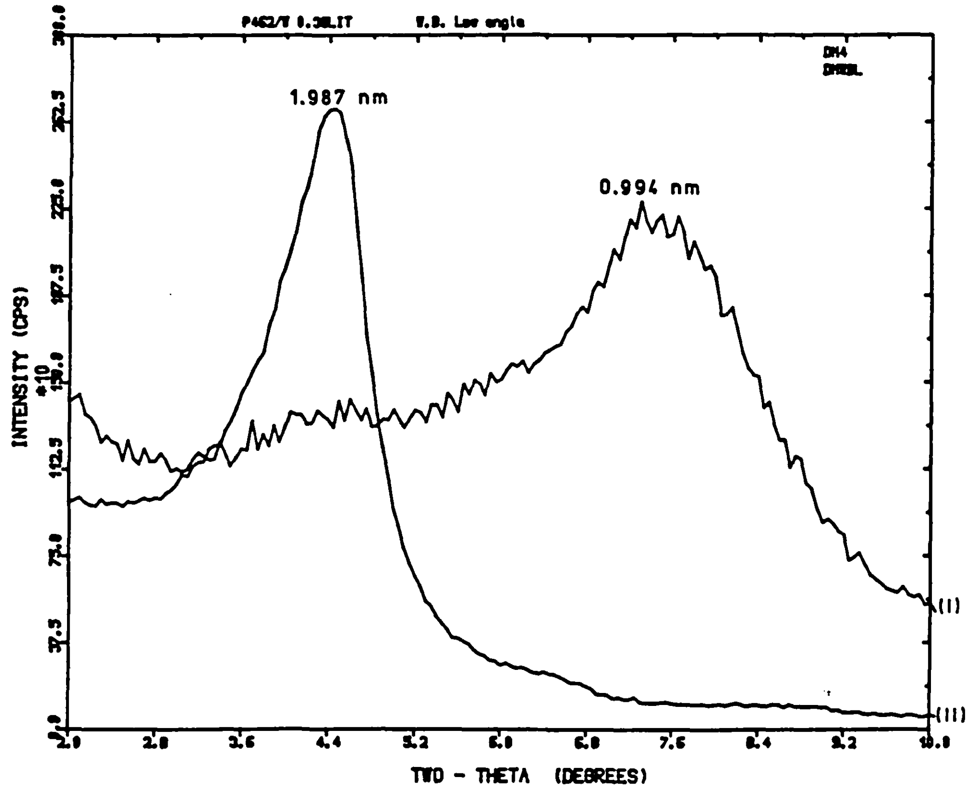


Figure 5.2: XRD Pattern of (I) Wyoming Bentonite and (II) Perchem 462 Exchanged Clay.

of the exchanged clay was greatly increased, to 1.987 nm in the presence of the QAS, compared to 0.994 nm for the unexchanged Wyoming bentonite. The interlamellar spacing of Perchem 462 was similar in size to that of BODDMAM, and the sharpness of the peak indicated little variation in the spacing of the silicate layers. When chloronaphthalene was adsorbed into Perchem 462 swelling occurred, and the interlamellar space increased to 2.506 nm (Figure 5.3). The swelling of exchanged clays in the presence of organic liquids has been well documented (Raussell-Colom & Serratosa, 1987).

Figure 5.4 shows the SEM micrographs of Wyoming bentonite and washed Perchem 462. Wyoming bentonite (Figure 5.4(I)) contains a mixture of flaky particles and fewer large smooth particles. The flaky particles appeared layered in structure and the EDS spectra showed that they contained the elements silicon, calcium and aluminium, hence indicating that they were mainly the clay particles. The EDS spectra of the larger particles contained a greater amount of silicon than the layered particles, and these were probably quartz impurities in the clay. The SEM micrograph of Perchem 462 (Figure 5.4(II)) was representative of the whole sample and showed small flaky particles with similar EDS spectra to those of the clay particles in Wyoming bentonite.

5.3.2 Effect of Organic Compounds on Cement Hydration

3-Chlorophenol and chloronaphthalene were mixed with cement paste in a range of concentrations and examined to determine the effect of these organic compounds on cement hydration, and to find which of the hydration products were most affected by their presence. For XRD analysis 3-chlorophenol and chloronaphthalene at "high" (0.1 mol) and "low" (0.02 mol) concentrations were mixed with OPC (50 g) and water (17.5 ml) and cured for 7 or 28 days. The "low" concentration was chosen because it corresponded to the concentration of 3-chlorophenol used in the leach tests (Section 4.2.3), the "high" concentration was five times the "low" concentration. For SEM

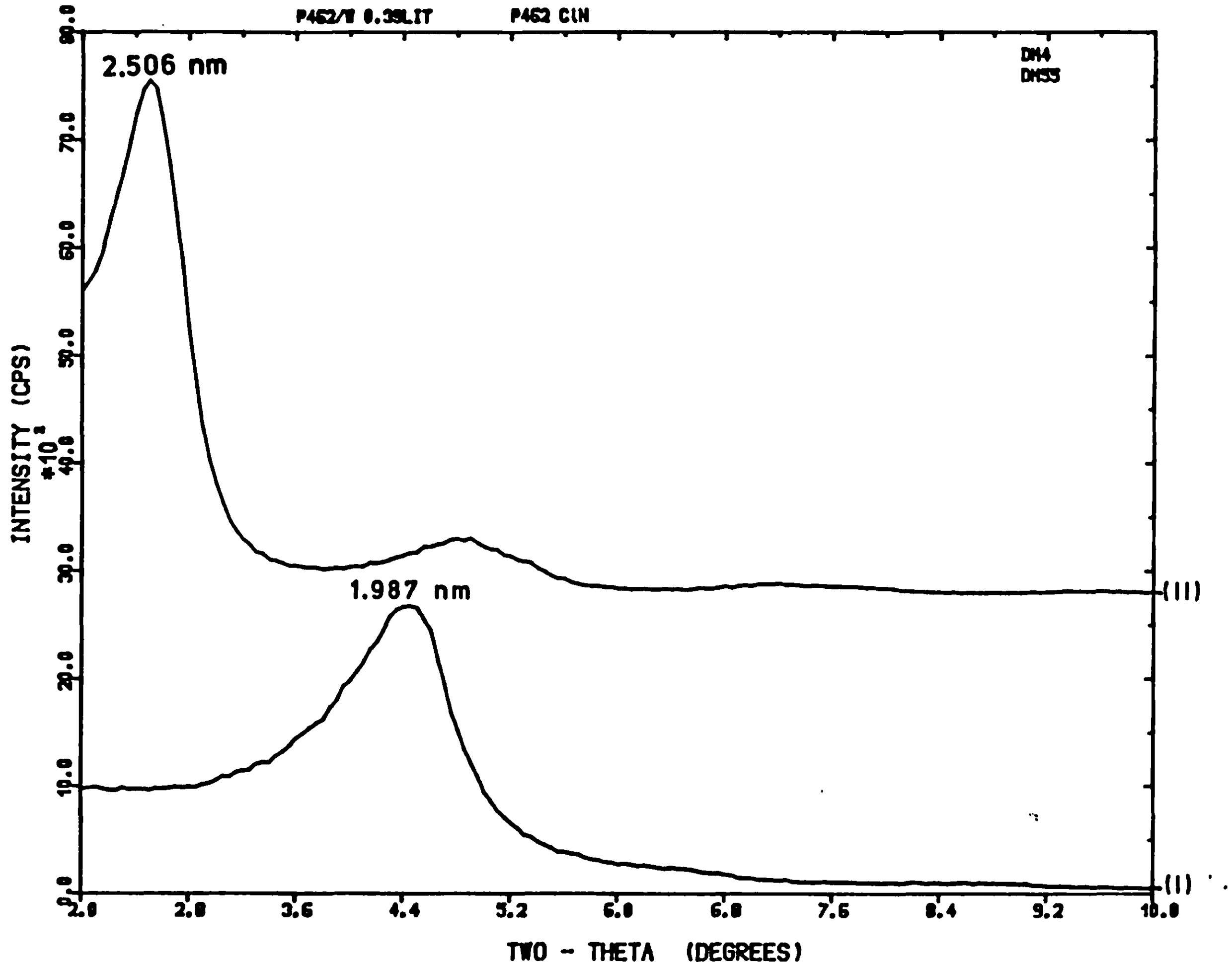


Figure 5.3: XRD Pattern of (I) Perchem 462 and (II) Perchem 462 with Adsorbed Chloronaphthalene.

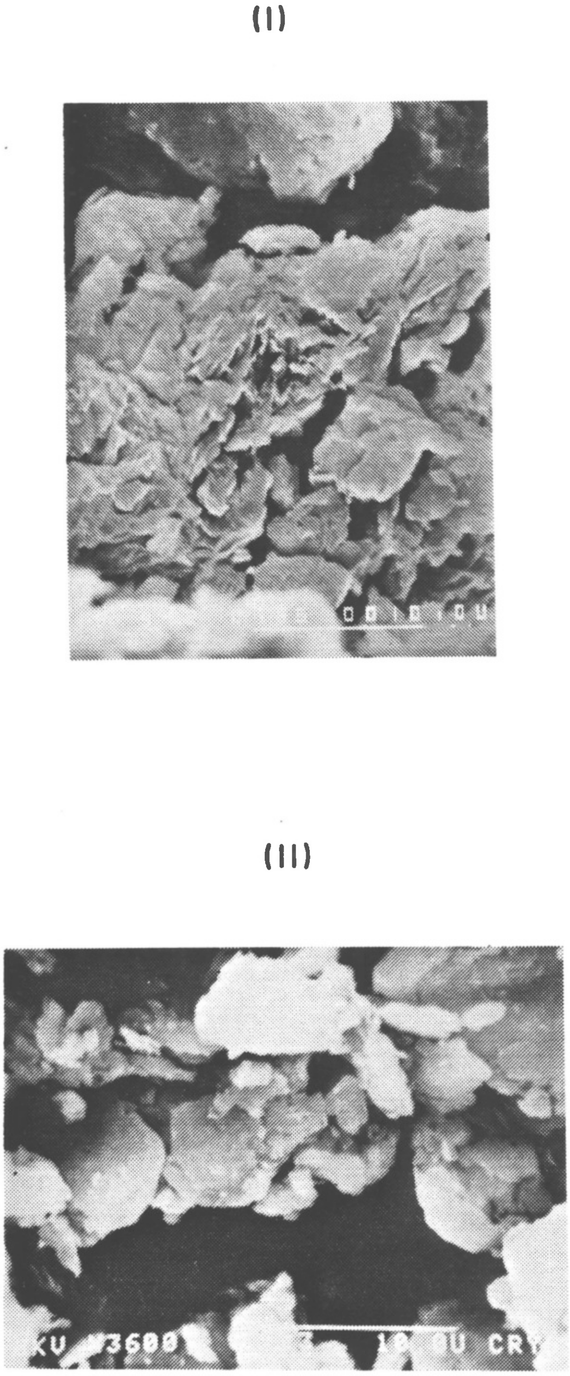


Figure 5.4: SEM of (I) Wyoming Bentonite and (II) Perchem 462 Exchanged Clay Showing the "Flaky" Clay Particles and Smooth Silica Impurities.

analysis a range of 3-chlorophenol concentrations from 0.001 M to 0.1 M were mixed with 50 g OPC and 17.5 ml water (w/c 0.35).

The XRD patterns of the 3-chlorophenol dosed samples were very different from the undosed cement sample, especially at the higher chlorophenol concentrations (Figure 5.5(I), 7 day old samples and 5.5(II), 28 day old samples). The spectra of the 3-chlorophenol dosed samples showed great increases in the C_3S and ettringite peaks compared to the undosed samples, and weak reflections not previously discernable became distinct peaks. C_3S was present in unhydrated cement, and as hydration continued was converted principally to C-S-H gel. Ettringite, a hydration product which forms in the early stages of hydration, slowly converts to monosulphate over the curing period. The heights of the C_3S peaks in the cement samples (Figure 5.5) were measured to give an indication of how far hydration had progressed compared to the unhydrated sample (Figure 5.6). Measurement of the progress of hydration is conventionally carried out by measuring the formation of CH, however in the XRD spectra obtained the CH peaks were too small to be measured. Calculation of the relative peak heights has been carried out and the results, expressed as the percentage of C_3S remaining compared to the unhydrated sample, are shown in Table 5.1

Table 5.1: Percentage of C_3S remaining in the sample after 7 and 28 days

Sample	Percentage of C_3S Remaining	
	7 Days Curing	28 Days Curing
OPC Only	53	50
OPC + Chlorophenol (Low)	68	41
OPC + Chlorophenol (High)	100	92

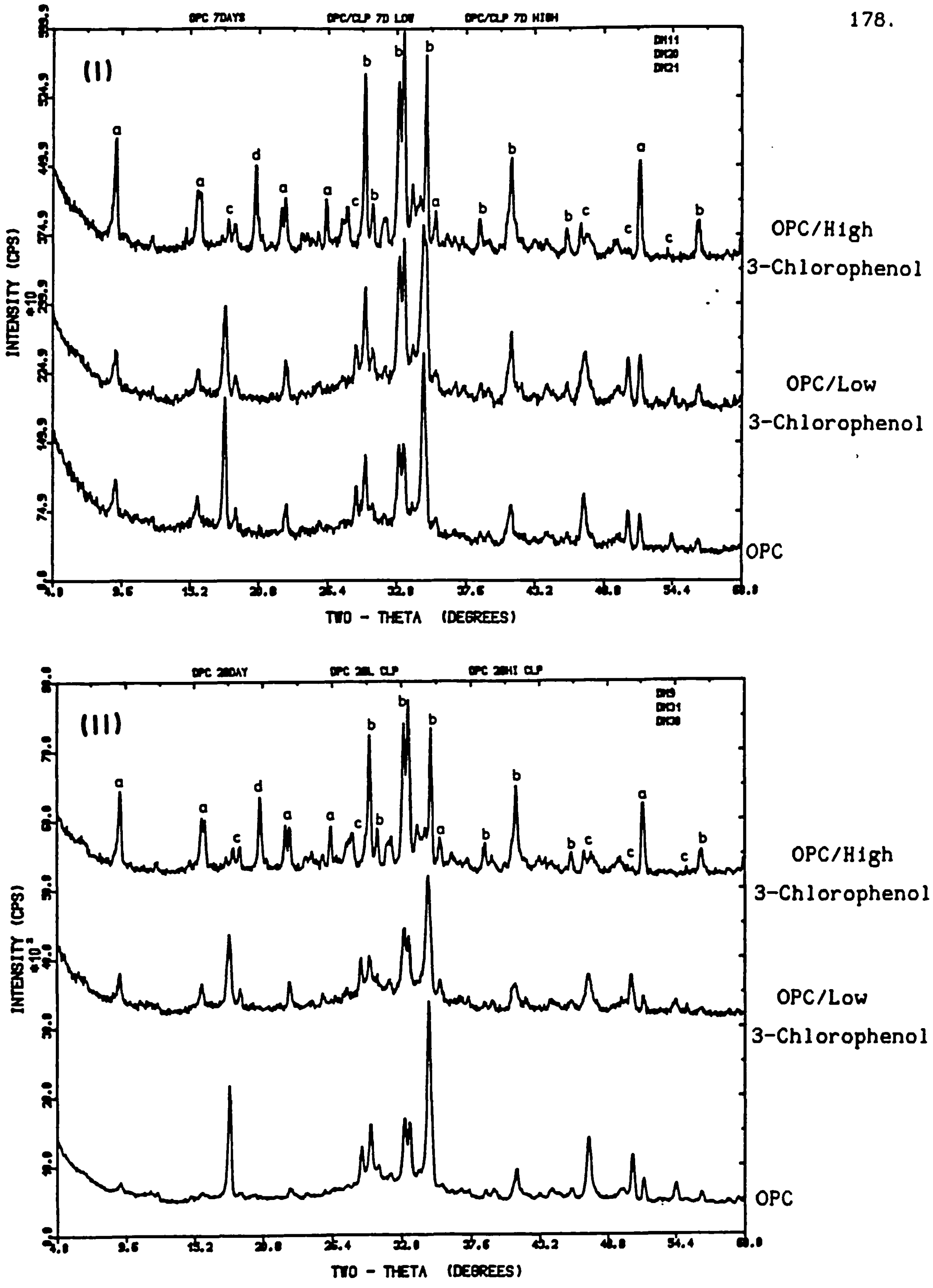


Figure 5.5: XRD Pattern to Show the Effect of 3-Chlorophenol on Cement Hydration after (I) 7 Days and (II) 28 Days of Curing.

a = Ettringite; b = Tricalcium Silicate (C_3S);

c = Calcium Hydroxide and d = 3-Chlorophenol

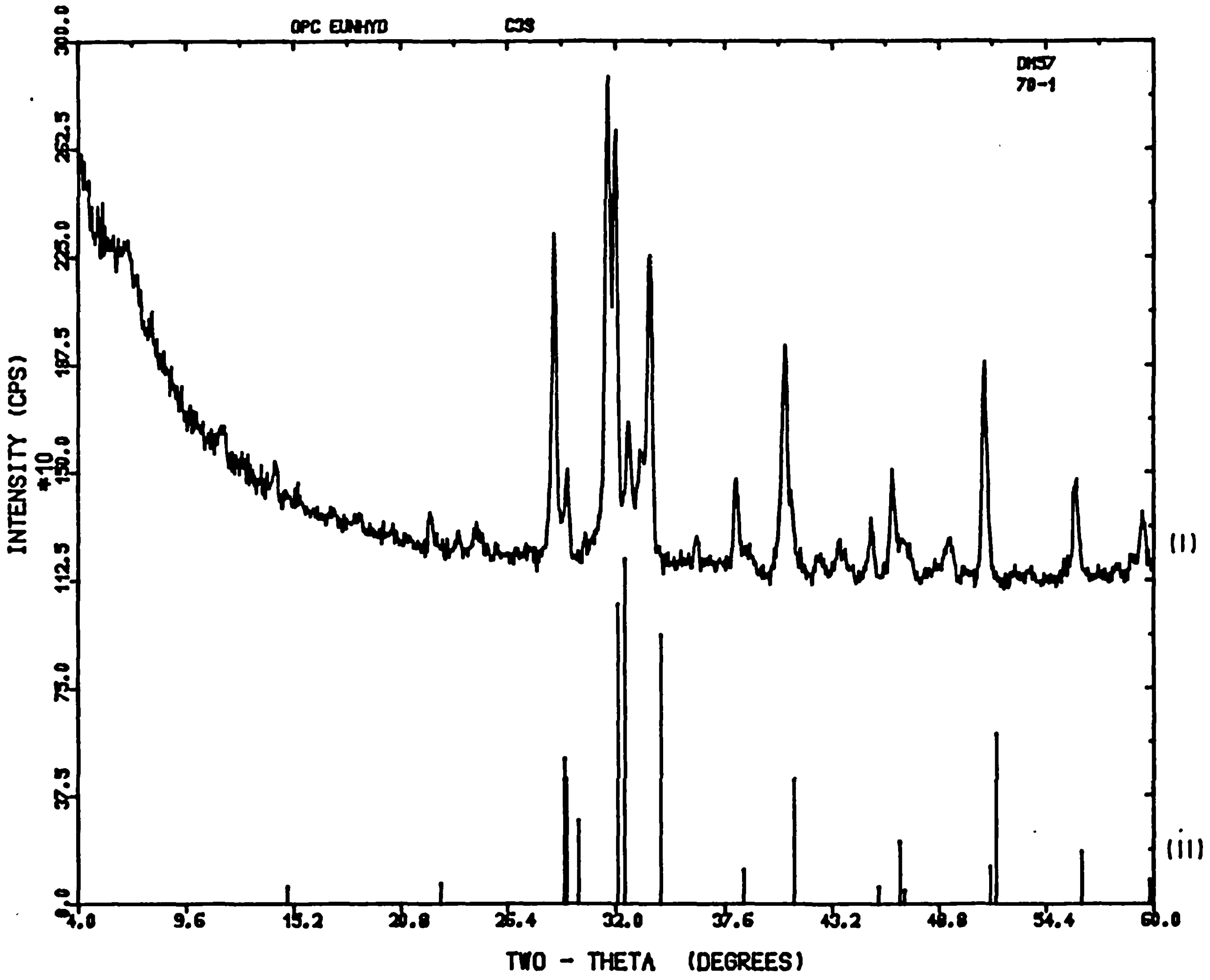


Figure 5.6: XRD Pattern of (I) Unhydrated Cement Showing
(II) Tricalcium Silicate Reflections.

Ettringite was present in the chlorophenol dosed samples in larger amounts than in the unhydrated samples. For the low dosed samples approximately 120% more ettringite was present at 7 days and 313% more at 28 days than in the OPC only samples. In the high dosed samples approximately 533% more ettringite was present at 7 days and 1433% at 28 days.

These results suggest that high concentrations of 3-chlorophenol inhibit the hydration of cement over the 28 day period as higher percentages of C_3S remain in the sample. This inhibiting effect was borne out by evidence of a decrease in the calcium hydroxide peaks in the chlorophenol dosed samples, calcium hydroxide being a final hydration product. At low chlorophenol concentrations the percentage of C_3S at 7 days was considerably higher than the undosed sample suggesting, once again, inhibition of hydration. After 28 days, however, the C_3S had been reduced to below the level in the undosed sample which suggested that the chlorophenol had either caused the hydration to be accelerated in the later stages or allowed hydration to proceed further towards completion by making the C_3S in the unhydrated cores of the cement particles available. The large amounts of ettringite present in the samples at 28 days not only suggest inhibition of hydration, but also the possibility of an interaction between the chlorophenol and ettringite which stabilised the ettringite and slowed, or stopped, its conversion to monosulphate.

The SEM micrographs of 7 day old cement paste, dosed with 3-chlorophenol, are shown in Figure 5.7(I). The micrographs show that as the concentration of 3-chlorophenol increased, the amorphous nature of the cement paste changed to a more crystalline form. The "rod-shaped" crystals present at the higher 3-chlorophenol concentration were shown, by EDS, to contain chlorine and calcium or a mixture of calcium, sulphur and aluminium. The crystals were mainly composed of the calcium salt of 3-chlorophenol or of ettringite. The 28 day old samples (Figure 5.7(II)) closely resembled the 7 day old samples, showing the same distinctive crystallinity at high 3-chlorophenol concentrations.

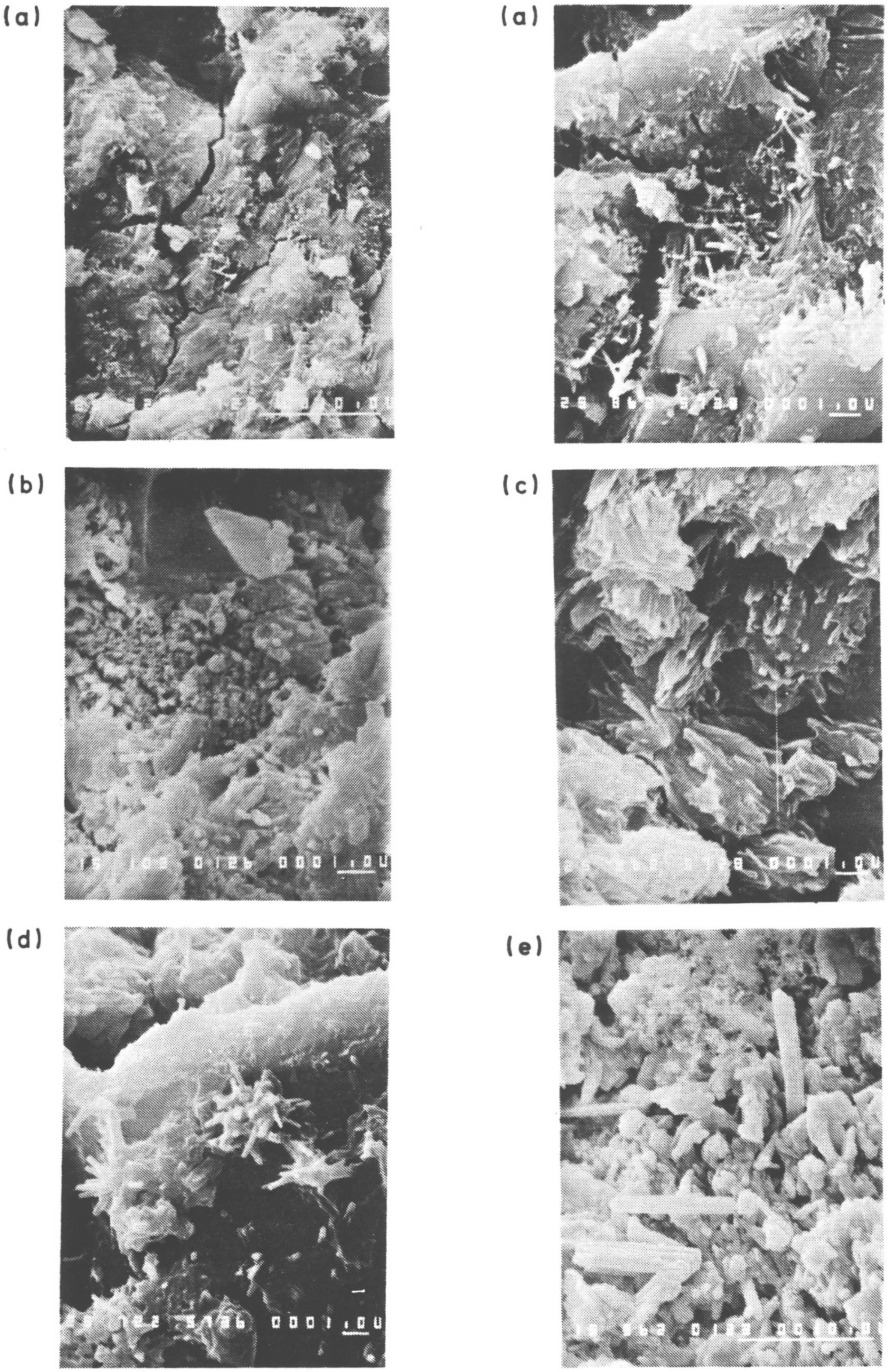


Figure 5.7(I): SEM of Cement Containing 3-Chlorophenol after 7 Days

a= 0.001 mol, b = 0.05 mol, c = 0.02 mol, d = 0.05 mol
and e = 0.1 mol.

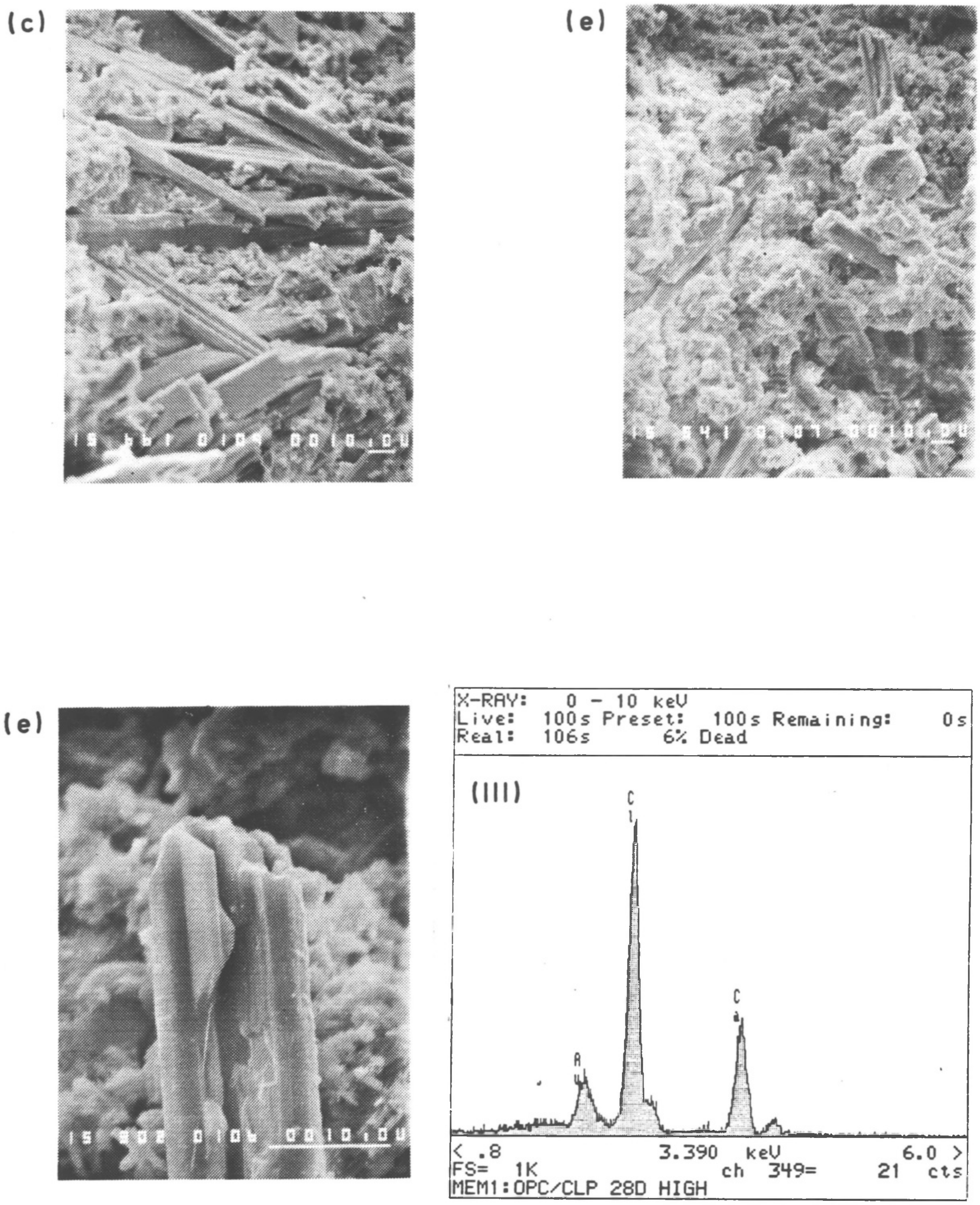


Figure 5.7(II): SEM of Cement Containing 3-Chlorophenol after 28 Days
(III) Shows the EDS Spectrum of (e)

c = 0.02 mol and e = 0.1 mol

The addition of chloronaphthalene to cement paste had little effect upon the microstructure of the cement. The XRD patterns showed that even at very high concentrations there was only a slight increase in the C_3S and ettringite peaks compared with the undosed samples (Figure 5.8). Similarly the SEM micrographs (Figure 5.9) showed that the cement had an amorphous structure characteristic of the undosed cement paste samples.

The major difference in the way 3-chlorophenol and chloronaphthalene affect the hydration of cement was due to the differences in miscibility of the two organic compounds with the cement paste and their different structures. 3-chlorophenol was well miscible with the cement paste even at the higher concentrations, whereas chloronaphthalene formed a layer on the surface of the specimen, so thatlittle of the chloronaphthalene would have been in contact with the cement itself. Structurally the organic compounds are different as 3-chlorophenol is a polar molecule containing a hydroxyl group which can be ionised to form the phenolate ion. Chloronaphthalene, on the other hand, is non-polar and so is hydrophobic in nature.

5.3.3 Effect of Cement on the Exchanged Clay

When the exchanged clay was mixed with cement there was a change in the XRD pattern of the clay at low angles (Figure 5.10). The cement/clay mix had a broader asymmetric peak which corresponded to an interlamellar spacing of 1.988 ± 0.014 nm, compared to the exchanged clay alone (1.987 ± 0.002 nm). The broadness of the peak indicates that either there was a great variation in the interlamellar spacings or that the clay particles had broken down into much smaller crystallites.

In the cement/clay mixes the clay particles could not be identified by SEM. To aid recognition of the clay in the cement matrix a small amount of clay paste (w/clay 1.0) was poorly mixed with cement paste

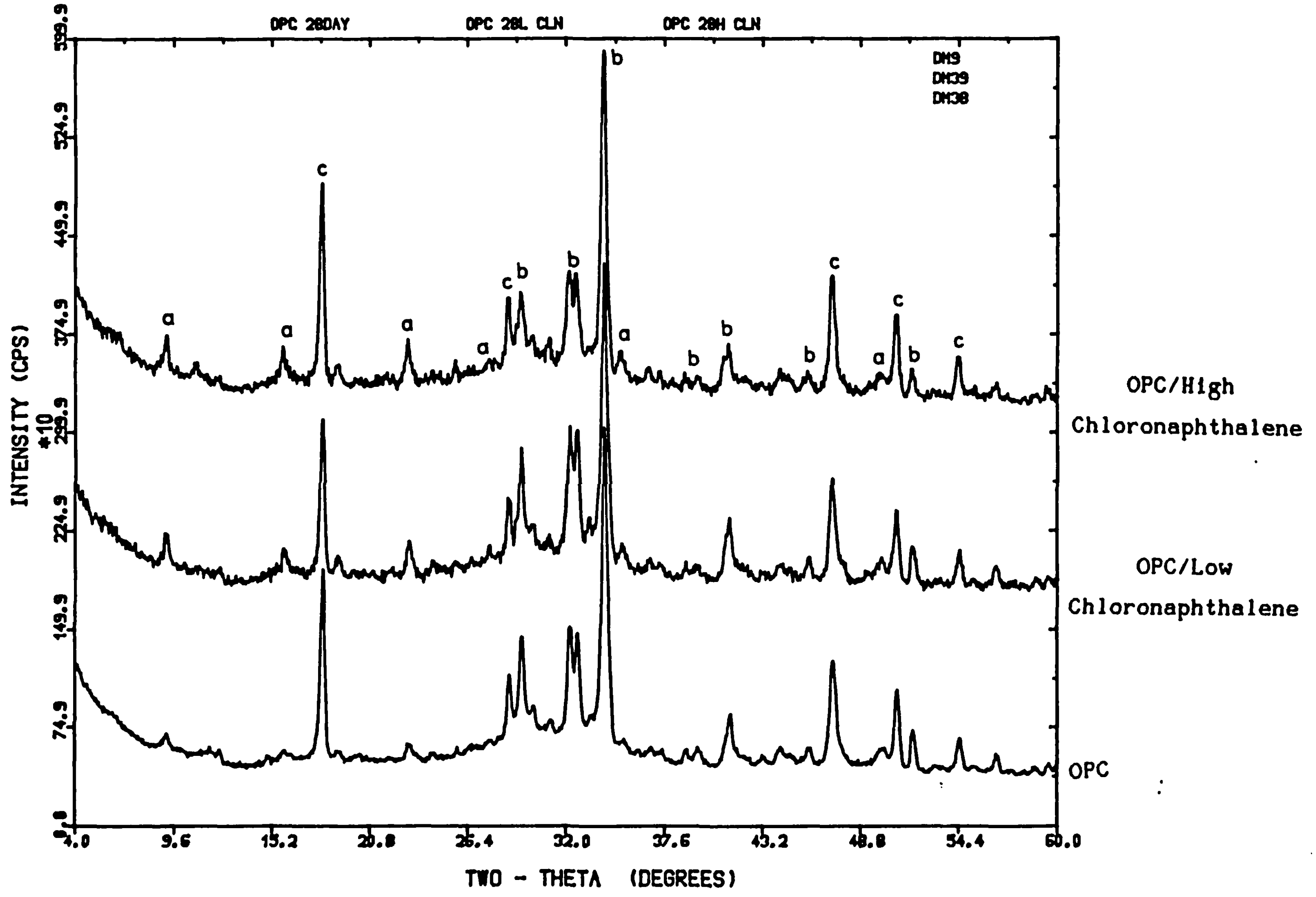


Figure 5.8: XRD Pattern of Cement Samples Containing Chloronaphthalene after 28 Days of Curing.
a = Ettringite; b = Tricalcium Silicate (C_3S); c = Calcium Hydroxide

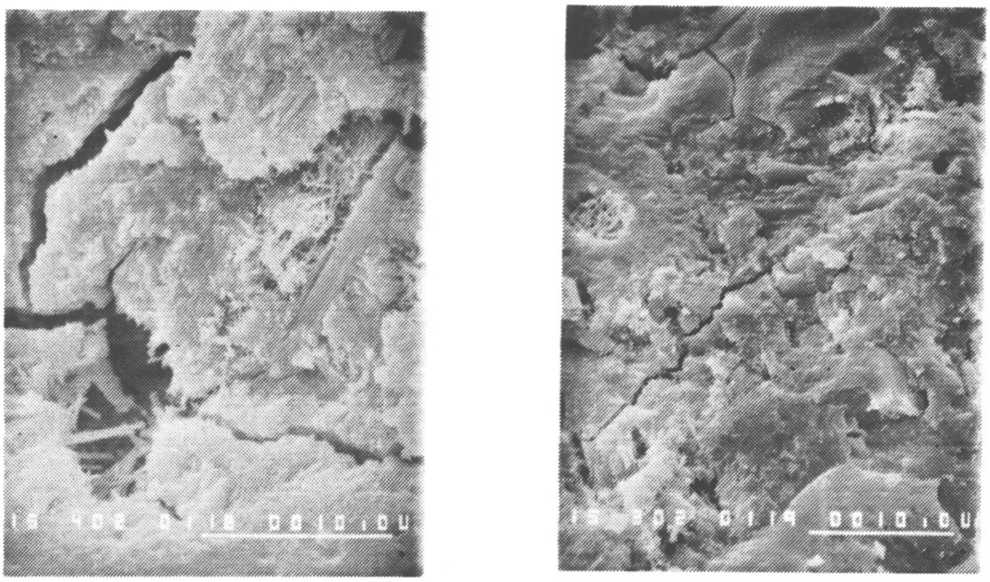


Figure 5.9: SEM of Cement Paste Containing a High Concentration of Chloronaphthalene, after 28 Days Curing.

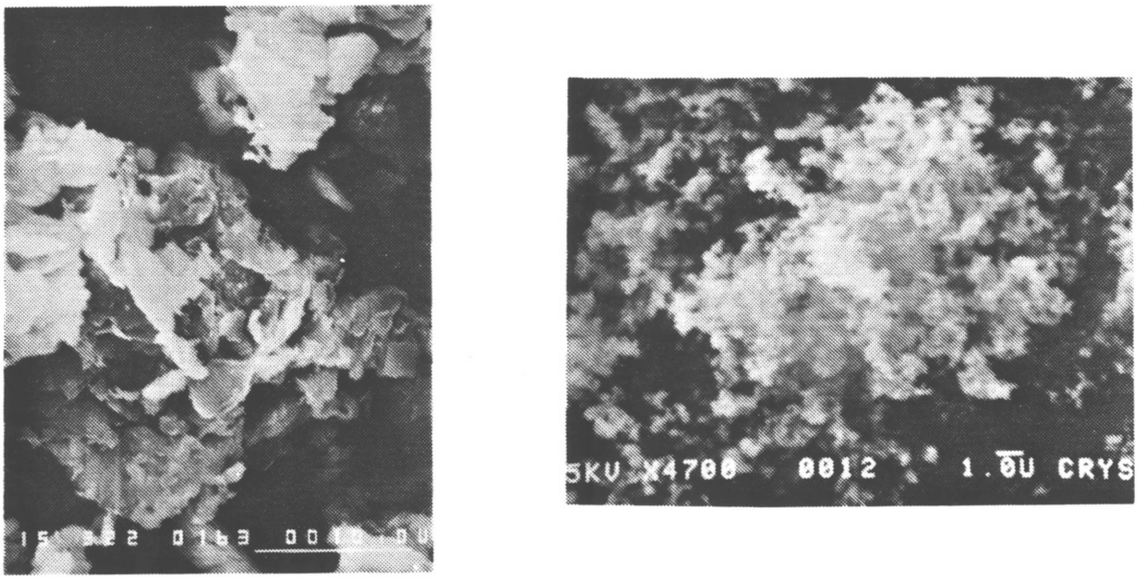


Figure 5.11: SEM of the Exchanged Clay in Contact with the Cement Paste.

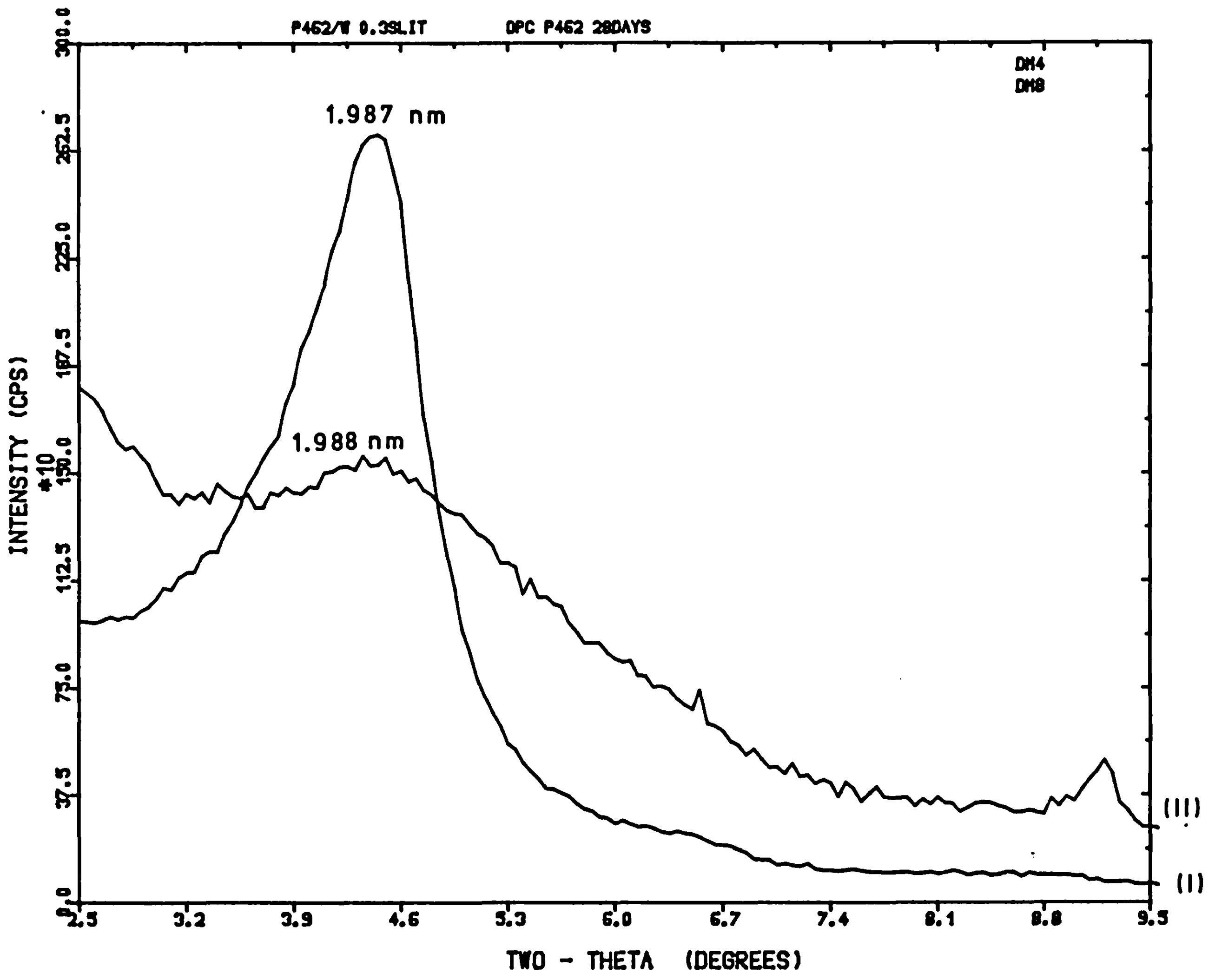


Figure 5.10: XRD pattern to Show the Effect of Incorporating Exchanged Clay into a Cement Matrix. (I) Perchem 462 only and (II) Perchem 462 in Cement Matrix.

(w/c 0.35). This gave a "marbled" solid in which the areas of clay could readily be identified. The SEM micrographs of the exchanged clay which had been in contact with cement paste showed that the clay, previously in the form of discrete particles approximately 10 µm across, had been broken down to form smaller flaky particles (Figure 5.11). The cause of the breakdown of the clay was thought to be the highly alkaline nature of the cement paste. To test whether this was the case the exchanged clay was treated with 0.1 M potassium hydroxide. The XRD patterns of the treated clay at five different ages are shown in Figure 5.12 and the SEM of the clays in Figure 5.13. The potassium hydroxide treatment produced clay which was similar to the untreated clay, but with a less sharp peak and a slightly higher interlamellar spacing than the untreated clay. Treatment of the exchanged clay with a saturated solution of calcium hydroxide had a similar effect upon the width and position of the peaks (Figure 5.14) in the XRD spectra. This was probably because although the calcium hydroxide, although only sparingly soluble in aqueous solution, forms a solution of approximately pH 12. Calcium hydroxide would be less soluble in a mixed solution such as a pore solution in cement paste.

5.3.4 Effect of the Exchanged Clay on Cement Hydration

The XRD pattern of pure cement paste as it cured from 7 to 28 days is shown in Figure 5.15. There were no major changes in the diffraction patterns over this period, all of the cement phases being present throughout the hydration period. There was, however, a steady decrease in the peaks which correspond to ettringite as the cement paste aged. Figure 5.16 shows the same curing time pattern for the Perchem 462/OPC samples. The ettringite peaks, unlike in the pure cement samples, were very weak or not visible at 7 days but grew steadily up to 28 days. The diffraction pattern of the exchanged clay alone is shown at the bottom of Figure 5.16. Figure 5.17(I) and (II) shows a direct comparison between the Perchem 462/OPC and cement-only samples after 7 and 28 days of curing respectively.

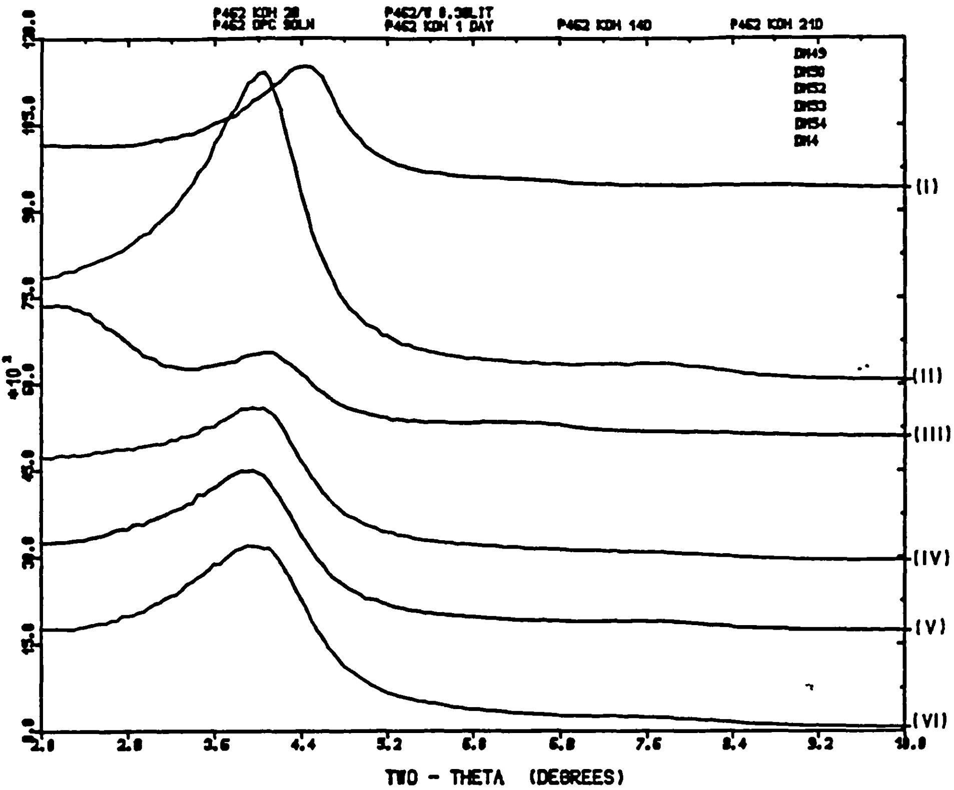


Figure 5.12: XRD pattern of Perchem 462 treated with 1.0 M potassium hydroxide for (I) 0 days, (II) 1 day, (III) 7 days, (IV) 14 days, (V) 21 days and (IV) 28 days.

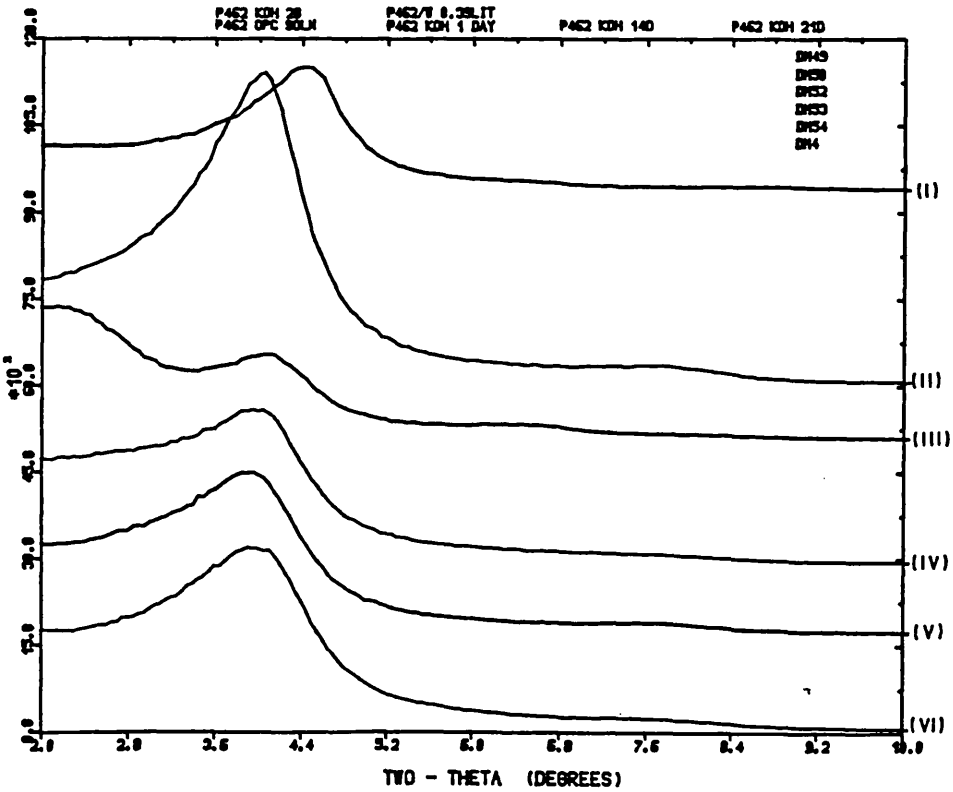


Figure 5.14: XRD Pattern of Perchem 462 Treated with Calcium Hydroxide for (I) 0 Days, (II) 7 Days, (III) 14 Days, (V) 21 Days and (V) Perchem 462 in the Cement Matrix for 7 Days.

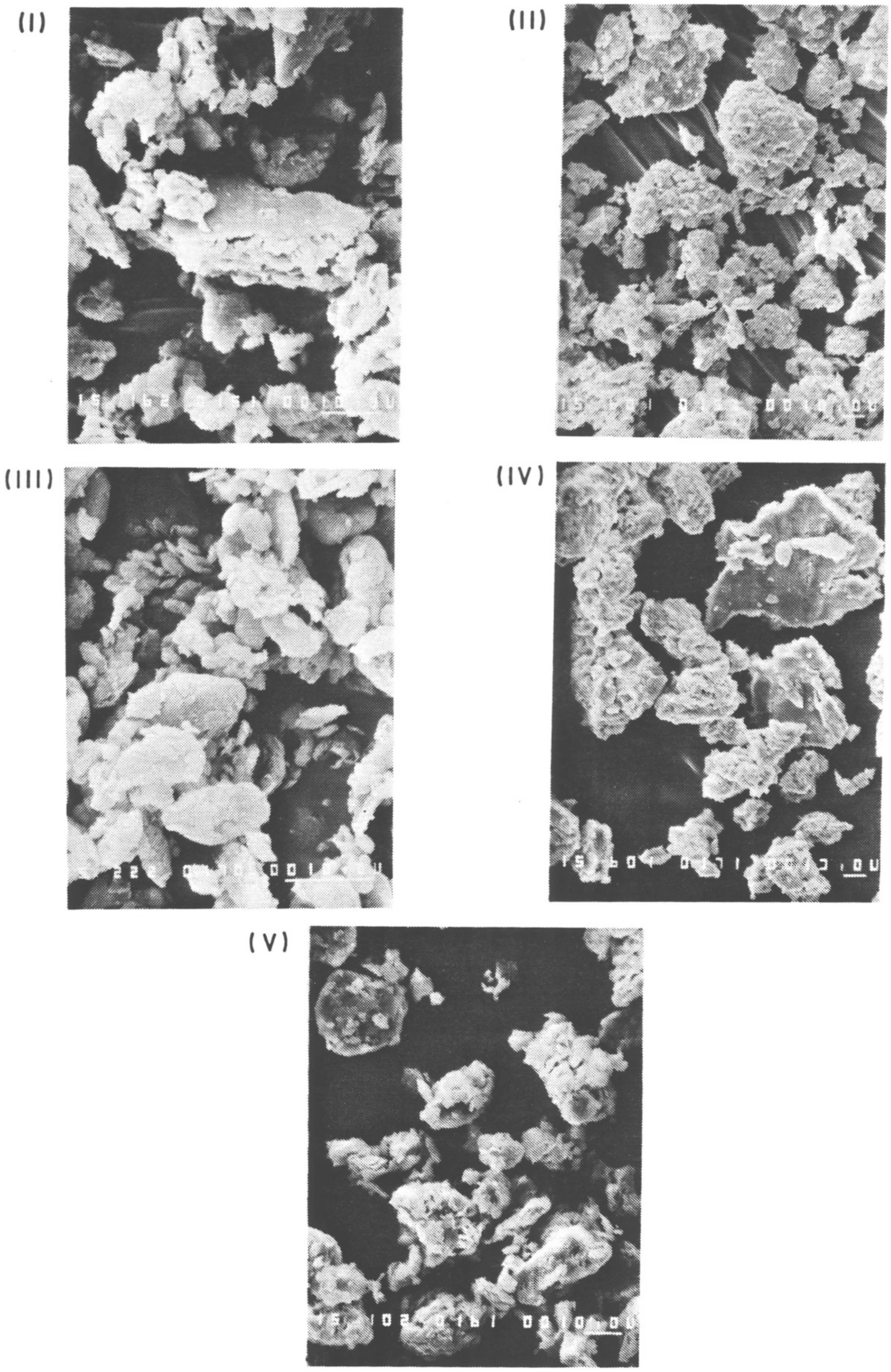


Figure 5.13: SEM Pattern of Perchem 462 Treated with 1.0 M Potassium Hydroxide for (I) 1 Day, (II) 7 Days, (III) 14 Days, (IV) 21 Days and (V) 28 Days.

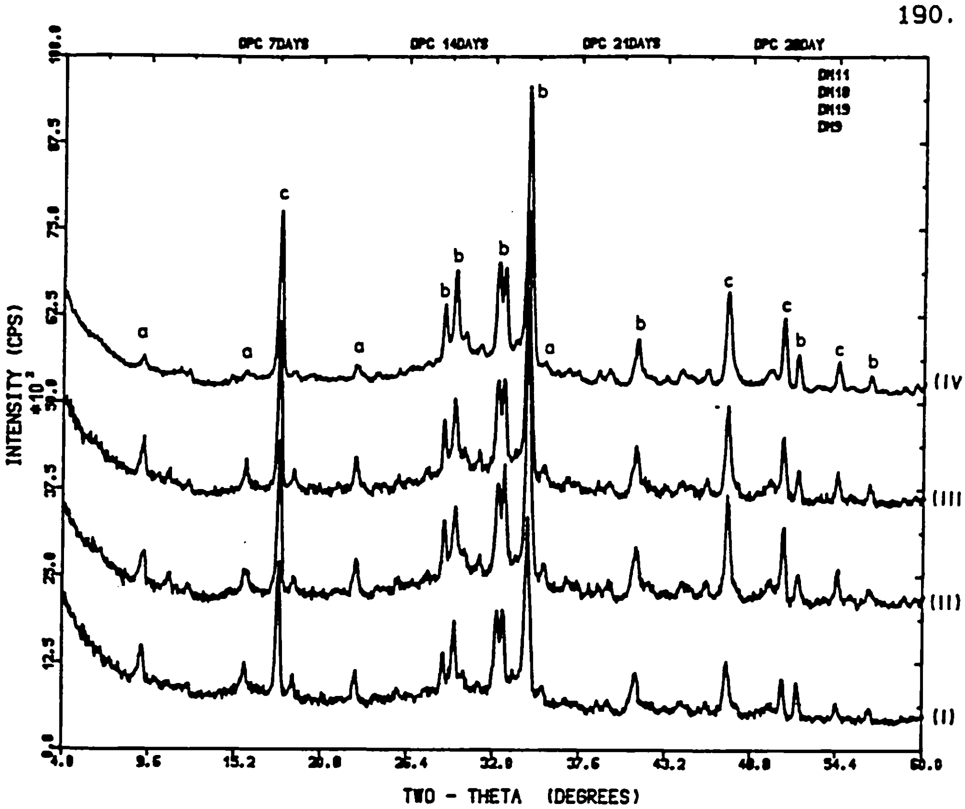


Figure 5.15: XRD Pattern of OPC Paste after Curing for (I) 7 Days, (II) 14 Days, (III) 21 Days and (IV) 28 Days.

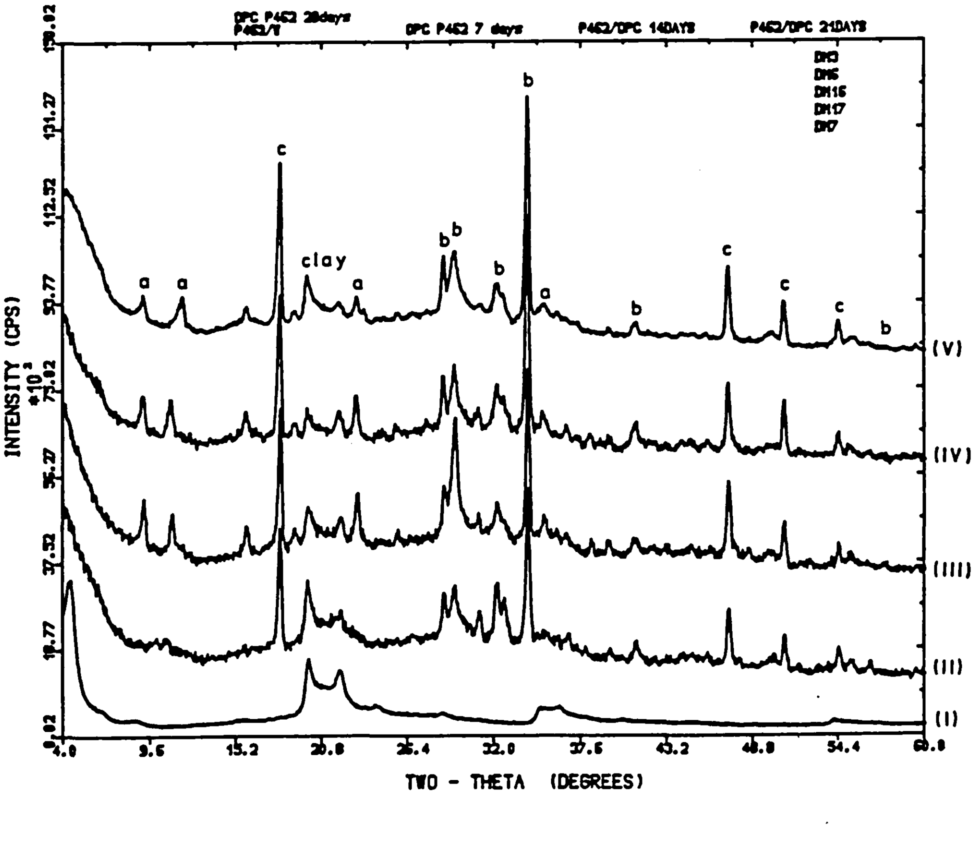


Figure 5.16: XRD Pattern of Perchem 462/OPC (I) Perchem 462, (II) 7 Days, (III) 14 Days, (IV) 21 Days and (V) 28 Days of Curing.

a = Ettringite; b = Tricalcium Silicate (C_3S);
c = Calcium Hydroxide and d = 3-Chlorophenol

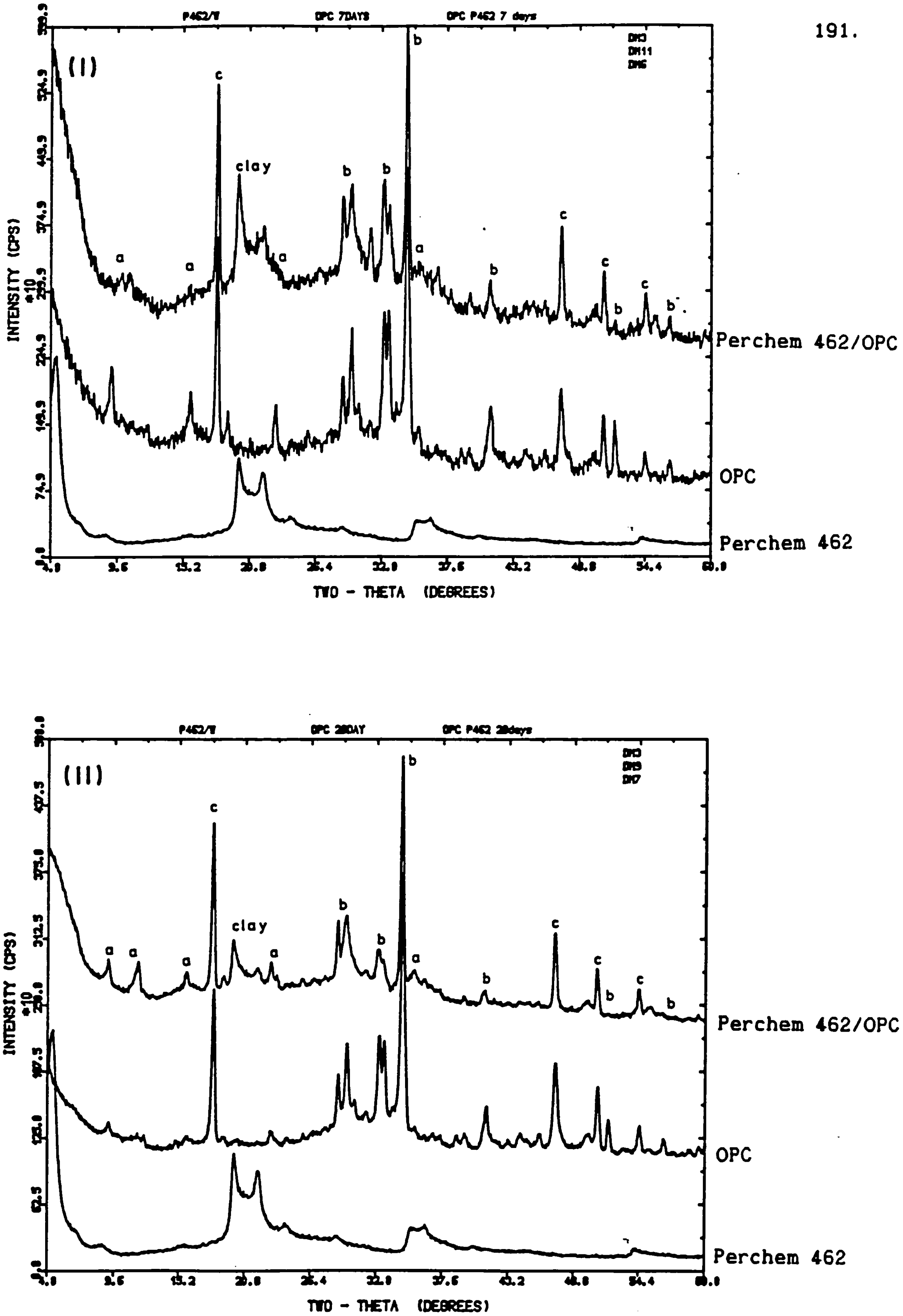


Figure 5.17: XRD Pattern to Compare Perchem 462, OPC and Perchem 462/ OPC after (I) 7 Days and (II) 28 Days of Curing.

a = Ettringite; b = Tricalcium Silicate (C_3S);
c = Calcium Hydroxide and d = 3-Chlorophenol

After 7 days the cement-only samples showed peaks, absent in the Perchem 462/OPC sample, which corresponded to the ettringite diffraction pattern. After 28 days the Perchem 462/OPC sample had developed the ettringite pattern. In the cement-only samples the ettringite peaks had greatly reduced intensities at 28 days, and was consistent with conventional cement paste curing. Table 5.2 shows the percentages of ettringite present in the Perchem 462/OPC samples expressed as a percentage of that in the OPC paste at the same age. The table shows that after 7 days of curing there was much less ettringite in the clay samples than in the OPC paste, however by 14 days there was 119% more ettringite present in the Perchem 462/OPC samples. The presence of C_3S in both sets of samples remained relatively constant over the 28 day period (Table 5.2), but in the Perchem 462/OPC samples almost 90% of the C_3S originally present in the unhydrated samples remains.

Table 5.2: Percentage of Ettringite and C_3S in OPC and Perchem 462/OPC samples.

	Percentage of Ettringite			
	7 Days	14 Days	21 Days	28 Days
Perchem 462/OPC	3	119	104	144
	Percentage of C_3S Remaining			
OPC Only	53	48	47	48
Perchem 462/OPC	89	86	92	88

The above effects suggest that the presence of the exchanged clay retards the cement hydration process, since the 28 day old OPC/Perchem 462 sample more closely resembled the 7 day old cement-only sample than a sample of comparable age. To test whether the effects on the cement hydration were due to the clay alone or were a consequence of the presence of the QAS in the exchanged clay, the XRD pattern of Wyoming bentonite mixed with cement was determined (Figure 5.18). This spectrum had a very similar pattern to the OPC/Perchem 462 sample of the same age, showing that the QAS had no significant effect on the cement hydration reactions.

The SEM micrographs of cement at 7, 14, 21 and 28 days are shown in Figure 5.19. Figure 5.19(I) showns the cement paste after 7 days of curing. The growth of the hydration products typical of the middle and late hydration periods, such as calcium hydroxide and calcium silicate hydrate, can be seen as well as the unhydrated core. As hydration continued, a gradual decrease in the unhydrated cement can be seen at 14 and 21 days respectively (Figures 5.19(II) and 5.19(III)). The 28 day old sample (Figure 5.19(VI)) showed the typical morphology of mature cement paste, e.g. featureless Type III calcium silicate hydrate and a few calcium hydroxide crystals. SEM of the OPC/Perchem 462 samples showed a strikingly different appearance to the cement-only samples. The micrographs after 7, 14, 21 and 28 days (Figure 5.20) showed that the whole cement surface was covered with short "needle-like" crystals interspersed with larger thicker "rod-like" crystals. Isolated areas of the samples contained groups of hexagonal crystals or platelets. The Wyoming bentonite/OPC samples (Figure 5.21) show the same prevalance of "needle-like" crystals and hexagonal plates. Analysis of the larger crystals by EDS indicated that they were mainly ettringite, while the hexagonal plates were monosulphate. Analysis of the smaller crystals could not be carried out because of beam penetration problems. The small crystals should have been identifiable from the XRD spectra, but the spectra indicated only an increase in ettringite compared to the cement-only samples. The crystals are probably calcium silicate hydrate, ettringite or the exchanged clay.

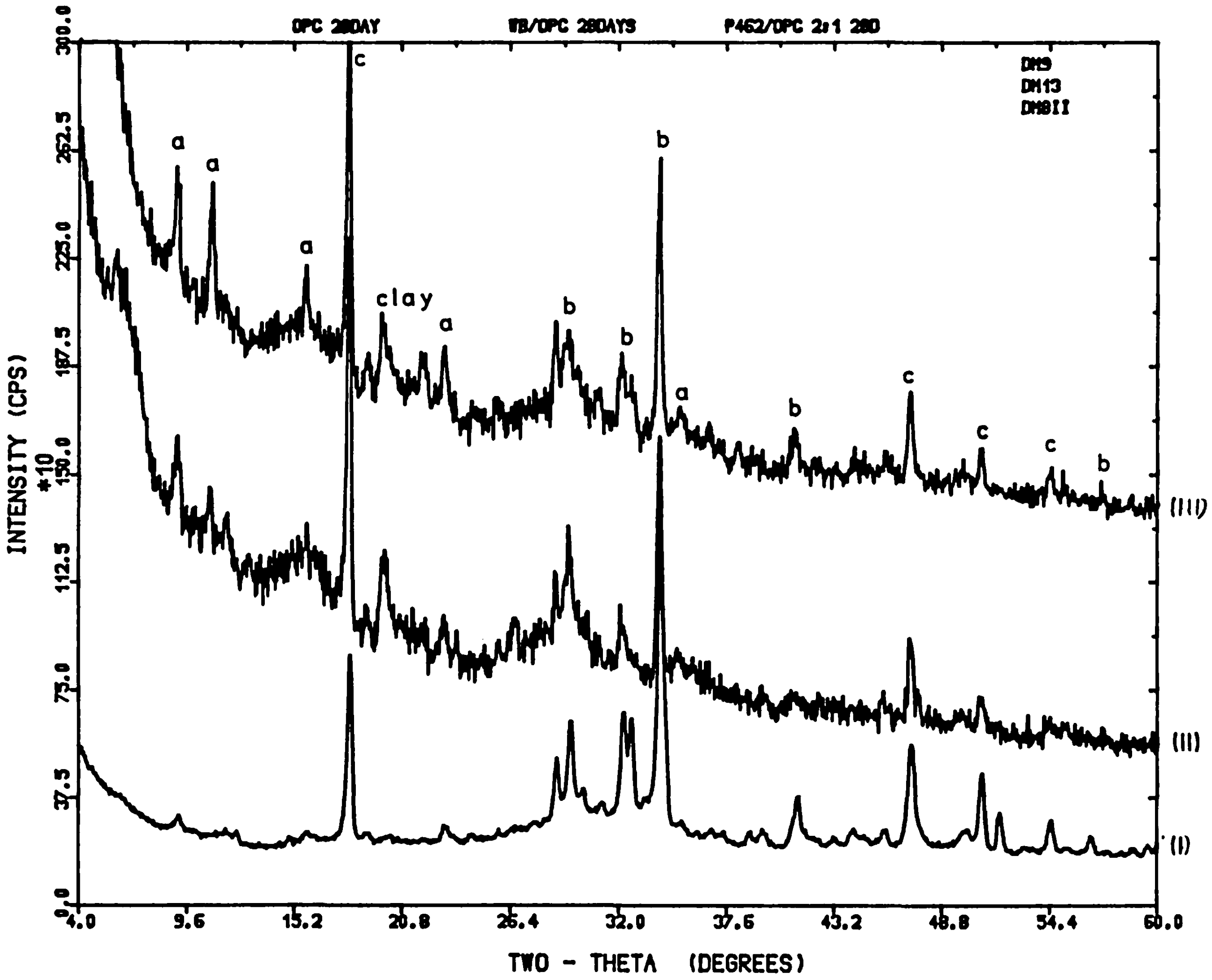


Figure 5.18: XRD Pattern to Compare (I) OPC, (II) Perchem 462/OPC with (III) Wyoming Bentonite after 28 Days of Curing.

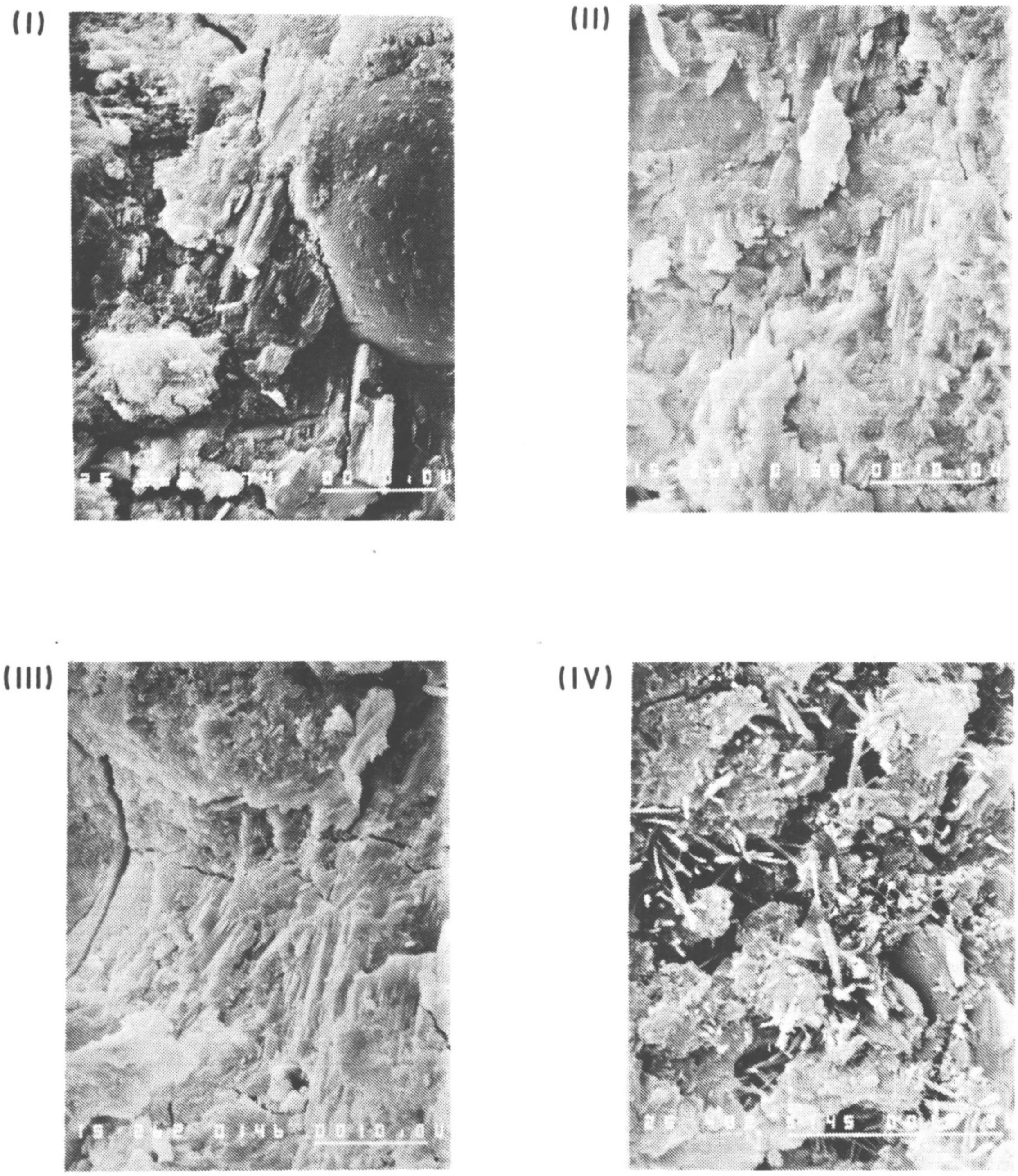


Figure 5.19: SEM Pattern of Cement Paste (I) 7 Days, (II) 14 Days, (III) 21 Days and (IV) 28 Days of Curing.

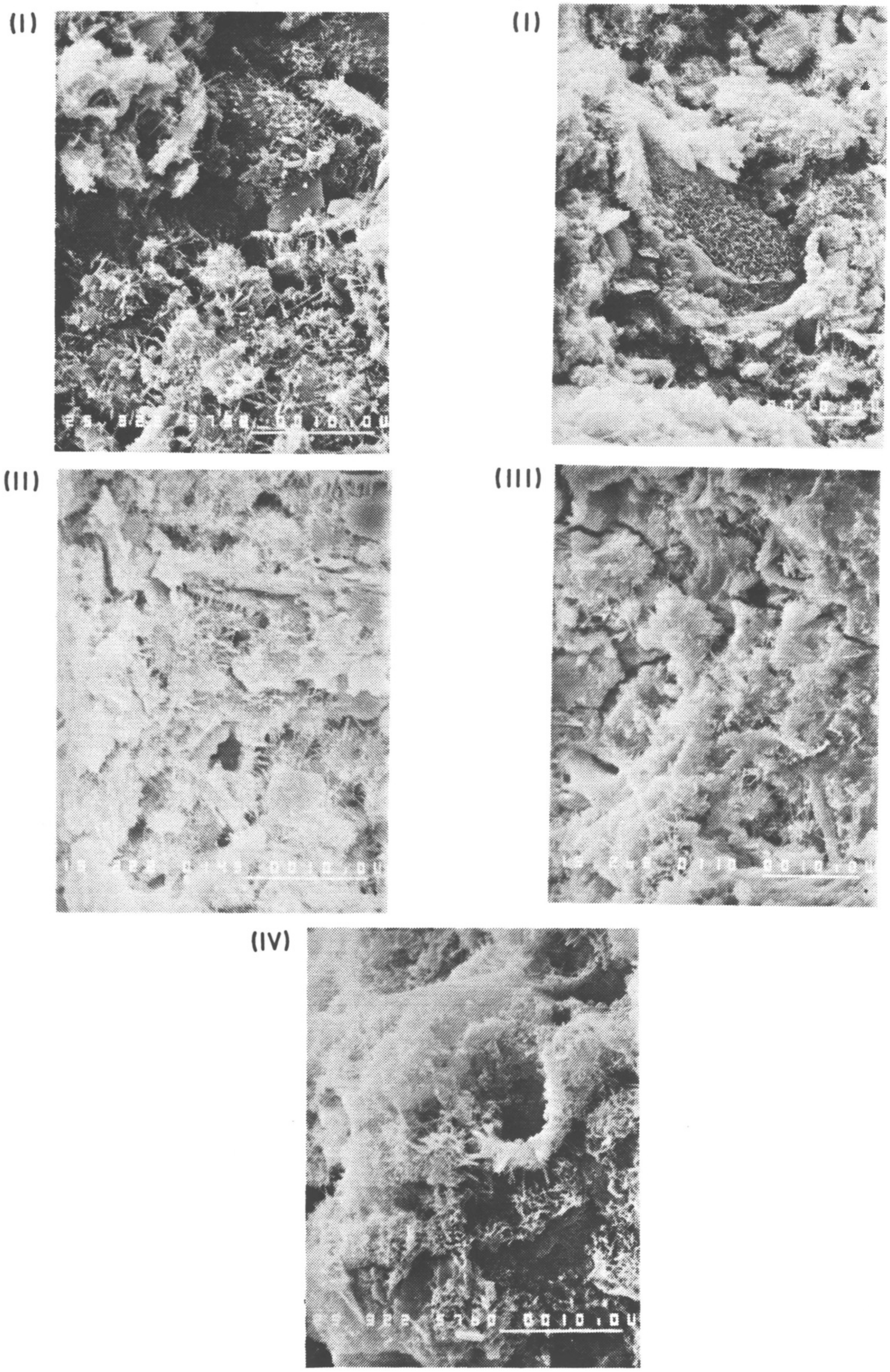
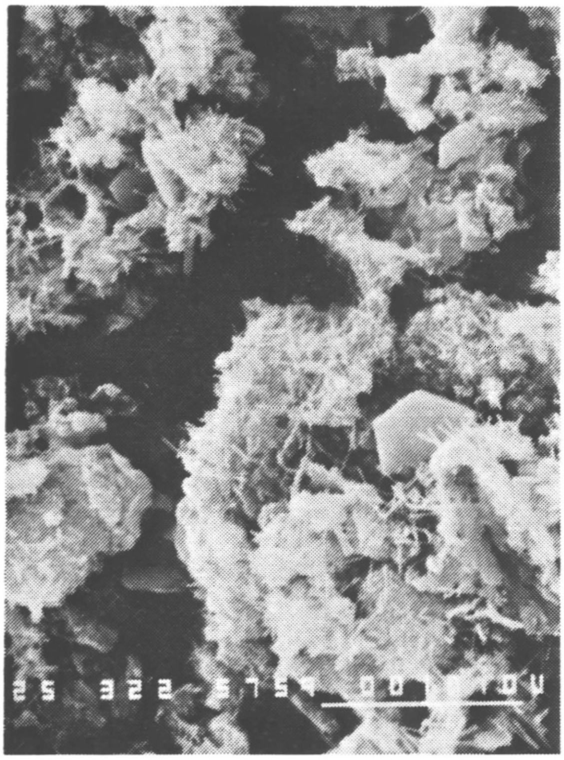


Figure 5.20: SEM of Perchem 462/OPC after (I) 7 Days, (II) 14 Days, (III) 21 Days and (IV) 28 Days of Curing.

(I)



(II)

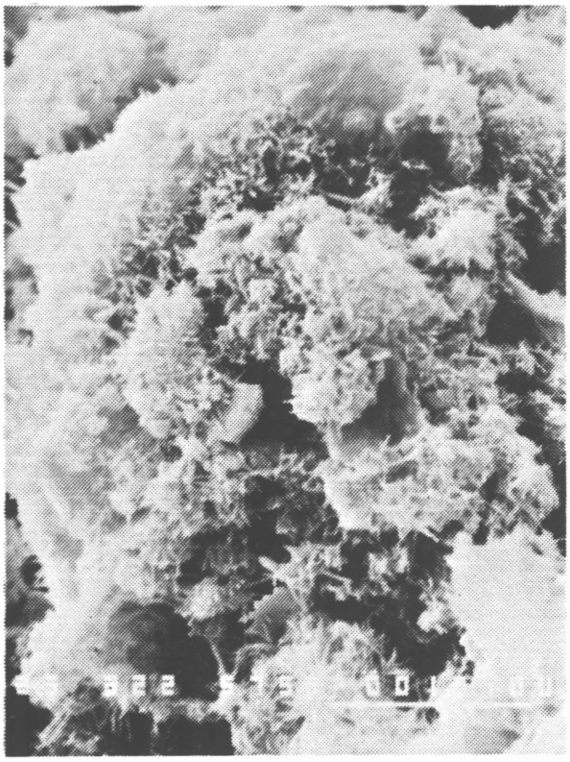


Figure 5.21: SEM of Wyoming Bentonite/OPC after (I) 7 Days and (II) 28 Days of Curing.

5.3.5 Stabilisation/Solidification of 3-Chlorophenol and Chloronaphthalene

The XRD spectra of 3-chlorophenol at low and high concentrations solidified in a Perchem 462/OPC mix at 7 and 28 days are shown in Figure 5.22. The exchanged clay containing adsorbed 3-chlorophenol at low concentrations had no effect upon the XRD spectra at 7 or 28 days compared with the Perchem 462/OPC samples. This suggests that 3-chlorophenol was adsorbed into the clay and did not come into contact with the cement during hydration, otherwise a similar effect would have been noted to the effect of 3-chlorophenol on OPC (Figure 5.6). At very high 3-chlorophenol concentrations, well in excess of the capacity of the exchanged clay, the 3-chlorophenol inhibited cement hydration in the same way as the high 3-chlorophenol/OPC mix (Figure 5.6).

Solidification of chloronaphthalene with exchanged clay and cement produced a solid sample with no immiscible layer of chloronaphthalene on the surface even at the high concentrations. The XRD spectra of the solidified chloronaphthalene at the two concentrations are shown in Figure 5.23. All three spectra were very similar, indicating that the chloronaphthalene had no effect on cement hydration, even when it was present in excess of the known exchange capacity of the clay.

5.4 SUMMARY

Using XRD analysis, the change in interlamellar spacing of the montmorillonite clay was observed upon the introduction of the QAS. Further swelling was caused by the introduction of chloronaphthalene but not by chlorophenol.

Chlorophenol retards the hydration of cement paste and stabilises the ettringite phase, slowing its conversion to monosulphate. Chlorophenol was found to crystallise in the cement

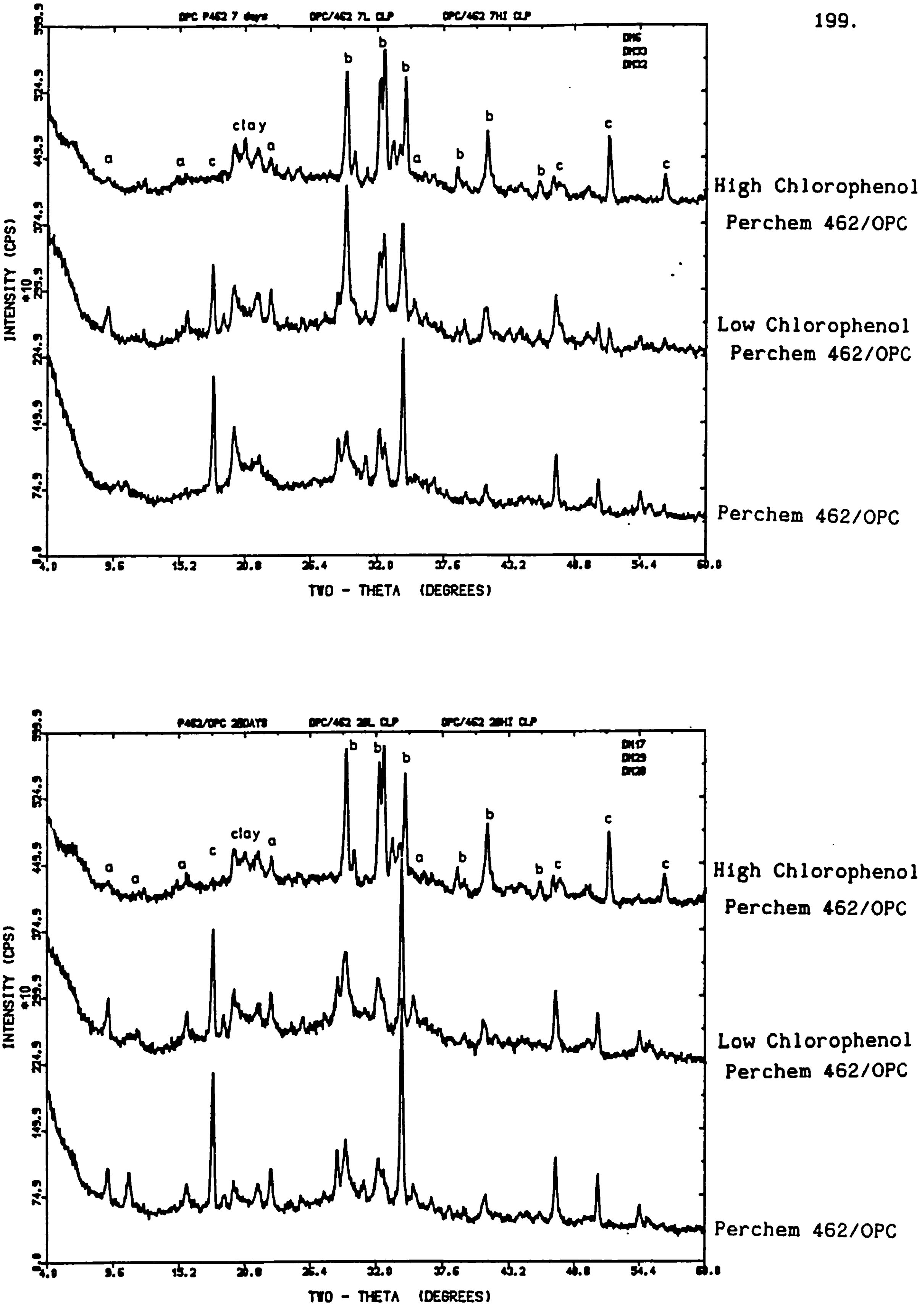


Figure 5.22: XRD Pattern to Show the Effect of 3-Chlorophenol Adsorbed onto Perchem 462, or Cement after (I) 7 Days and (II) 28 Days of Curing.

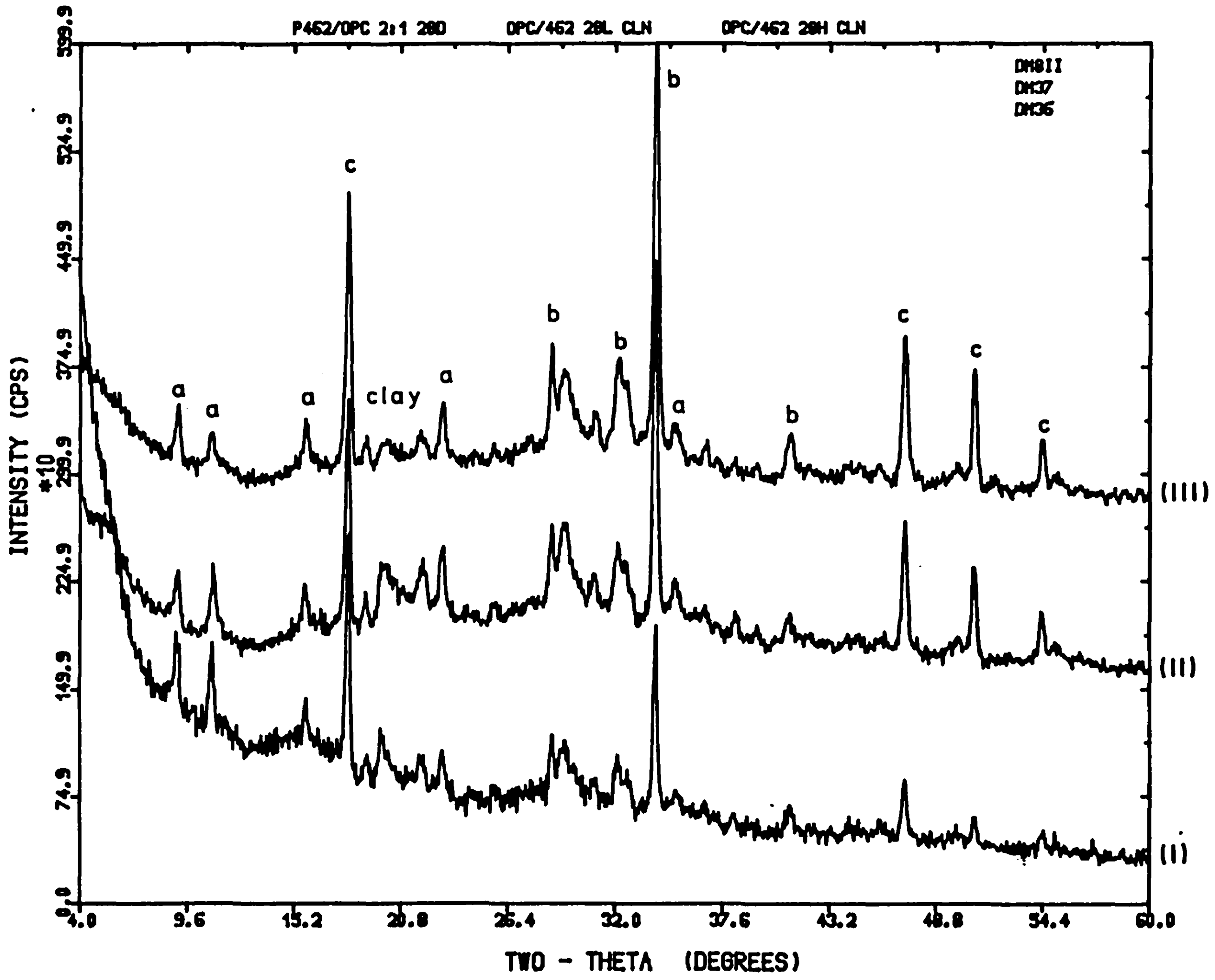


Figure 5.23: XRD Pattern to show the Effect of Chloronaphthalene, Adsorbed onto Perchem 462, after 28 Days Curing. (I) Perchem 462/OPC only, (II) plus Low Concentration Chloronaphthalene and (III) Plus High Concentration Chloronaphthalene.

paste as its calcium salt. Chloronaphthalene was immiscible with the inorganic cement matrix and had no effect on hydration.

The introduction of the exchanged clay into the cement matrix slowed the formation of the ettringite and increased its stability. Small crystals were observed by SEM covering the cement surface, these were either caused by the clay or were ettringite. The high alkalinity of the cement caused peptization of the clay, but did not interfere with the adsorbed quaternary ammonium cations.

Chlorophenol solidified with an exchanged clay/cement mix showed that up to the adsorption capacity of the exchanged clay the chlorophenol had no effect upon cement hydration. Above the adsorption capacity, the excess chlorophenol inhibited hydration.

Chloronaphthalene, which was immiscible with cement paste, could be incorporated into the exchanged clay/cement mix. The chloronaphthalene had no effect upon cement hydration.

6. SOLIDIFICATION OF INDUSTRIAL WASTES

6.1 INTRODUCTION

The work described in preceding chapters has studied the adsorption and solidification of organic "model" solutions that contained only the compounds under investigation. It was now thought to be important to study the use of the exchanged clays for the adsorption of real industrial organic contaminated wastes, and to use a cement-based solidification process similar to the processes used commercially to treat the waste.

Three industrial wastes were studied, which could not be solidified by conventional cement-based processes because the organic content of the wastes would inhibit cement hydration and would be rapidly leached from the matrix. The adsorption of the metals and organics by the exchanged clay, the physical characteristics of the samples and the chemical stability of the wastes in the solidified mixes were investigated.

6.2 MATERIALS AND METHODS

6.2.1 Materials

(a) Waste

Three liquid industrial wastes were chosen for use in this study. Two of the wastes came from single chemical processes and one, Waste C, was a mixture of effluents from a number of original sources. The wastes contained up to 12% by weight organic compounds with traces of heavy metals and inorganic anions. The main characteristics of the wastes are shown in Table 6.1.

Table 6.1: Properties of Industrial Wastes

	Waste A	Waste B	Waste C
Origin	Process effluent from diazotization process	Process effluent from glycid ether production	Mixed inorganic/ organic effluent
Appearence/ Comments	Thermally unstable organic liquid. Decomposes over 7 days giving off BF_3 and sulphates precipitate.	Brown/red sludge containing chlorinated solvents.	Oily black sludge containing solvents, amines and latex products.
pH	0.15	9.91	7.64
TOC (mg/l)	18060 13227*	37140	123,200
Inorganic Carbon(mg/l)	0	81	68
Zinc(mg/l)	43.6	48.3	216
Copper(mg/l)	6.8	24.3	8
Nickel(mg/l)	13.2	15.4	<0.2
Cadmium(mg/l)	<0.05	2.0	<0.05
Lead(mg/l)	<0.5	<0.5	<0.5

*After 7 days

(b) Solidification Materials

The work utilised the commercially available exchanged clay, Perchem 462, for solidification where the quantities required made laboratory production of the exchanged clay both time consuming and uneconomic.

The other materials used for solidification were Type 1 ordinary Portland cement (Blue Circle, UK) and "GPR" grade calcium carbonate, mesh size <200 µm (BDH Ltd., UK). The role of the calcium carbonate in the solidification mix was to act as an aggregate to decrease the amount of OPC needed to produce a bulk mix, similar to the role of sand in mortar, thus making the process more commercially realistic.

6.2.2 Adsorption Experiments

Adsorption isotherms for the organic and metal components of the wastes were determined to find the maximum concentration of each waste that could be adsorbed onto the exchanged clay. The exchanged clay was first washed by mixing 200 g with 2 l of distilled water for 24 hours. This was done to remove any excess QAS arising from the manufacturing process from the surface of the clay. After this period the clay was allowed to settle, the supernatant and any surface foam removed and the suspension filtered under vacuum through a Whatman No. 1 filter paper. The filter cake recovered was dried (105°C/12 h) and then ground to <0.5 mm. Any loss of the QAS from the clay during the adsorption studies was monitored by the use of exchanged clay/distilled water controls.

Adsorption isotherms were determined by the addition of 1.0 g of the exchanged clay to 100 ml of waste which had been diluted to give a range of organic/ metal concentrations. The exchanged clay and waste were mixed by end-over-end rotation for 24 hours and then filtered. The filtrate was analysed for total organic carbon concentration and for the metal concentrations by atomic absorption spectrometry. Control samples containing waste only and exchanged clay only were also run.

A second type of adsorption experiment was carried out to determine if all of the TOC content of the waste could be adsorbed by the exchanged clay. The exchanged clay (10 g) was suspended in 100 ml of waste and shaken for 24 hours. The suspension was filtered to remove the exchanged clay and a second sample of exchanged clay (10 g) added to the filtrate. The adsorptions were repeated on five successive days, the filtrate being analysed for TOC on each day and the volume change noted.

The third adsorption experiment was carried out with a view to assessing the practicality of scaling up the adsorption work to produce an exchanged clay filter cake with adsorbed waste in sufficient quantities to permit cement-based solidification. The adsorption experiments were repeated using between 1.0 g to 20 g of exchanged clay in 100 ml samples of the waste. These samples were mixed, filtered and analysed as described above.

6.2.3 Mix Development

Mix development was undertaken to optimise the parameter for a commercial type mix prior to use of the real wastes. The aim of this experiment was to minimise the OPC content of the mix and maximise the amounts of clay with adsorbed waste and inert filler. At this stage, physical integrity, as measured by unconfined compressive strength, was used to assess the success of the optimisation experiments.

To determine the minimum ratio of OPC to water, exchanged clay and filler needed to meet these criteria, a series of test mixes were prepared, as shown in Figure 6.1. Mixes 1 to 4 and 13 to 16 investigate the effect of total insoluble solids (TIS) on the strength of the mix at a fixed percentage of OPC, in the absence and

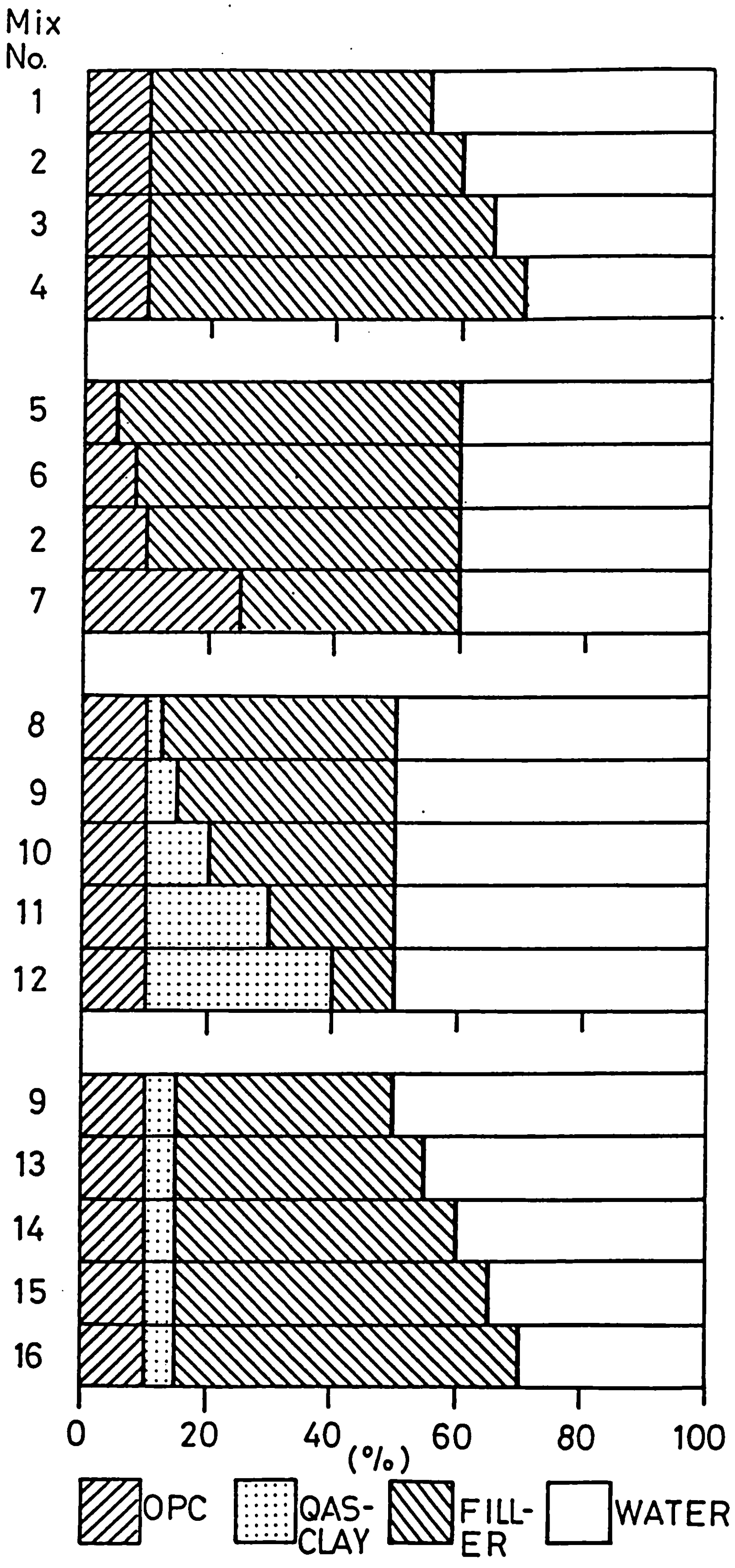


Figure 6.1: Composition of Mix Development Samples.

presence of the exchanged clay. Mixes 2, 5, 6 and 7 contain variable amounts of OPC, at a constant TIS so that the optimum OPC content could be determined. Mixes 8 to 12 show the effect of increasing the percentage of exchanged clay at constant percentages of TIS and OPC.

The exchanged clay used was prewashed, dried and reground prior to use, to minimise the effect of foam in the cement matrix caused by excess QAS, as described in Section 4.3.2. The solids were mixed in a domestic mixer and then the water added. Mixing was continued for approximately 3 minutes until a homogeneous mix had been obtained. The samples were cast in polystyrene cylindrical moulds (54 x 62 mm), which had prevously been coated with PTFE to prevent the samples adhering to the internal surfaces and also to prevent interaction of the waste with the polystyrene itself. Care was taken to exclude air during casting. The samples were allowed to cure for 3 days, the moulds were then removed and the samples placed in sealed polythene bags to finish curing. Any bleed water on the surface of the moulds was measured before unmoulding and the amount used to calculate the true TIS of the solidified samples. Four replicates of each mix were prepared. Two were allowed to cure for 7 days and two for 28 days prior to testing.

The UCS of the samples was determined using a compressive strength machine manufactured by Wykeham-Farrence, Slough, UK. Prior to testing the tops of the cylinders were ground to provide smooth parallel surfaces to prevent point loading. The loading rate was controlled manually and failure of the samples taken to occur when no further load could be applied.

6.2.4 Stabilisation/Solidification

Each of the wastes described in Table 6.1 were stabilised by mixing 200 g of the exchanged clay with 2 l of waste for either 24 or 48 hours. The two time periods were used and the results compared to check that the shorter, 24 hours, adsorption time was sufficient to allow maximum adsorption of the organics. After the required time the exchanged clay suspensions were filtered under vacuum until no free liquid was visible on the filter cake. The filter cake was weighed and the waste:exchanged clay ratio calculated to be 1.25:1 in each case, indicating that excess waste, above the adsorptive capacity of the exchanged clay (as determined in the previous adsorption experiments), was present. This excess liquid was, in preliminary work with Waste A, assumed to take part in the hydration of the OPC. The mixes produced were unsatisfactory, however, presumably due to interference between the unstabilised waste present in the excess liquid and the OPC setting process. In order to remove this excess non-adsorbed waste from the filter cake, the exchanged clay was washed with 2 l of distilled water and refiltered, the liquid to exchanged clay ratio being maintained at 1.25:1 by the addition of distilled water, if necessary. The filtrate obtained from the 24 hours adsorption of the waste by the exchanged clay mixtures was used as a second low concentration waste sample. Fresh samples of exchanged clay were added, the volume being made up to 2 l by the addition of small quantities of the washings. The regime of mixing, filtration and washing were carried out as described above.

The three wastes were solidified using the mixes shown in Table 6.2. The mixes were based on the results of the mix development work, but higher weights of OPC had to be added to the exchanged clay/waste mix to give the necessary strength. The filter cake, plus additional water for hydration of the OPC, was mixed to a smooth paste in a domestic mixer and then added to premixed dry OPC and filler. When the paste was homogeneous, subsamples were transferred to cylindrical moulds.

Three sets of control samples were prepared, following the protocol outlined above. One set of control samples contained waste which had been mixed with the exchanged clay followed by immediate addition of the OPC (mixes C4 and C5, Table 6.2). This was done to assess the effect of the absence of a pre-mixing adsorption stage on product integrity. The second set of control samples contained exchanged clay and OPC mixed with distilled water replacing the waste (mixes D1 to D5, Table 6.2). The third set of control samples contained cement, filler and waste only (A4, B4 and C7), to show the effect of the wastes on mixes similar to conventional cement-based solidification processes.

Table 6.2: Solidification Mixes

Sample	Clay[1] %	OPC %	Filler %	Total Liquid Content %	TIS %	Free Liquid to OPC Ratio %
WASTE A						
A1[4]	11	12	26	52	49	3.7
A2	7	26	17	50	50	1.7
A3	7	26	17	50	50	1.7
A4	0	26	24	50	50	1.9
WASTE B						
B1	9	26	20	45	55	1.5
B2[2]	9	26	20	45	55	1.5
B3[3]	9	26	20	45	55	1.5
B4	0	26	29	45	55	1.7
WASTE C						
C1	9	26	20	45	55	1.5
C2[2]	9	26	20	45	55	1.5
C3[3]	9	26	20	45	55	1.5
C4[4]	9	12	34	45	55	3.2
C5[4]	9	26	20	45	55	1.5
C6[4]	9	12	34	45	55	3.2
C7	0	26	29	45	55	1.7
CONTROLS						
D1	11	12	26	52	49	3.7
D2	7	26	17	50	50	1.7
D3	9	26	20	45	55	1.5
D4	9	12	33	50	50	3.2
D5	0	26	29	45	55	1.5

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[1] As dry solids
[2] Waste adsorbed for 48 hours
[3] Filtrate and washings adsorbed onto clay
[4] Waste alone used for hydration

(a) Unconfined Compressive Strength Testing

After 7 days the samples were unmoulded, and allowed to cure at 18 ± 2°C and 100% relative humidity. The setting rates of the mixes were measured using a pocket concrete penetrometer on a subsample of each mix (Section 4.2.4(a)). Unconfined compressive strength tests were carried out on the samples after 7 and 28 days curing as described in Section 4.2.4(b).

(b) Leach Testing

After testing for UCS the samples were ground in a pestle and mortar and sieved to achieve a particle size between 0.5 and 2 mm. Subsamples (40 g) were placed in polypropylene screw capped containers and exactly four times the weight of distilled water added. The containers were shaken by rotation for 7 days, filtered and the filtrate analysed for TOC and metal concentrations.

6.3 RESULTS

6.3.1 Adsorption Experiments

Isotherms showing the adsorption of TOC from the three wastes by the exchanged clay are shown in Figure 6.2. The isotherms represent the amount of TOC adsorbed by 1 g of exchanged clay from 100 ml of aqueous waste solution. The results show that as the concentration of the waste increased, the amount of TOC adsorbed also increased and no maximum capacity was reached even when using undiluted waste. This suggests that a concentration effect was operating, and although the adsorption capacity of the exchanged clay may have been

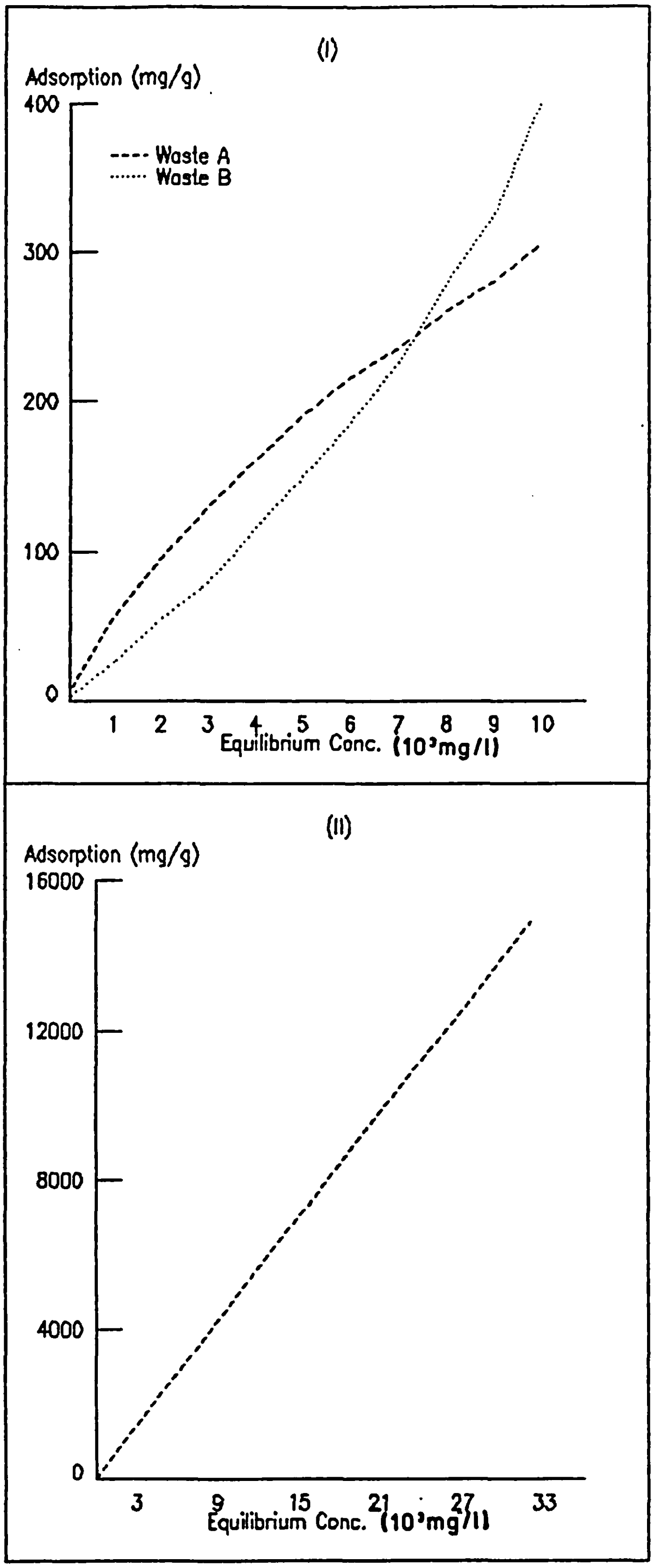

Figure 6.2: Adsorption Isotherms for (I) Wastes A & B and (II) Waste C.

satisfied, as the concentration of the solution increased some of the organic compounds were able to adhere to the outer surface of the exchanged clay. The adsorption isotherms suggest that, even at the lowest concentrations of waste tested, some of the TOC was not adsorbed by the exchanged clay.

To investigate whether the exchanged clay could adsorb all of the TOC from the wastes two different experiments were carried out. The first experiment, to discover if all of the TOC could be adsorbed, involved using 10 g of the exchanged clay in 100 ml of Waste B and replacing the exchanged clay on each day for five successive days. The results of this experiment are shown in Figure 6.3 which shows that up to 80% of the TOC could be adsorbed by the exchanged clay from Waste B, although the results again suggest that some organic compounds were adsorbed poorly or not at all. In the second experiment, increasing weights of exchanged clay were added to a constant concentration of waste solution and the adsorption of TOC monitored. The results of the experiment are shown in Figure 6.4. The results for both wastes show that as the weight of exchanged clay was increased the removal of TOC increased, although the concentration remaining in solution never reached zero but tended towards a constant value of TOC. This TOC concentration made up approximately 2% of the original TOC of the solution. At higher exchanged clay masses, the samples did not form homogeneous colloidal suspensions but instead the clay agglomerated, thus greatly reducing its surface area. The TOC adsorbed by higher weights of exchanged clay (10 g, for example) was not therefore ten times that adsorbed by 1 g of the exchanged clay.

The adsorption of metals by the exchanged clay was measured for Wastes B and C. Five metals were determined, but cadmium and lead were found to be below the detection limit of the analytical method for both wastes and nickel was also below the detection limit in Waste C. The amounts of the zinc, copper and nickel adsorbed from Waste B by the exchanged clay are shown in Figure 6.5 and from WasteC in Table 6.3. Adsorption of the metals from the wastes was good

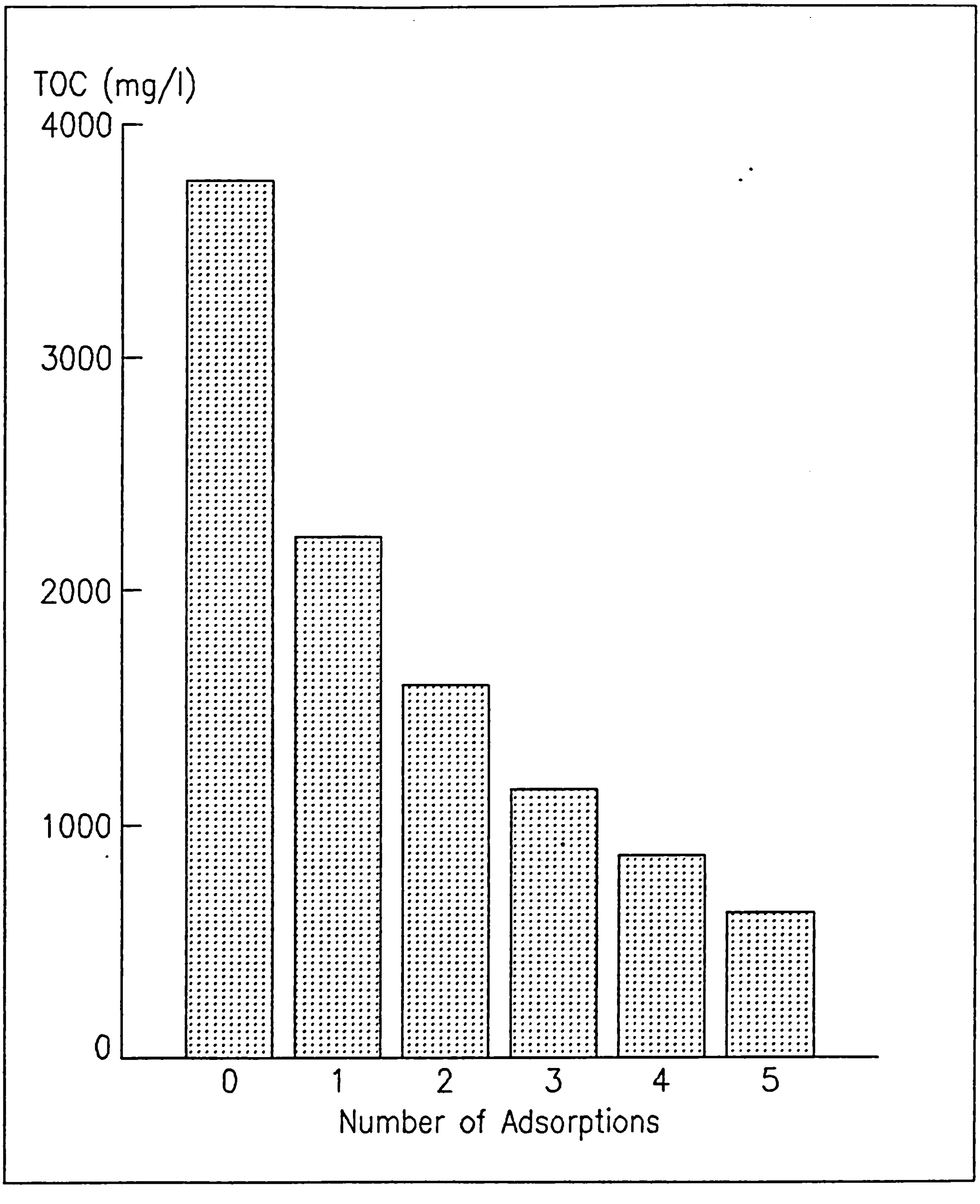

Figure 6,3: Adsorption of Industrial Waste B by Exchanged Clay (Constant Weight).

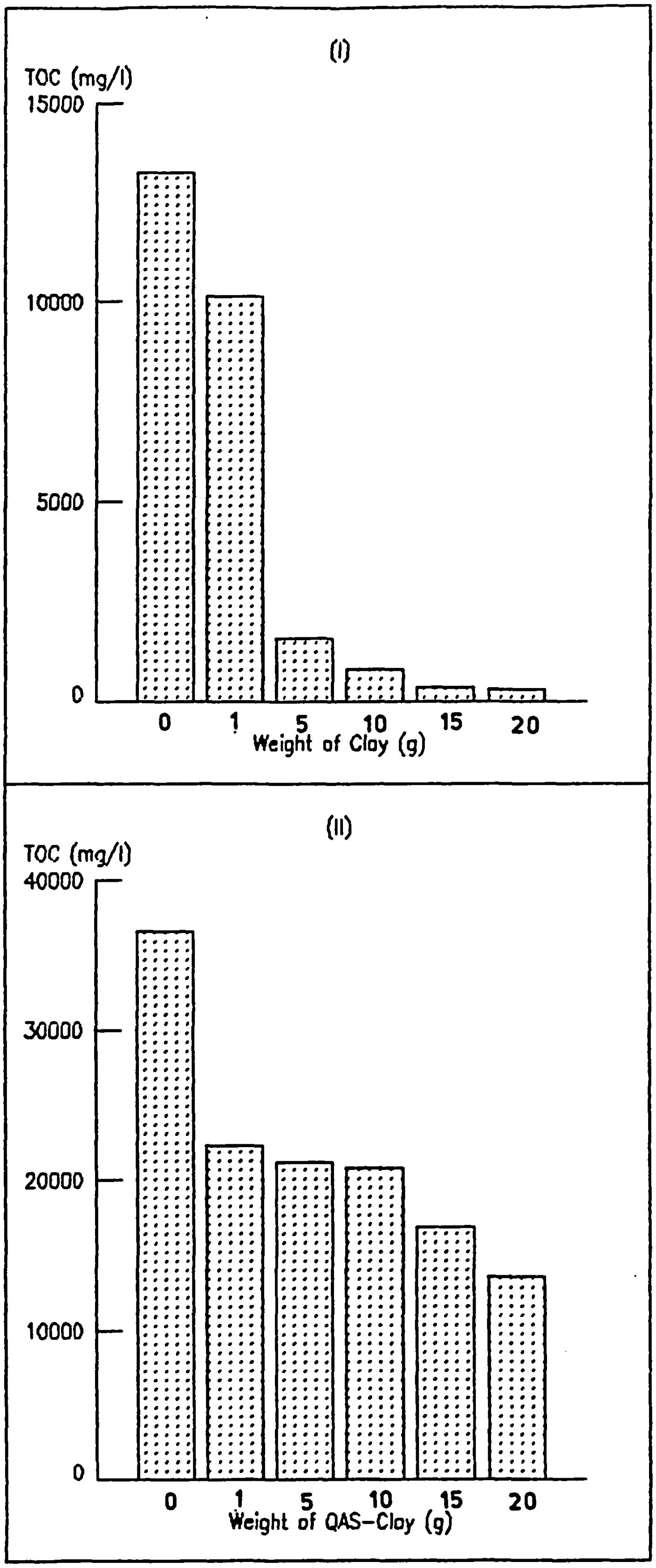

Figure 6.4: Adsorption of Industrial Wastes by Increasing Weights of Exchanged Clay, (I) Waste B and (II) Waste C.

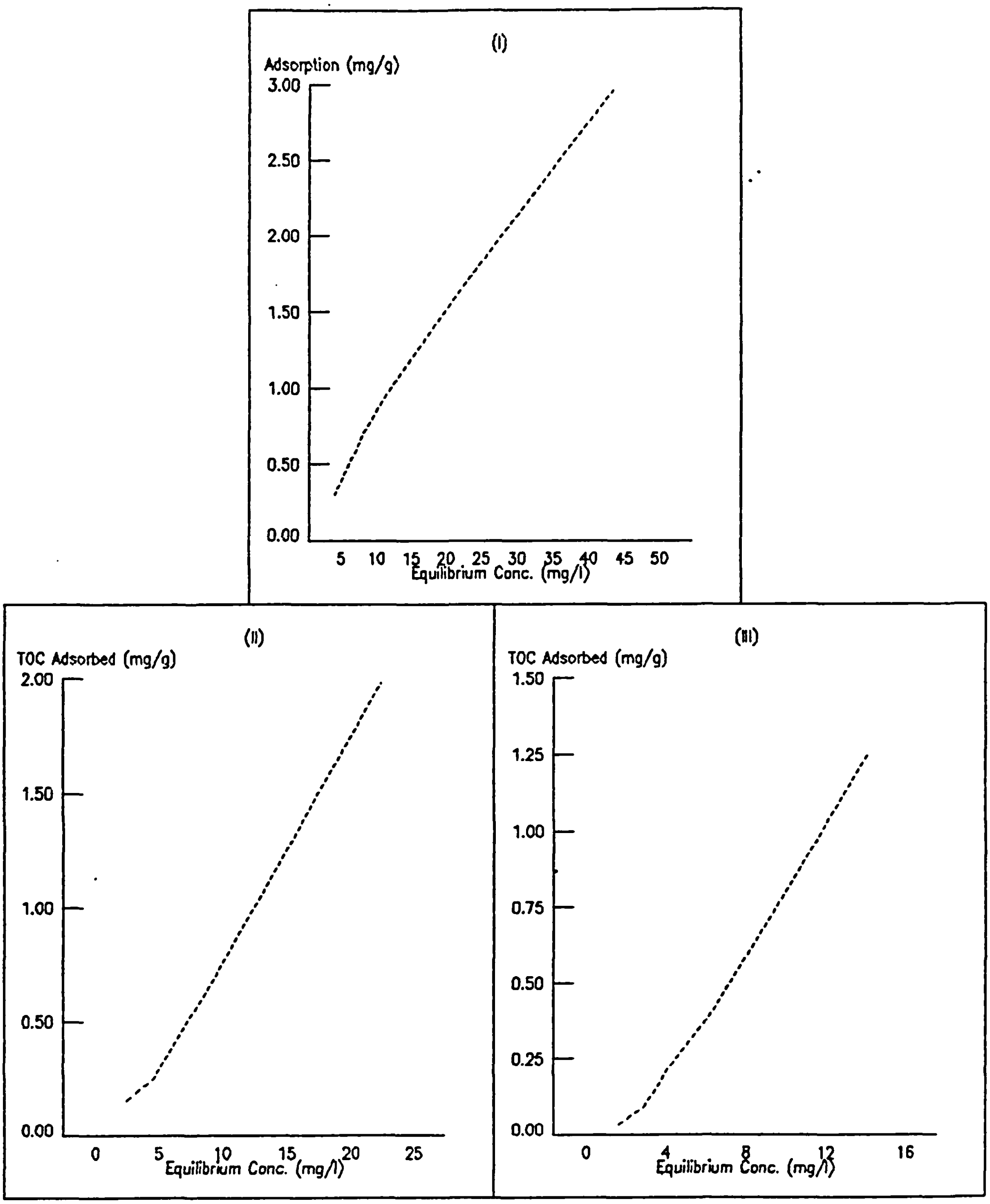

Figure 6.5: Adsorption of (I) Zinc, (II) Copper and (III) Nickel from Waste B.

for zinc and copper at low metal concentrations but the percentage adsorbed decreased as the metal concentration increased. Nickel, from Waste B, was well adsorbed at higher concentrations but showed a poor affinity for adsorption at lower waste concentrations.

Table 6.3: Adsorption of Metals from Waste C

	Initial Conc. (mg/l)	Final Conc. (mg/l)	Amount Adsorbed (mg/g)	% Adsorbed
ZINC				
	2.1	0.5	0.16	76.0
	10.8	2.7	0.81	75.0
	216.0	21.0	19.50	90.0
COPPER				
	0.8	<0.1	0.07	>87.5
	1.6	<0.1	0.15	>94.0
	2.0	<0.1	0.19	>95.0
	8.0	2.2	0.58	72.5

6.3.2 Mix Development

The aim of this work was to optimise the OPC:filler:exchanged clay:liquid ratios to give a good solidification mix with an UCS in excess of 350 kNm^{-2}. At present, no statutory limit for unconfined compressive strength of solidified materials exists, although discussions on fixing guideline values are in progress both in the UK and USA. Nevertheless a "rule of thumb" value of 350 kNm^{-2} (50 lb ins^{-2}) has been used by commercial solidification operators (Wilkinson, 1988), and although somewhat arbitrary, this Figure has therefore been used in the present work to assess the strength of the mixes produced.

The aim of mix development for solidification of industrial wastes requires that the OPC and exchanged clay content be minimised with respect to the wastes, i.e. the filler and liquid, to prevent a large increase in the final bulk of the product and to give a cost-effective process.

The effect of varying the TIS of the mixes was investigated in Mixes 1 to 4. The results of this work are shown in Figure 6.6(i). Generally, as the TIS content of the mixes was increased there was an increase in strength over both the 7 day and the 28 day curing period. The exception to this was the 60% TIS (Mix 2) which showed the highest strength of all of the mixes. This high strength was considered to be due to insufficient water being present in the mix to fully hydrate the OPC whilst not causing excessive bleed.

The effect of varying the OPC content of the mix is shown in Figure 6.6(ii). The TIS of these mixes was kept as close to 60% as possible and the only filler used was calcium carbonate. The UCS of the samples after 7 days of curing showed that the mixes with 10% and 25% OPC (Mixes 2 and 7) showed similar and considerably higher strengths than the mixes with lower OPC contents. After 28 days curing the UCS of the 25% OPC mix was greatest, although the 10% OPC also reached a very satisfactory strength. Mix 6, which contained 7.2% OPC, reached a strength in excess of 350 kNm^{-2} after 28 days, but it was decided that a 10% OPC content would be used for the remaining mixes to ensure the required strength development. For some of the waste solidification mixes the highest OPC content was necessary (Mix 7) to produce samples of the required strength.

The introduction of exchanged clay into the mix reduced the overall strength of the mixes (Figure 6.6(iii)). The TIS of the mixes was kept constant at 50%. This low TIS was chosen because at high exchanged clay:filler ratios, the water was absorbed by the clay and higher TIS contents were too stiff to be workable. The results show that as the exchanged clay:filler ratio was decreased, i.e. as the amount of the exchanged clay in the mix increased, the strength of the mixes fell. The presence of the exchanged clay in the mix

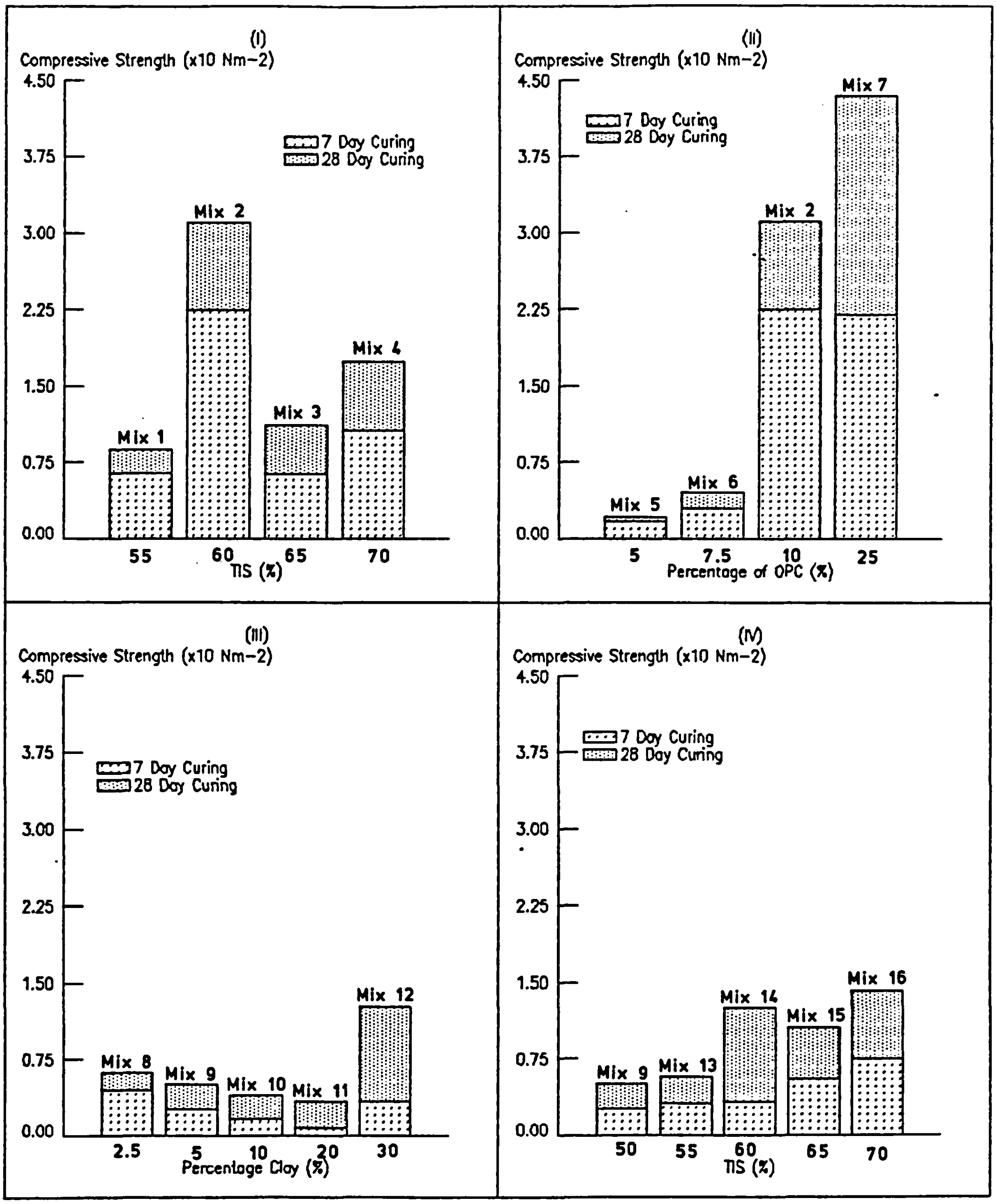

Figure 6.6: Unconfined Compressive Strengths of Mix Development studies.

(I) Variation of TIS for OPC/Filler mixes,

(II) Determination of Optimum Percentage of OPC

(III) Variation of Exchanged Clay:Filler Ratio

(IV) Variation of TIS at Constant Clay:Filler Ratio.

appeared to act as a water-store, and the samples with the most exchanged clay reached their final strength more slowly than the samples with only a little exchanged clay. The final mix (Mix 12) had a very high strength compared to the other samples, and the 7 day strength was comparable in strength to that of the mix with very small quantities of exchanged clay present (Mix 8). The 28 day strength exceeds that of Mix 8 by a factor of two.

The effect of TIS on the mixes in the presence of a small constant percentage of exchanged clay (Figure 6.6(iv)) was very similar to that found in the non-clay mixes except that the final strengths were slightly lower (Figure 6.6(i)).

6.3.3 Stabilisation/Solidification

The composition of the stabilisation/solidification mixes are given in Table 6.2. The setting rates of these mixes, as measured by the penetrometer results are given in Table 6.4. The results show that the mixes using exchanged clay with the excess waste removed by washing set satisfactorily (A2, B1, B2, C1, C2, C4), whilst the unwashed exchanged clay (Mix A1) shows a much reduced rate of setting compared to the corresponding control samples (D1). This retarding of the setting rate is also evident with the "washed" samples (A2 and A3), but after 7 days these samples displayed a strength similar or equivalent to that of their controls (D2). For Wastes B and C the exchanged clay samples set at a higher rate than the equivalent controls (D3 and 4) and this effect was reflected in the UCS data. Mixes C5 and C6 contained OPC, waste (which had not been pre-adsorbed on to the exchanged clay) and exchanged clay. Unlike the mixes that had the wastes adsorbed on to the exchanged clay prior to solidification, these samples did not set even after 28 days curing, presumably due to the inhibition of the OPC hydration by the organic content of the waste. The control samples which contained the unstabilised wastes, OPC and filler (A4, B4 and C7) also did not set, even after 28 days curing (Table 6.4). This shows the inhibiting

Table 6.4: Penetrometer Measurements (1.27 cm depth)

	Penetrometer Results (KNm^{-2})		
	1 Day	3 Days	7 Days
Waste A			
A1	0	0	0
A2	550	1930	4140
A3	830	2620	>4820
A4	0	0	0
Waste B			
B1	2760	>4820	>4820
B2	2760	>4820	>4820
B3	2890	>4820	>4820
B4	0	0	0
Waste C			
C1	2620	>4820	>4820
C2	2760	>4820	>4820
C3	2760	>4820	>4820
C4	2290	>4820	>4820
C5	0	0	0
C6	0	0	0
C7	0	0	0
Controls			
D1	0	550	1580
D2	2620	>4820	>4820
D3	2620	3310	>4820
D4	2200	4820	>4820
D5	>4820	>4820	>4820

effect of the wastes on the cement hydration. Unconfined compressive strength tests and leach tests could not be run on these samples as they were semi-liquid.

The UCS of the cylindrical samples are shown in Figure 6.7. All of the exchanged clay/OPC mixes reached the required strength after 28 days although Mix A2, which used the excess waste on the exchanged clay to hydrate the cement, and Mix C4 which contained only a small percentage of OPC, barely met the criterion. Mix B3 was found to form two definite layers which separated when the sample was demoulded. Both of the layers has similar strengths and compositions, but the reason for the separation is not known.

The leach tests carried out on the crushed solidified samples showed the ability of the exchanged clay to stabilise the organic contaminants of the waste. The retention of TOC during the leach tests on 7 and 28 day old samples are shown in Figure 6.8. The retention of TOC by the solidification mixes was greater than 70% for all the mixes of Waste A and B and well in excess of 80% for Waste C. For Waste A the concentration of TOC leached from the solidified samples was compared with the concentration of the waste of the same age to account for the decomposition of the waste with time.

All of the wastes showed an increase in retention after 28 days of curing compared to 7 days, particularly in those samples where the main strength development had occurred between those times. This suggests that the setting of the samples was contributing to the retention. The interaction of the OPC and exchanged clay leads to a decrease in the permeability of the matrix with time so making the adsorbed waste less accessible to the leaching fluid.

Analysis of the leachate of both the 7 and 28 day cured samples for zinc, copper, nickel. cadmium and lead on all of the waste samples showed that the metals were below the detection limit of the analytical method. The two exceptions to this were the two mixes that contained the unstabilised waste (C5 and C6). These samples

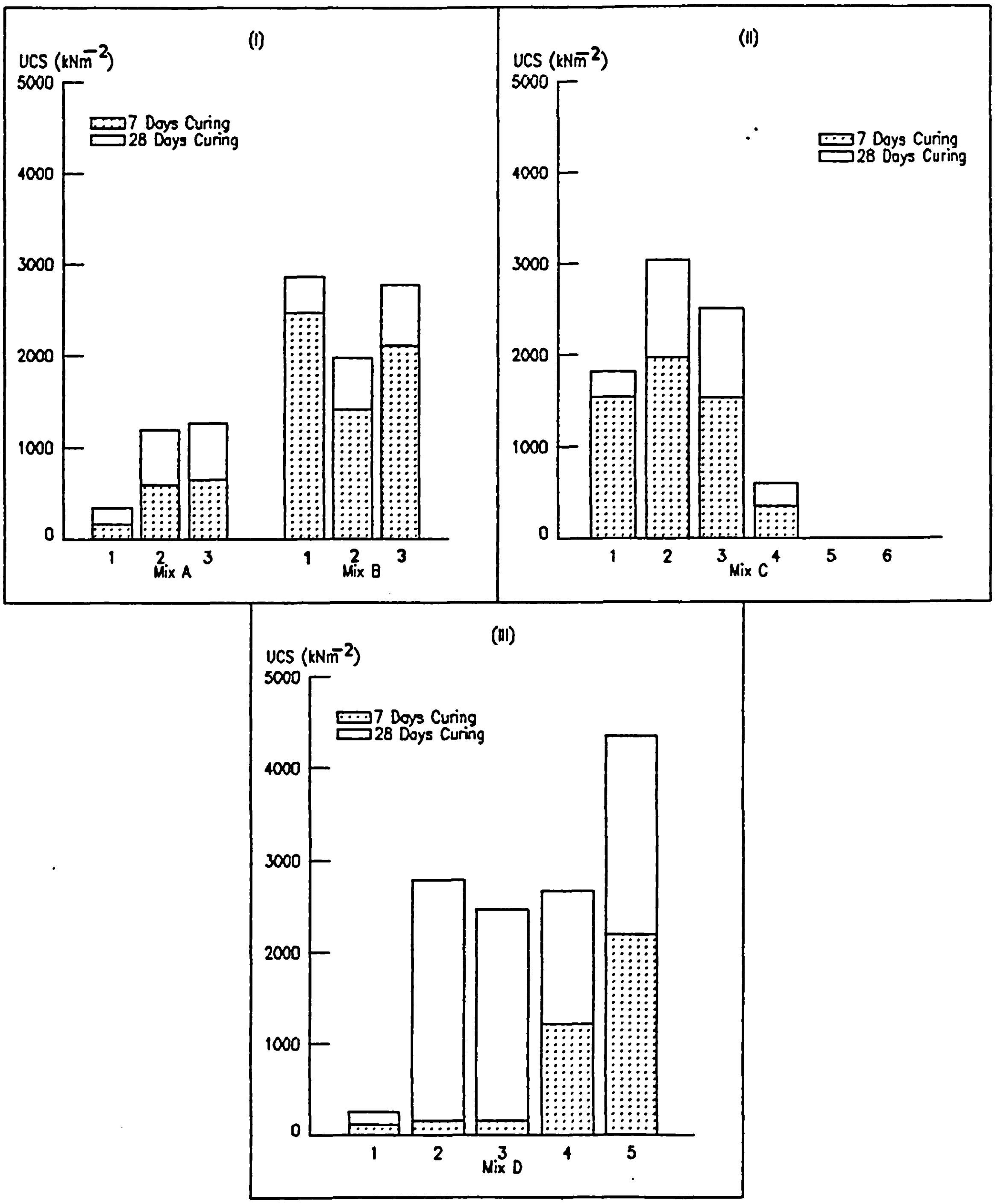

Figure 6.7: Unconfined Compressive Strength for Solidified Industrial Wastes, (I) Waste A & B, (II) Waste C and (III) Control (D).

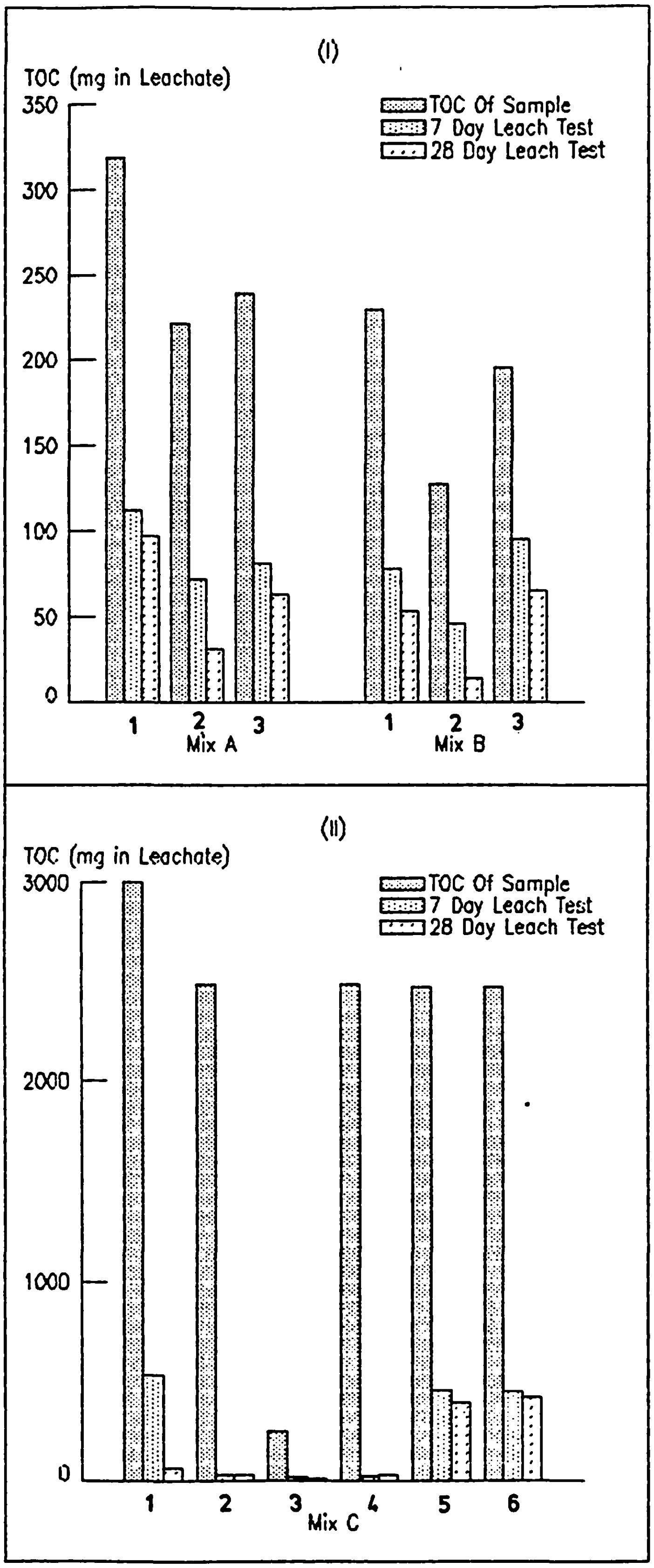

Figure 6.8: TOC Leaching from Raw Waste and Solidified Mixes (I) Wastes A & B and (II) Waste C. (For each sample, data refers to the same weight of waste.)

were found to release approximately 0.5 mg/l of copper into the leachate from both the 7 and 28 day cured samples.

6.3.4 Industrial Application

An appreciation of the potential economic advantages of the exchanged clay/OPC stabilisation/solidification of organic contaminated wastes can be gained from comparing some preliminary estimates of material costs (the main cost factor in stabilisation/solidification) with the likely range of incineration costs for the same materials. The following calculations give an approximate costing of the S/S of two of the wastes studied in this work, based upon the successful mixes developed.

Prior to treatment each batch of waste must be sampled and the percentage of organic carbon determined. A simple adsorption experiment would be performed on the waste to determine the amount of exchanged clay required to adsorb the organic compound and the time to reach equilibrium. Based upon these results the required quantities of exchanged clay would be added to the waste. The waste/exchanged clay slurry would be stirred for the predetermined time to allow complete adsorption. When the adsorption of the organic compounds is complete the slurry could be solidified by any commercial cement-based solidification process.

Example 1: Treatment of Waste B

TOC of Waste = 37140 mg/l
1 g of exchanged clay removes 1418.9 mg TOC/l waste, therefore 1 l of waste requires 26.2 g exchanged clay.

To solidify 1 tonne of liquid waste and 775 kg solid waste required approximately:-

26 kg Exchanged Clay @ £2000/T = £ 52.00
200 kg OPC/PFA @ £ 60/T = £ 12.00

Total material cost = £ 64.00

Example 2: Treatment of Waste C

TOC of Waste = 123200 mg/l
1 g of exchanged clay removes 2705.0 mg TOC/l waste, therefore 1 l of waste requires 45.5 g exchanged clay.

To solidify 1 tonne of liquid waste and 755 kg solid waste required approximately:-

45.5 kg Exchanged Clay @ £2000/T = £ 91.00
200 kg OPC/PFA @ £ 60/T = £ 12.00

Total material cost = £ 103.00

From the calculations above it has been shown that mixed industrial wastes could be stabilised for as little as £100 to £200 per tonne using conventional stabilisation/solidification technology. Additionally, it is envisaged that, if exchanged clay became widely used in waste treatment in this way their costs would fall as demand increased and the market became more competitive. Incineration of similar wastes with a low calorific value could cost up to £1000 per tonne (Ryan, 1989).

The calculation does not take into account factors such as the need to treat any waste filtrate or clay washings, which themselves would contain some organic and metal constituents. The cost also does not include transport, labour or the cost of depositing the S/S product. Clearly, however there is some economic advantage in stabilisation/solidification which would warrant its further development for pilot plant testing.

6.4 SUMMARY

This work used Perchem 462 to adsorb the organic component of three organically-contaminated industrial wastes. In the mixes which were subsequently made up, an inert filler (calcium carbonate) was used to reduce the cement content to as low as 12% and thereby more accurately simulate a commercial solidification mix.

The most successful S/S mixes were achieved by (i) pre-adsorbing the waste onto the clay and (ii) washing the clay following this to remove residue of the waste remaining when the adsorption capacity of the clay had been saturated. If this were not done, hydration of the mixes was found to be inhibited and setting delayed. The work with the three wastes indicated that there was, in all cases, a residual organic element which was not adsorbed, and this was presumed to be the cause of delayed hydration with the unwashed clay. Nonetheless, all the mixes which were produced using washed clay exhibited compressive strengths which were greater than the value of 350 kN/m^2 which is at present used as a "bench mark" value in at least one commercial operation in the UK. Leaching tests indicated that the amount of TOC leached from a unit weight of solidified waste could in some cases be as low as 1% or less of that present in an equivalent weight of unsolidified raw waste. This was considered to be an extremely encouraging result for the wastes tested, which would otherwise be impossible to solidify satisfactorily using present commercial formulations.

7. CONTAMINATED SOIL TREATMENT

7.1 INTRODUCTION

The problems of contaminated land, how to deal with it and the limitations it places on new developments have become increasingly important issues in recent years (Institute of Environmental Health Officers, 1988). Contaminated land consists of land formerly used for industry, mining or waste disposal which has been shown to contain sufficient quantities or concentrations of a substance or substances such as to pose a direct hazard to a specified target or targets (I.E.H.O., 1988). As the requirement for land in cities and towns increases it has become necessary to develop such sites for commercial and industrial uses or for domestic housing. One of the major sources of contaminated land in urban areas is due to the redevelopment of former town gas production sites which fell into disuse after the introduction of natural gas (DoE, 1985).

Town gas works were often sited close to rivers or railways to facilitate delivery of the raw material, coal and the export of, for example, coke. Although the gas works sites were originally situated on the edge of towns, they have usually been engulfed as the towns expanded and now occupy prime positions in, or near, town centres. Hence there is considerable interest in their redevelopment. The major problem which faces potential developers of gas works sites are the presence of chemical contaminants which could pose a health hazard to permanent occupants of the site and the workers employed during redevelopment (Beckett & Simms, 1985). The gas making process produced a wide range of by-products such as tar, ammoniacal liquors, coke and aromatic organic compounds. During the course of the gas works operation these materials tended to be dispersed around the site. The aromatic compounds present in the soil contain, predominantly, polyaromatic hydrocarbons (PAH), many of which are known carcinogens and are adsorbed into the human body through skin contact, drinking contaminated water or inhalation of contaminated dust (Lee et al., 1981). To clean up a gas works site it is necessary to either remove or contain the hazardous chemicals, such as the PAH, to prevent contamination of ground and surface waters, and to avoid dust hazards or adsorption into the vegetation to be planted.

Exchanged clays have been shown, in the prevous chapters, to be able to adsorb many organic compounds from industrial wastes. In this work it was hoped that the clays could be used to stabilise hazardous constituents of contaminated soils, either prior to cement-based solidification of the contaminated soil or as a stabilising additive. The initial work used soil samples dosed with phenol, 3-chlorophenol and 2,3-dichlorophenol. Phenols and the substituted phenols have been shown to be adsorbed by soils with high clay contents (Boyd, 1982; Selvakumar et al., 1987) and models for the adsorptions have been derived (Lagas, 1988; Ollinger & Ahlert, 1987). It was hoped that, by using the exchanged clay mixed with the contaminated soil, the sorptive properties of the clay would prevent release of the phenols from the soil and would also act to reduce the permeability of the soil, so reducing the rate of transport through the soil. The phenol dosed soils were solidified using the exchanged clay and the cement-based solidification mixes developed in Section 6.3.2.

The study was then extended to look at the stabilisation of a soil from a derelict gas works site contaminated with PAH, using the exchanged clay. Dozombak & Luthy (1984) showed that PAH could be adsorbed by clay soils, but their adsorption contributes to the transport of these hydrophobic molecules through the site. Hosler et al. (1988) showed that small PAH, such as naphthalene and anthracene, could be biodegraded in the soil. Larger PAH such as the highly carcinogenic benzo(a)pyrene, however, remain largely unchanged, hence methods for containing such compounds are required.

7.2 MATERIALS AND METHODS

7.2.1 Materials

The solvents used were "HPLC" grade from Rathburn Chemicals, Walkerburn, Peebleshire, UK. Reagents were Analar grade obtained from BDH Ltd, Poole, UK, unless otherwise stated.

(a) Soils

Uncontaminated soil was obtained from Silwood Park, Surrey, UK. Contaminated soil was obtained from the site of a derelict gas works, which was being redeveloped, near St Albans, U.K. This soil was contaminated with coal tar and other waste products from gas production and contained, for example, PAH in concentrations in excess of 1.88 g kg^{-1} dry soil. The soil sample was taken from an area used for coal tar storage and so contained large amounts of coal tar that had leaked from the storage tanks.

Both of the soil samples were dried (105°C/24 h), crushed manually in a pestle and mortar and sieved to between 0.5 and 2 mm. The uncontaminated soil was divided into four subsamples, three of which were dosed with a range of phenolic compounds at concentrations well in excess of the Greater London Council's definition of unusually heavily contaminated soils (G.L.C., 1979) as follows. Solutions (0.1 M) of phenol, 3-chlorophenol, and 2,3-dichlorophenol in hexane were prepared. Aliquots of the stock solutions (125 ml) were mixed with 500 g of the uncontaminated soil and additional pure hexane added to allow the soils to be stirred by magnetic stirrers. After 24 hours the hexane was evaporated by gently heating the soil, leaving the phenols as residues on the soil at concentrations of 25 m mol/kg. The soil samples were recrushed to less than 2 mm and dried in a dessicator.

7.2.2 Characterisation of the Soils

The pH values of the dosed, undosed and gasworks contaminated soils were measured after 10 g of each soil was stirred for 24 hours in 100 ml of distilled water. The metal concentrations in the soils were determined by inductively coupled plasma spectrometry (ICP). The soil samples were prepared by manual grinding to <0.75 μm, digesting in a mixture of concentrated perchloric and nitric acids, filtering and diluting the filtrate to the appropriate concentration for analysis.

The concentration of PAH in the contaminated gasworks soil were determined by a method adapted from that used by Baek (1988) for PAH analysis of solid particulate samples. Soil (1.0 g) was extracted for 16 hours with 120 ml of dichloromethane in a Soxhlet apperatus. The cycle time was approximately 10 minutes. The extract, a clear deep yellow solution, was concentrated to about 3 ml using a rotary evaporator at 30°C, and finally evaporated to near dryness with a stream of oxygen-free nitrogen. The residue was then re-dissolved in about 3 ml of hexane and stored at -18°C prior to clean-up and analysis by reverse-phase high performance liquid chromatography (HPLC).

7.2.3 Analytical Procedure for Polyaromatic Hydrocarbons

The analytical procedure for the PAH was adapted from the method developed by S. Baek (1988) for eighteen individual low and medium molecular weight PAH ranging from phenanthrene to coronene. The method involved a clean-up stage using SEP-PAK silica cartridges (Waters Associates Ltd., Hertford, UK) prior to analysis by HPLC with fluorescence and ultraviolet (UV) detection. The nomenclatures, abbreviations, formulae and water solubilities (where known) of the 18 PAH determined are shown in Table 7.1.

The extraction of the soil to determine the total PAH present was carried out in standard Soxhlet apparatus using dichloromethane

Table 7.1: Formulae, Abbreviations and Water Solubility (where known) of the PAH Analysed in this Study.

Nomenclature (IUPAC)	Abbreviation	Formula	Molecular Weight	Solubility Water*(µg/l)
Phenanthrene	PHEN	$C_{14}H_{10}$	178	1290.0[a]
Anthracene	ANTHR	$C_{14}H_{10}$	178	73.0[a]
Fluoranthene	FLUR	$C_{16}H_{10}$	202	260.0[a]
Pyrene	PYR	$C_{16}H_{10}$	202	135.0[a]
Benzo(c)phenanthrene	BcPH	$C_{18}H_{12}$	228	-
Cyclopenta(cd)pyrene	CcdP	$C_{18}H_{10}$	226	-
Benz(a)anthracene	BaA	$C_{18}H_{12}$	228	14.0[a]
Chrysene	CHRY	$C_{18}H_{12}$	228	2.0[a]
Benzo(b)naphtho -(2,1-d)thiophene	BNTH	$C_{16}H_{10}S$	234	-
Benzo(e)pyrene	BeP	$C_{20}H_{12}$	252	5.5[b]
Benzo(b)fluoranthene	BbF	$C_{20}H_{12}$	252	-
Benzo(k)fluoranthene	BkF	$C_{20}H_{12}$	252	-
Benzo(a)pyrene	BaP	$C_{20}H_{12}$	252	3.8[a]
Dibenz(a,h) -anthracene	DahA	$C_{22}H_{14}$	278	2.49[c]
Benzo(ghi)perylene	BghiP	$C_{22}H_{12}$	276	0.26[a]
Indeno(1,2,3-cd) -pyrene	I123P	$C_{22}H_{12}$	276	-
Anthanthrene	ANTHN	$C_{22}H_{12}$	276	-
Coronene	Cor	$C_{24}H_{12}$	300	0.14[a]

* = at 25°C
a = Mackay and Shiu (1977)
b = Schwarz (1977)
c = Means et al. (1980)

as the solvent (Section 7.2.2). Extraction of the aqueous samples, from both batch and column tests, was carried out at pH 2 using diethyl ether. This solvent was chosen after preliminary studies had been carried out to select the best solvent by extracting PAH-dosed aqueous samples. Prior to clean-up the diethyl ether/pentane mix was evaporated off and the sample re-suspended in hexane, a non-polar solvent suitable for use as an eluent in silica minicolumn chromatography (Section 7.2.3(a)). After clean-up the PAH fraction was collected, reduced to dryness in a stream of oxygen-free nitrogen and re-suspended in 1ml acetonitrile for analysis.

Acetonitrile and water, used as the mobile phase in the HPLC analysis, were prefiltered through a 0.22 µm hydrophilic organic membrane filter (Millipore 'type GV', Millipore Ltd, Harrow, UK) using a Millipore solvent filtration kit, and then all trapped air was removed by ultrasonication for 15 minutes.

Glassware used for all analytical work was made of borosilicate. Before use the glassware was cleaned by soaking in 10% (v/v) Decon 90 detergent for 24 hours, rinsing with distilled water and then soaking in 10% chromic acid for 24 hours, and finally rinsing at least twice in distilled water. Exposure to air was avoided when the glassware was stored before use.

(a) Clean-up

The clean-up and fractionation of extracted samples was carried out using Waters SEP-PAK cartridges (Waters Associates Ltd., Hartford, UK). The silica SEP-PAK cartridge, a radially compressed mini column, was used as an alternative to a conventional purification methods such as thin layer chromatography (TLC) clean-up or a silica gel open column.

Prior to use, each SEP-PAK cartridge was rinsed with 10 ml of hexane, a non-polar solvent. The concentrated extract was then loaded onto the cartridge, and the vial containing the residue rinsed twice with 1 ml hexane. These rinsings were also loaded onto the cartridge. After discarding the hexane eluent, the cartridge was eluted with 5 ml of 15% dichloromethane in hexane, a more polar solvent, and the eluent collected in a 10 ml test tube. The cartridge eluent was evaporated slowly to near dryness under a stream of oxygen free nitrogen, and re-dissolved in 1 ml of acetonitrile. The sample was then ready for HPLC analysis.

(b) Preparation of Standard Solutions

PAH standard materials (more than 99% purity) were obtained from the following suppliers and were used without purification: PHEN, BeP, DahA, BghiP and COR from Aldrich Chemical Co. (Gillingham, U.K.); BkF and I123P from Phase Separation Ltd (Clwyd, UK); ANTHR, FLUR, PYR, BaA, CHRY and BaP from Ralph N. Emmanuel Ltd. (Wembley, UK); BcPH, Ccdp, BNTH, Bbf and ANTHN from the Community Bureau of Reference of the Commission of the European Communities (Brussels, Belgium).

These standards, which were available as powders, were dissolved in acetonitrile at a range of 2 to 50 µg ml^{-1}. A mixture of PAH standards were made up from the individual stock solutions. Table 7.2 shows the concentrations of PAH in stock solutions and in the mixed standard. The concentrations of individual PAH in the mixed standards were chosen to be comparable with those used by S. Baek (1988) which gave similar fluorescence and UV responses with selected chromatographic conditions and wavelength programmes. Portions of the stock mixture of standards were diluted 1:2, 1:5, 1:10 and 1:20 with acetonitrile for appropriate use as standards.

(c) HPLC Analysis

The chromatographic analysis was carried out by reverse-phase HPLC using a gradient elution. The details of instrumental specifications and chromatographic conditions used are presented in Table 7.3.

Table 7.2: Concentrations ($\mu g\ ml^{-1}$) of PAH in Stock Standard Solutions.

PAH	PAH Number	Stock Solution ($\mu g\ ml^{-1}$)	Mixture of Standards ($\mu g\ ml^{-1}$)
PHEN*	1.	4.0	0.101
ANTHR	2.	10.9	0.136
FLUR	3.	15.0	0.188
PYR	4.	24.0	0.600
BcPH	5.	9.3	0.116
CcdP*	6.	14.6	0.365
BaA	7.	6.1	0.076
CHRY	8.	9.0	0.230
BNTH	9.	18.4	0.460
BeP	10.	5.0	0.063
BbF*	11.	10.0	0.250
BkF	12.	2.0	0.025
BaP	13.	8.6	0.110
DahA*	14.	5.0	0.125
BghiP*	15.	6.2	0.160
I123P*	16.	21.6	1.350
ANTHN	17.	5.4	0.068
COR	18.	3.0	0.300

* = Determined by UV.

Table 7.3: Instrumental Specifications and Chromatographic conditions used for the HPLC analysis.

HPLC System	
Pumps	*Waters 6000A LC Pump Waters M45 LC Pump
Controller	Waters model 680 Automated Gradient Controller
Injector	Waters Model U6K Universal Injector with 2 ml Sample Loop
Analytical Column	Waters PAH Analysis Radial-PAK Cartridge, 5 mm x 10 cm, 10 µm particle size C_{18} Packing, installed in Z-module Radial Compression Separation System
Guard Column	Waters Guard-PAK with C_{18} Inserts
Chromatographic Conditions	
Mobile Phase	Acetonitrile in Water
Gradient Elution	35% to 92% for 42 mins (Non-linear Gradient*) 92% to 92% for 6 mins
Equilibration	100% to 100% for 5 mins 35% to 35% for 7 mins
Flow Rate	2 ml min^{-1}
Temperature	18 ± 2°C
Detectors	Perkin-Elmer LS-4 Programmable Fluorescence Spectrometer (Perkin-Elmer Ltd., Beaconsfield, U.K.) with a Phillips PM8251 Recorder (Phillips, Netherlands)
	Waters 480 UV-Visible Spectrophotometer with a pontentiometric Recorder (Labdata Instrument Ltd., Croydon, U.K.)

*Waters (Millipore Ltd., Harrow, U.K.)

* Programme No. 5 on the Waters Automated Gradient Controller.

The HPLC system consisted of two solvent delivery pumps, an automatic gradient controller, an injector with a 2 ml sample loop, an analytical column with a guard column and two detectors. A Waters Radial-PAK PAH analysis cartridge (5 mm x 10 cm), 10 µm particle size C_{18} packing (Millipore Ltd., Harrow, UK) was used for the analytical column, while the mobile phase consisted of acetonitrile and water, which were delivered into a mixing chamber by separate pumps. A guard column containing a C_{18} insert (Millipore Ltd., Harrow, UK) was installed between the injector and the analytical column in order to prevent the deterioration of the analytical column resulting from the accumulation of chemicals or particles from the injected samples.

The mobile phase was run from 35% to 95% acetonitrile in water over 42 minutes, using a non-linear gradient (curve 5 on the Waters Automatic Gradient Controller), followed by 92% acetonitrile from 42 to 48 minutes. In order to equilibrate the column for the next run, the mobile phase was run with 100% acetonitrile for 5 minutes, followed by 35% acetonitrile for 7 minutes isocratically. Identical equilibration times between injections were maintained to obtain reproducible retention times. The flow rate was 2 ml/min and the column pressure was typically 620 kNm^{-2}, ranging from 330 kNm^{-2} to 1000 kNm^{-2}.

(d) Detection

The spectra of fluorescence emission and UV absorption from the eluting fractions were monitored by two detectors connected to the analytical column in series: a wavelength programmable fluorescence spectrometer and a UV-visible spectrophotometer. The fluorescence detector was programmed into 4 pairs of wavelength conditions in order to give a good response to each PAH of interest as it eluted, while the UV detector was set at 290 nm. The fluorescence and UV spectral characteristics of a number of PAH were obtained from the literature (Baek, 1988 and Wise, 1983). The specific excitation and emission wavelength conditions used for the fluorescence detection of each PAH are shown in Table 7.4, where the PAH are listed in their order of elution.

Table 7.4: Wavelength Conditions used for the Detection of PAH

Wavelength (nm) Excitation	Wavelength (nm) Emission	PAH
260	430	PHEN, ANTHR, FLUR, PYR
285	385	BcPH, CcdP, BaA, CHRY, BNTH, BeP, BbF
295	410	BkF, BaP
300	455	DahA, BghiP, I123P, ANTHN, COR

(e) Identification and Quantification

The chromatographic peaks of the samples were identified by two methods. Firstly, individual PAH were tentatively identified on the basis of their retention times by referring to those of standards. Secondly, the ratios between fluorescence and UV response were used to confirm the identification by comparison with those of corresponding standards.

The quantification of the PAH in the samples was also made by comparing the measured peak heights with those of the standards of known concentrations. The concentration of a PAH per kg dry soil was calculated using the following formula:

$$C_i = \frac{h_i \times r_i}{f \times m}$$

where, C_i was the concentration in ng kg^{-1} of i^{th} PAH in dry soil or ng/vol of leachate, h_i was the peak height in mm of the i^{th} PAH, r_i was the response factor of the i^{th} PAH in ng, f was the ratio of the injected volume to the volume of final solution and m was the ratio of the weight of soil extracted to the weight of dry soil in kg.

The response factor, defined as the ratio of the known amount of a standard PAH injected to the corresponding peak height, was applied to calculate the concentration of each PAH. The response factors for each PAH were determined each day by injecting 100 µl of a mixture of standards. The response factor was calculated by measuring the ratio of the height of the UV and fluorescence peaks multiplied by the known concentration of the i^{th} in the standard,

(f) Quality Control of the Analytical Methods

Carefully prepared mixtures of PAH standards and a blank were routinely injected to check column performance and to optimize operating conditions for each batch of analyses. The day-to-day precision, the reproducibilities of retention times and the response factors were determined by analysing the same standard mixture on consecutive days. In order to evaluate losses of PAH during extraction and clean-up procedures for the aqueous samples, recovery tests were performed with water samples spiked with known amounts of the mixed PAH standard, below the estimated maximum solubility of each individual PAH. The spiked samples were subjected to the entire analytical procedure identical to the actual samples and the chromatographs compared directly with the injected standards. Water blanks were also tested to ascertain whether there was any contamination during the clean-up and testing procedure. The results of the blank runs were subtracted from each of the samples.

7.2.4 Batch Tests

Subsamples (10.0 g) of each of the phenol dosed soils were mixed with BODDMAM (0, 0.5, 1.0, 2.0 and 5.0 g) or Perchem 462 (1.0 g) in polypropylene screw-capped containers. To each container was added ten times the combined soil and clay's weight of water. The containers were rotated, end-over-end, for 24 hours, filtered through Whatman No. 1 paper and the filtrate analysed colourimetrically for phenol concentration. The effect of mixing a clay slurry with the soil and allowing time for adsorption of the phenols prior to leach testing was also investigated. BODDMAM (1.0 g) was mixed with 10 ml water to form a smooth paste, the paste was combined with 10.0 g of dry dosed soil, mixed well and left to stand for 24 hours. After 24 hours 110 ml distilled water was added and the samples shaken for 24 hours, filtered and analysed for phenol concentration.

Subsamples (10.0 g) of the gasworks soil were mixed with Perchem 462 (0.0, 0.5, 1.0, 2.0 and 5.0 g) in conical flasks. To each flask was added twenty times the weight of water, the flasks sealed and then stirred by magnetic stirrers. After 24 hours the samples were filtered through 0.45 µm membrane filters and the filtrate extracted for PAH.

(a) Extraction of PAH from Aqueous Solution

The aqueous samples were transfered, with ether washings (2 x 10 ml) to separating funnels and the pH adjusted to 2 by the addition of approximately 2 ml of 20% phosphoric acid. A total volume of 60 ml ether was added and the samples shaken for approximately 3 minutes. Following separation of the phases, the aqueous phase was returned to the original vessel and subsequently re-extracted with 2 x 30 ml ether. The extracts were combined and diluted with approximately 60 ml pentane. The water was removed from the extracts by freezing out at -18°C overnight. The organic fraction was decanted into a Kuderna/Danish evaporator and concentrated using macro and micro 3-ball Snyder columns to approximately 500 µl (Alltech (Associates)

Applied Science, Lancs., U.K.). Further evaporation, to near dryness, was achieved using a stream of oxygen-free nitrogen. The residue was then re-dissolved in about 3 ml hexane and stored at -18°C prior to clean up and HPLC analysis.

7.2.5 Column Tests

The results of the batch tests showed that the minimum ratio of exchanged clay to soil that retained >98% of three phenols was a 1:10 ratio. To scale up the experiment to make it closer to a real site situation, soil columns were used to test the retention of the organics. For the gasworks soils a range of clay:soil ratios were investigated because greater volumes of water passing through the soil would allow greater solution of the sparingly soluble PAH if they were not stabilised. The columns were packed with glasswool and sand to provide a firm base for the soil and prevent particles flowing into the leachate. Twelve different soil samples were introduced into the columns (Table 7.5). A further 50 g of sand was poured on top of each soil column and the column compacted by gentle agitation. Glasswool was placed in the top of the column to prevent the water forming channels and the columns were filled with water. In order to maintain a constant hydraulic head was achieved in each column the water level was kept as constant as possible throughout the experiment.

For the phenol dosed soils, consecutive 100 ml aliquots of the leachate were collected and analysed for phenol concentration (Section 3.2.3). After 500 ml of leachate had been collected, the column was eluted with 0.1 M sodium hydroxide. The first alkaline fraction was collected when the pH of the leachate increased above 7. Two subsequent alkaline fractions were collected and analysed for phenol concentration.

The gasworks soils were eluted with distilled water only. Five 2.5 l fractions were collected over a period of 5 days from each column. The concentration of PAH in the leachate was determined by HPLC analysis as previously described.

Table 7.5: Composition of Soil Columns

Column	Soil Type	Weight P.462 Per 10g Soil (g)	Weight of Soil in Column (g)	Volume of Eluent (ml)
1	Phenol dosed*	0.0	200	700
2	Phenol dosed	1.0	200	700
3	3-Chlorophenol dosed	0.0	200	700
4	3-Chlorophenol dosed	1.0	200	700
5	2,3-Dichlorophenol dosed	0.0	200	700
6	2,3-Dichlorophenol dosed	1.0	200	700
7	Uncontaminated	0.0	200	700
8	Gasworks	0.0	100	2500
9	Gasworks	0.1	100	2500
10	Gasworks	0.5	100	2500
11	Gasworks	1.0	100	2500
12	Gasworks	2.0	100	2500

* = Dosed soil equal to 25 m mol/kg for each phenol.

7.2.6 Stabilisation/Solidification of Phenol-Dosed Soils

Cement-based solidification of the phenol-dosed soils was performed using the mixes shown in Table 7.6. The dry soil was mixed with the exchanged clay or filler and water added. The soil slurry was mixed well, the OPC added and mixed again. Each solidification mix was transfered to cylindrical moulds used in the dynamic leach tests and compressive strength tests (Sections 4.2.5 and 4.2.4 respectively). The residue was placed in a beaker for penetrometry tests and equilibrium leach tests. All of the samples were allowed to cure for 28 days in polythene bags to maintain the humidity and at 20±2°C.

Table 7.6: Stabilisation/Solidification Mixes for Contaminated Soils

Mix	Soil	Dosed Organic	Clay %	Filler %	Cement %	TIS %
1	50.0	Phenol	0.0	5.0	10	65
2	50.0	3-Chlorophenol	0.0	5.0	10	65
3	50.0	2,3-Dichlorophenol	0.0	5.0	10	65
4	50.0	Phenol	5.0	0.0	10	65
5	50.0	3-Chlorophenol	5.0	0.0	10	65
6	50.0	2,3-Dichlorophenol	5.0	0.0	10	65
7	37.5	Phenol	12.5	0.0	10	60
8	50.0	Uncontaminated	5.0	0.0	10	65
9	50.0	Uncontaminated	0.0	5.0	10	65

(a) Strength Testing

After 28 days curing the samples were demoulded and the UCS of the cylinders measured as previously described (Section 4.2.4(b)). The penetrometry measurements were also taken using a pocket concrete penetrometer, at 2.7 cm penetration, after 28 days (Section 4.2.4(a)).

(b) Leach Tests

Dynamic leach tests (Section 4.2.5(a)) were carried out on the samples after 28 days curing. The leachate in the test was analysed and replaced with fresh distilled water seven times in the 28 daytest period. The equilibrium leach tests (Section 4.2.5(b)) were carried out on 28 and 56 day old samples.

7.3 RESULTS

7.3.1 Phenol Dosed Soil

The uncontaminated soil was dosed with solutions of the phenols dissolved in hexane. The hexane was evaporated off and the soil tested to determine the concentration of phenol remaining (Table 7.7).

Table 7.7: Phenol Concentration and pH of Dosed Soil

	Weight phenol (m mol/kg)	pH
Phenol dosed soil	249	4.75
3-Chlorophenol dosed soil	235	5.16
2,3-Dichlorophenol dosed soil	282	5.87
Soil Only	95	5.87

The pH of the uncontaminated soil was measured to be 5.87. Dosing with the acidic phenols decreased the pH as shown in Table 7.7.

The soil was analysed by ICP for the principle metal concentrations. The results are given in mg/kg dry soil:-

Li	8.5	Na	231.0	K	3466.0	Rb	40.0	Be	1.0
Mg	1538.0	Ca	4718.0	Sr	33.4	Ba	108.0	Al	18150.0
La	24.8	Ti	752.0	V	55.5	Cr	69.9	Mo	<0.4
Mn	280.5	Fe	2312.0	Co	7.6	Ni	17.6	Cu	41.6
Ag	0.6	Zn	204.4	Cd	<0.2	Pb	153.0	P	1187.0

The results showed there was no significant contamination of the soil, since the metal concentrations are typical of those found in uncontaminated soils (G.L.C., 1979).

(a) Batch Tests

Batch extraction tests were performed on the phenol dosed soils to determine the amount of the phenols that could be adsorbed from the soils by BODDMAM. The results of these experiments for the adsorption of phenol, 3-chlorophenol and 2,3-dichlorophenol from 10.0 g soil by varying weights of BODDMAM (0.0, 0.5, 1.0, 2.0 and 5.0 g) are shown in Figure 7.1. The releases of phenols are expressed as a percentage of the release from the unstabilised sample. The results indicate that 2,3-dichlorophenol, which has been shown to be the best adsorbed of the three phenols, required far less exchanged clay to stabilise it compared to the smaller, more soluble phenols. In the batch test, it was considered most likely that the phenols dissolved off the soil into the leachate and were then readsorbed by the exchanged clay. All of the concentrations measured were found to be well below the maximum solubility of the phenols in water so the relative insolubility of 2,3-dichlorophenol compared to phenol does not seem to be directly responsible for this effect. Perchem 462

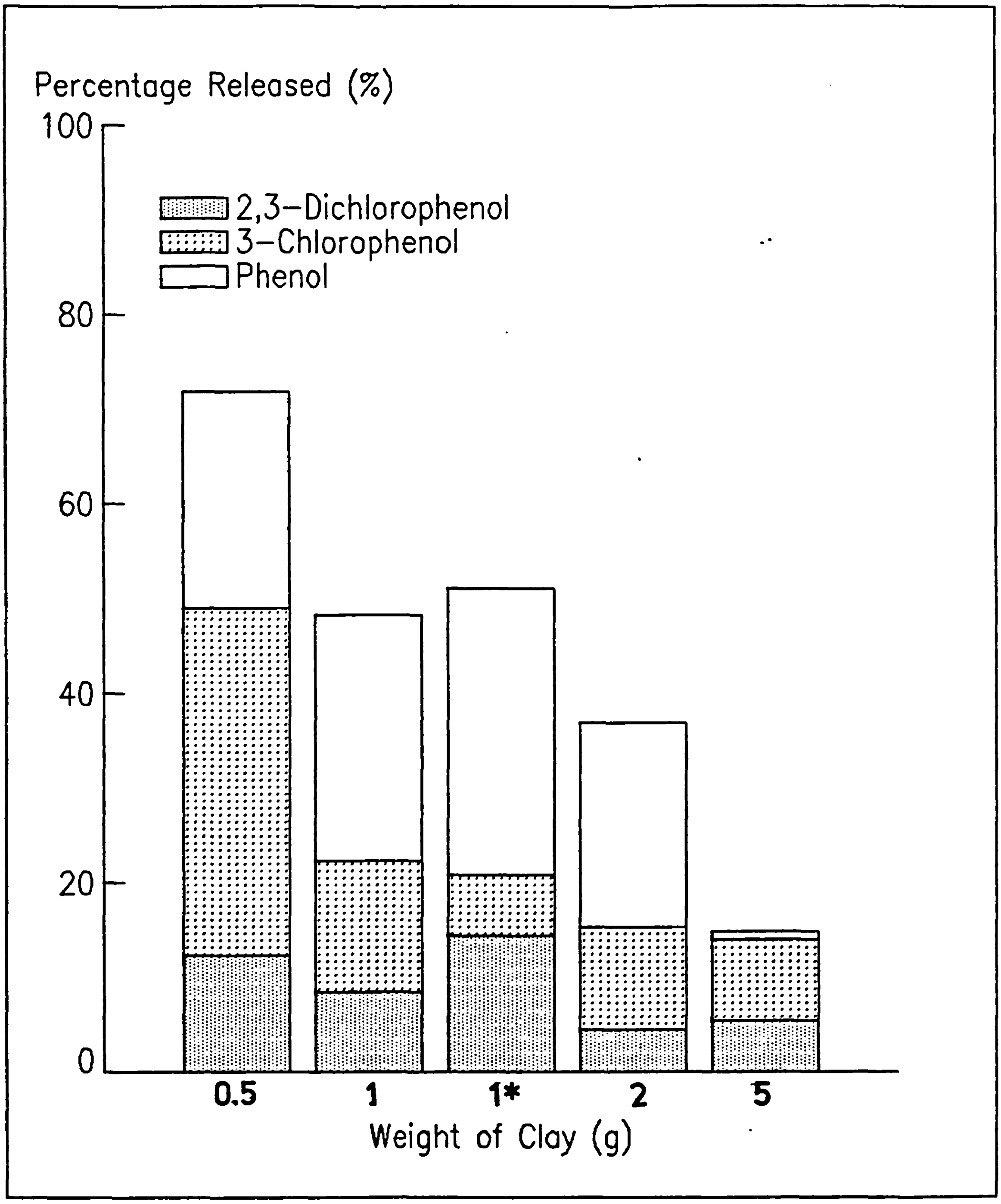

Figure 7.1: Results of Batch Test on Phenol Dosed Soil using BODDMAM (except 1* which uses Perchem 462).

adsorbs all three phenols in very similar quantities to BODDMAM (Figure 7.1), so Perchem 462 was once again used for the large scale column work. Mixing the clay as a wet slurry with the soil had no effect on the percentage of phenol adsorbed, indicated that adsorption takes place rapidly.

(b) Column Tests

The results of the column leach tests on the phenol dosed soils are shown in Figure 7.2(I). The retention of all three phenols by the exchanged clays in the soil are in excess of 95% of that released by the unstabilised soil columns. The pattern of release from the unstabilised soil (Figure 7.2(I) and (II)) showed a high concentration of phenols in the first few elutions, the concentration tailing off as the test progressed and most of the phenol had been removed from the soil. The pattern of release from the stabilised soil did not show the high maximum initial release of the unstabilised soil but a very gradual, almost constant, release of the phenols into the leachate. The slow release of the phenol by the stabilised samples would provide an opportunity for dilution of the leachate when the stabilised samples were finally disposed of.

7.3.2 Cement-based Stabilisation/Solidification

The soils were solidified with the exchanged clay, OPC and water. The mixes chosen were based upon the results of the mix development work (Section 6.3.2), the soil being substituted for dry filler.

(a) Unconfined Compressive Strength Tests

The results of the penetrometry and UCS tests are shown in Table 7.8. The results show that for the undosed soil the presence of the exchanged clay in the mix (Mix 8) gave a lower UCS than the mix with

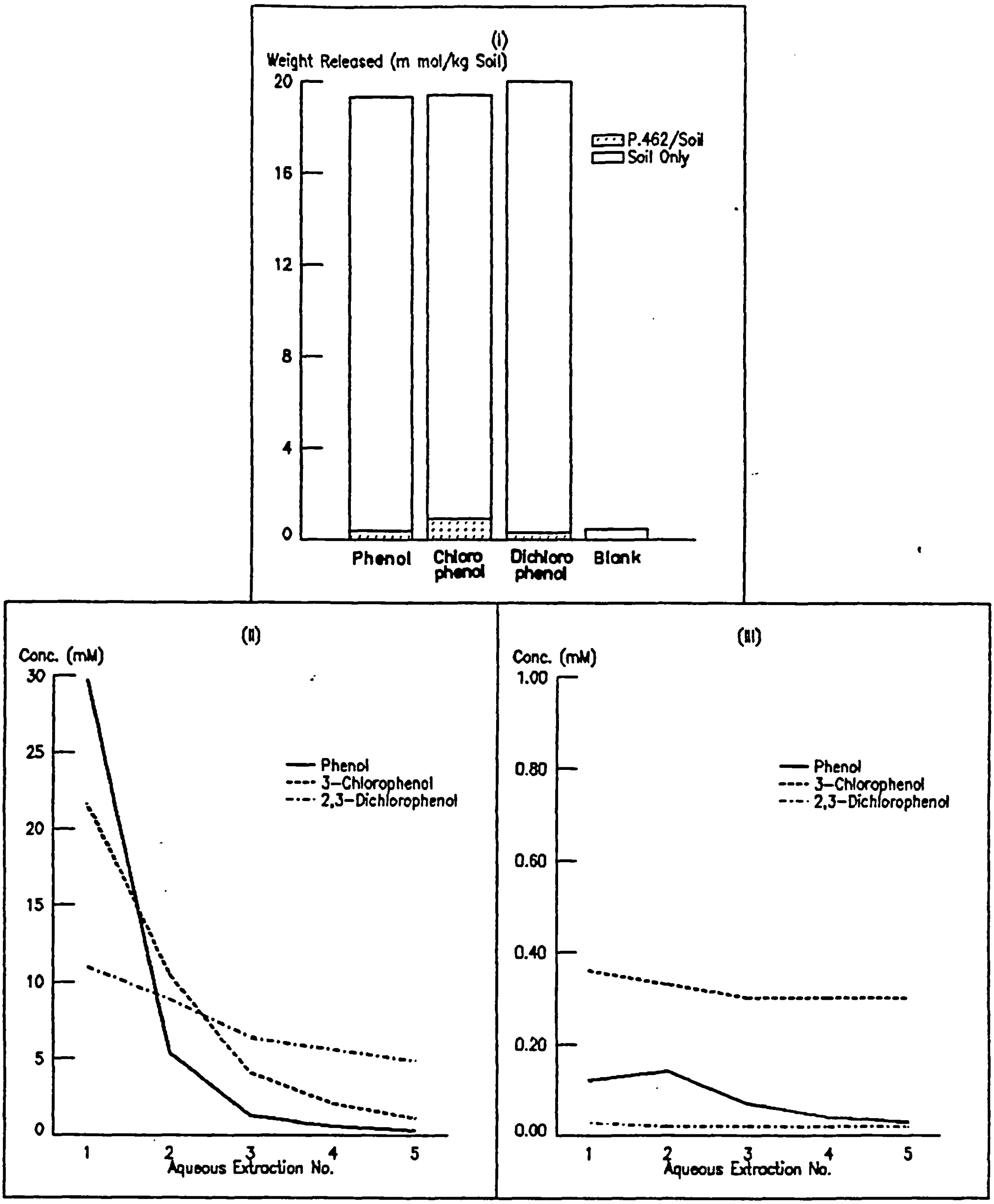

Figure 7.2: Release of Phenols from Soil Columns.

(I) Total Release from Soil and Perchem 462/Soil Columns

(II) Pattern of Release from Soil Column

(III) Pattern of Release from Perchem 462/Soil Colums

Table 7.8: Strength Test Results for Solidified Soil

Mix	Dosed Organic	Penetration (2.5cm) at 28 Days (10^6 Nm^{-2})	·Unconfined Compressive Strength (10^6 Nm^{-2})
1	Phenol	0.34	ND*
2	3-Chlorophenol	0.48	ND
3	2,3-Dichlorophenol	0.51	ND
4	Phenol	4.08	0.60
5	3-Chlorophenol	>4.76	0.27
6	2,3-Dichlorophenol	>4.76	0.66
7	Phenol	2.99	0.58
8	Uncontaminated	>4.76	0.59
9	Uncontaminated	>4.76	0.77

*Not determined as samples below minimum strength measurable on UCS machine.

inert filler ($CaCO_3$) (Mix 9). This is probably due to the detrimental effect of either the soil or the exchanged clay on cement hydration. The dosed soils with no clay had very low penetration strength even after 28 days (Mixes 1,2 and 3), demonstrating the effect of the phenols on the cement hydration. The UCS of the dosed control could not be measured as the samples crumbled as they were demoulded. The dosed soil samples with exchanged clay (Mixes 4, 5 and 6) showed a much greater strength than the controls and the samples were demoulded successfully to give satisfactory UCS values which were , except for the 3-chlorophenol samples, in excess of the "350 kNm^{-2}" rule-of-thumb. The UCS of Mixes 4 and 7, both of which contain phenol dosed soil but with different amounts of clay showed that Mix 4, with a lower weight of exchanged clay, gave a higher strength than Mix 7. This result was consistant with the results of the mix development work (Section 6.3.2) which found that increasing amounts of clay decreased the strength of the mix, although there must be a balance between the maximising phenol adsorption and minimising the amount of clay required.

(b) Dynamic Leach Test

The results of the dynamic leach test are shown in Figure 7.3. The Figure shows the amount of each phenol released from the control samples (Mixes 1, 2 and 3, Table 7.6) compared with the amount released by the stabilised samples (Mixes 5, 6 and 7), in a 28 day period. The results given are for equal weights of soil in all of the stabilised samples. The results are consistent with all previous experiments on the three phenolic compounds, 2,3-dichlorophenol being the best and phenol the least well stabilised (84% and 23% retained respectively compared to the controls). The addition of more exchanged clay to the phenol dosed soil gave a slightly improved retention (38%), this was due to the additional clay adsorbing the excess phenol present in the soil, above the maximum capacity of the clay. The control samples, unlike the stabilised samples, broke down after a few days of the test giving quasi-equilibrium conditions, with the consequent increase in surface area vulnerable to leaching.

(c) Equilibrium Leach Tests

Equilibrium leach tests were carried out after 28 and 56 days of curing (Figure 7.4(I) & (II) respectively). The amount of each phenol released after 56 days of curing is less than after 28 days. This effect was, presumably, due to continued hardening of the OPC matrix. The percentage of phenol and 3-chlorophenol released from the samples was higher than in the dynamic leach test due to the test requirement which ensured complete breakdown of the matrix. Conversely more 2,3-dichlorophenol was released during the dynamic leach test than from either of the equilibrium leach tests. This

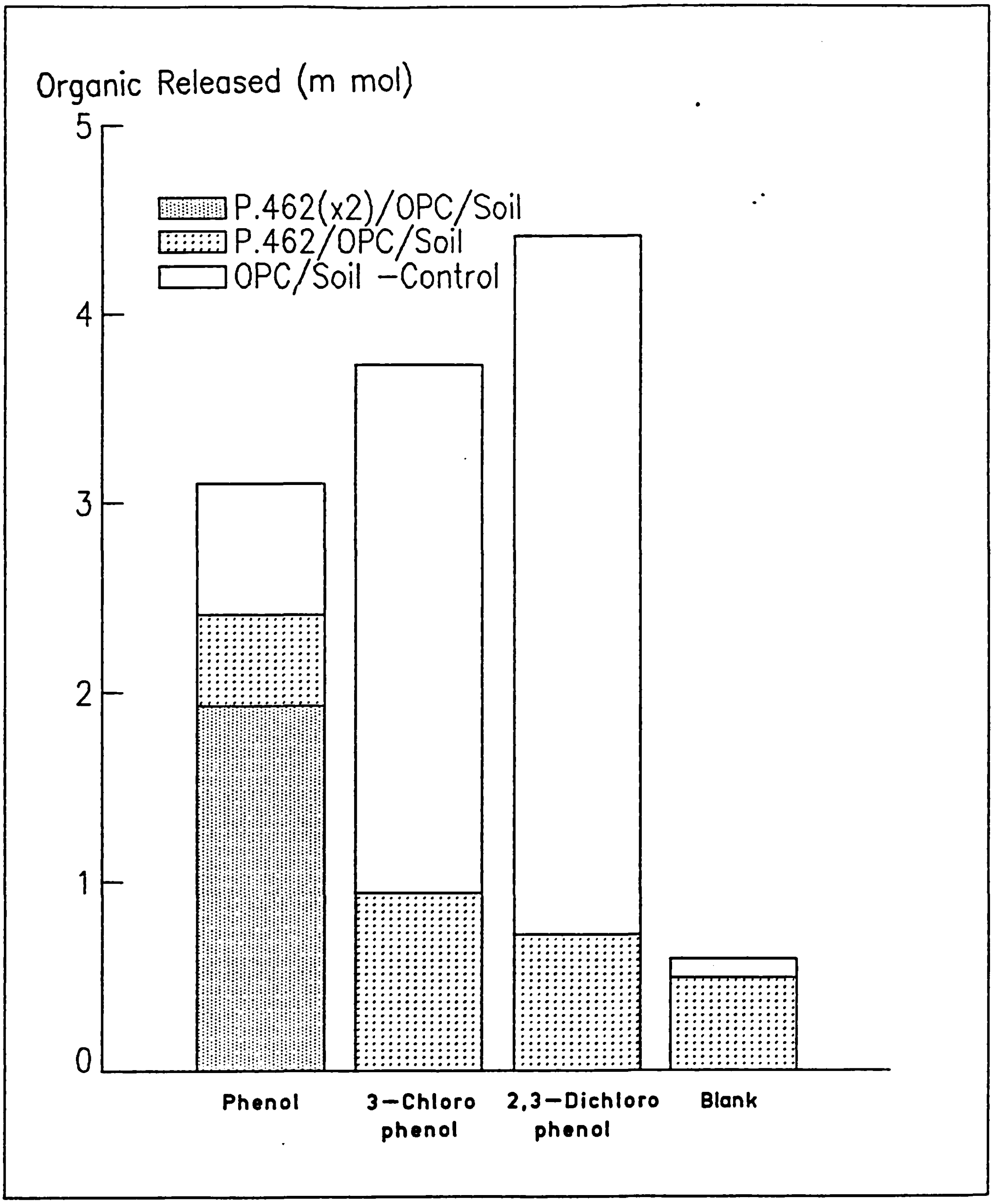

Figure 7.3: Dynamic Leach Test Results for Solidified Phenol Dosed Soil.

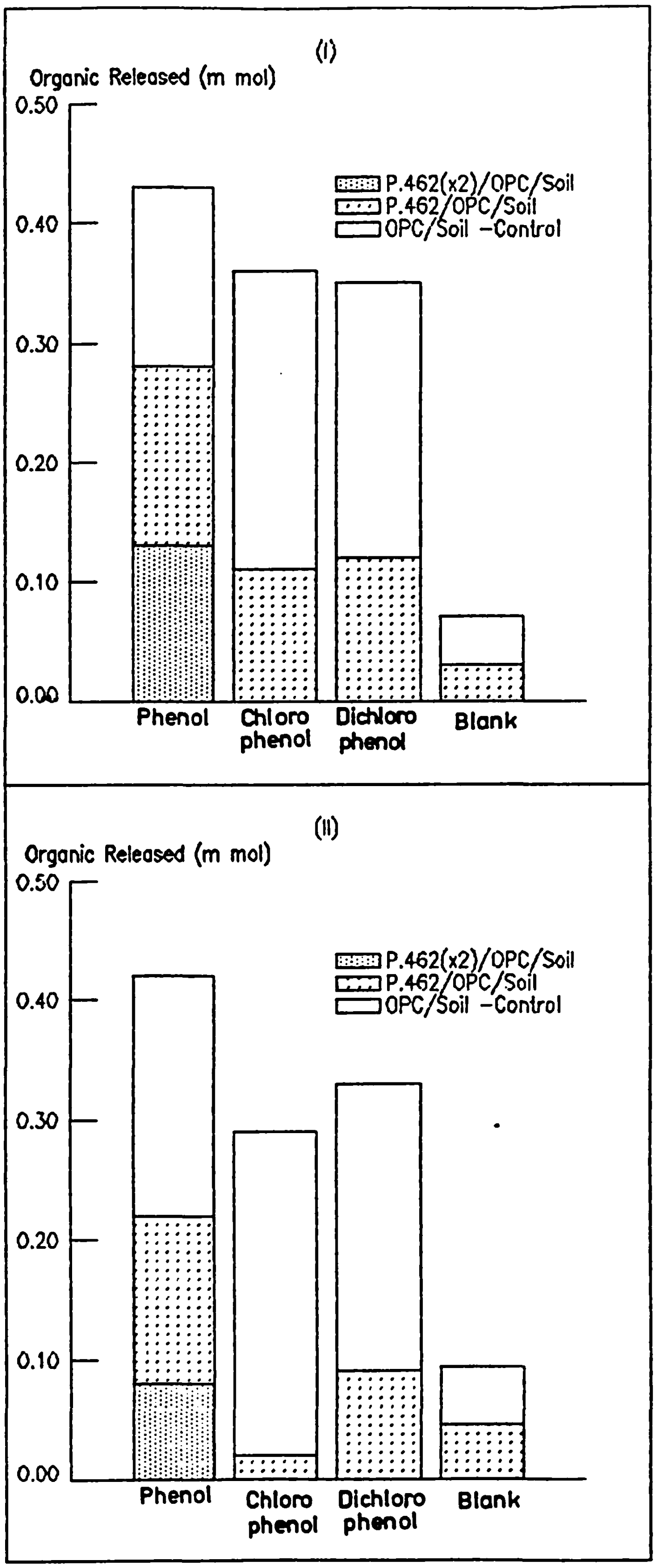

Figure 7.4: Equilibrium Leach Test Results for Phenol Dosed Soil after (I) 28 Days Curing and (II) 56 Days Curing.

effect was due to the low solubility of the 2,3-dichlorophenol in the limited amount of water used in the equilibrium leach tests compared to the dynamic leach tests.

7.3.3 Gasworks Soil

(a) Evaluation of Analytical Methods for PAH

Using the method devised by S. Baek (1988) eighteen PAH were characterised and the amount present quantified. Analysis showed that only 16 PAH could be detected in the aqueous samples the two final PAH having aqueous solubilities which were too low.

The recovery efficiencies of the 18 PAH are shown in Table 7.9. The overall recovery was 85.5 ± 5.0%. Table 7.9 also shows the concentration of PAH found in the blanks from batch and column tests. The blank was obtained by extracting distilled water in the volumes of leachate obtained from the batch and column experiments by the standard method. The clean-up and analysis of the blank samples was identical to that of the samples. The reproducibility of the analysis was checked by analysing the standard on four consecutive days. The results are shown in Table 7.9 as the percentage variation in peak heights.

(b) Soil Analysis

The contaminated gasworks soil was analysed for pH, the concentration of metals, the percentage of cyclohexane extractable material and the concentration of the 18 PAH. The results of this analysis are shown in Table 7.10. The extremely high concentrations of PAH in the soil sample were probably due to coal tar contamination from the storage tanks at the gasworks. Four metals were present in

Table 7.9: Evaluation of Analytical Method for PAH

PAH	Recovery from 1L Water (%)	Blank		Reproducibility over 4 days
		Batch Test	Column Test	
PHEN	53.4	1.50	3.75	90.5
ANTHR	71.4	0.75	0.76	87.7
FLUR	88.9	7.75	3.13	84.8
PYR	78.1	0.00	7.50	81.1
BcPH	84.2	0.40	1.05	99.6
CcdP	75.8	11.06	15.51	78.6
BaA	100.3	0.35	3.64	82.2
CHRY	102.0	0.00	3.11	87.5
BNTH	66.7	0.00	11.50	90.5
BeP	98.6	0.37	1.32	81.8
BbF	97.8	0.00	0.70	85.4
BkF	64.3	1.10	0.70	96.5
BaP	101.1	3.45	0.00	91.2
DahA	99.5	0.00	0.00	77.9
BghiP	90.0	0.00	0.00	92.7
I123P	107.2	0.00	0.00	79.4
ANTHN	70.3	0.00	0.00	86.7
Cor	51.8	0.00	0.00	89.3
Total PAH Released		26.73	52.67	

Average Recovery = 83.4 ± 4.1 %

Mean Reproducibility = 86.9 %

Table 7.10: Analysis of Contaminated Gasworks Soil

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pH 8.59

Concentration of Metals in Soil (mg kg^{-1} dry soil)

Metals in concentrations as "contaminants" - Cu 218.7; Ni 95.8; Zn 553.0; Pb 1373.0

Metals in soil at "typical" concentrations - Li 28.8; Na 1591.0; K 2808.0; Rb 16.0; Be 2.8; Mg 2326.0; Ca 10820.0; Sr 92.9; Ba 85.8; Al 21330.0; La 18.8; Ti 661.0; V 86.9; Cr 52.5; Mo 6.0; Mn 734.0; Fe 62300.0; Co 28.0; Ag 0.8; Cd 0.6; P 880.0.

Organic Constituents of Soil

Cyclohexane Extract (%) 9.46

Total PAH (mg/kg) 1882.39

Standard "6" PAH* Analysis (mg/kg) 694.98

Concentration of Individual PAH (mg/kg dry soil) - PHEN 8.36; ANTHR 89.40; FLUR* 111.28; PYR 104.08; BcPH 13.46; CcdP 63.28; BaA 197.18; CHRY 142.36; BNTH 342.20; BeP 35.86; BbF* 80.98; BkF* 61.70; BaP* 208.50; DahA 7.36; BghiP* 30.38; I123P* 202.50; ANTHN 27.88; COR 174.00.

PAH* = PAH defined by EEC Directive (1980) for analysis to give idea of total PAH concentration.

concentrations which would cause the soil to be classed as contaminated" by the GLC definitions, i.e. nickel, copper, zinc and lead. These metals were associated with coal tar storage (Rump et al., 1988).

(c) Batch Test

The total release of the PAH from the soil into the leachate is shown in Figure 7.5. The Figure gives the total weight of the PAH analysed and shows the dramatic effect of the exchanged clay on the PAH concentration, 90% of the PAH being retained with 10% clay (1.0 g/10 g soil). The EEC directive on PAH (1980) defines six PAH as "marker" compounds, and the concentration of each of these in the leachate are shown in Figure 7.5(II) from the soil alone and with the exchanged clay. The addition of larger quantities of exchanged clay i.e. up to 50% by weight, only slightly increased the percentage of PAH adsorbed from 90% to 94%

(d) Column Tests

The total release of PAH from the soil columns are shown in Figure 7.6(I). The Figure shows the sum of the PAH concentrations released into the leachate over the five extractions and also gives the PAH released by the exchanged clay/stabilised soil as a percentage of the amount released by the unstabilised control. In general, as the clay to soil ratio increased, the release of PAH decreased up to a 1:10 ratio, above which the additional clay seems to have only a very limited effect. All 18 PAH were found in the leachate from the first extractions of the control samples and the first 16 found for all of the stabilised samples. As the extractions progressed the higher PAH (14 - 18) were rarely found in the leachate in concentrations significantly greater than the background levels. This suggests that the higher molecular weight PAH were preferentially adsorbed compared to the smaller PAH.

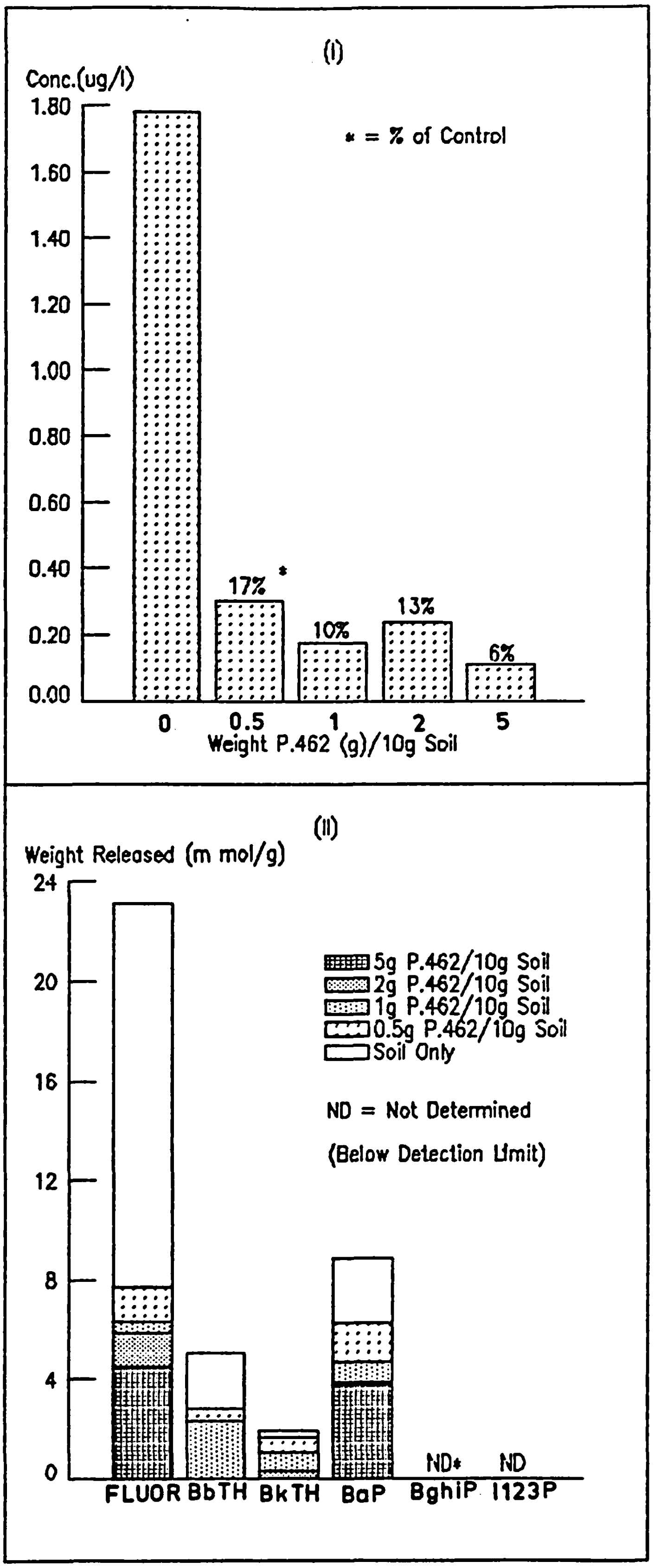

Figure 7.5: Release of PAH from Soil During Batch Tests showing (I) Total Release and (II) "Standard" Six PAH

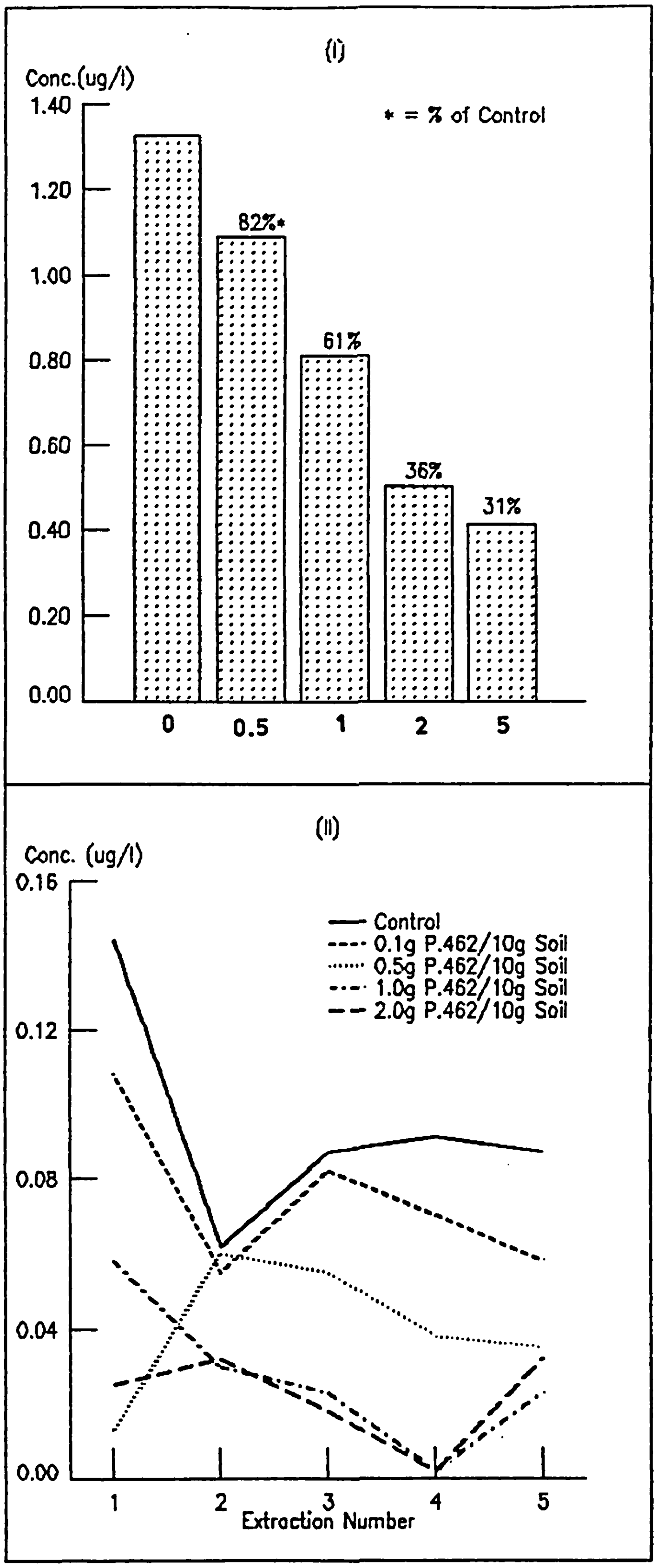

Figure 7.6: Release of PAH from Soil Columns showing (I) Total Concentration of PAH Released and (II) "Standard" Six PAH.

The release of individual PAH over the five extractions seemed irregular although the mean concentrations gave a constant order i.e. the control releases the most and the 2 g Perchem 462/10 g soil the least. Figure 7.6(II) shows the concentration of each of the 6 PAH, defined in the EEC directive (1980), in the leachate. Although the individual concentrations vary there were definite trends in release visible. These trends reflect those found for all 18 PAH and the order of retention remains the same.

7.4 SUMMARY

Phenol-dosed soils were stabilised using the quaternary ammonium exchanged clay. Batch tests showed that the release of the phenols was reduced to less than 15% for all three phenols. Column tests show that the adsorption of phenols by the clay was very high (>95% retained). Stabilisation/solidification of the phenol-dosed soils gave strengths higher than those with the soil alone, suggesting that the clay had a beneficial effect on the matrix. Leach tests on the solidified samples showed a reduction in the release of the phenols under both dynamic and equilibrium leaching conditions.

The soil from the gas works site showed considerable coal tar and PAH contamination. Stabilisation of the soil with the exchanged clay was successful, and the release of PAH in both batch and column leach tests was very low.

8.0 DISCUSSION

Inorganic industrial wastes which are contaminated with organic compounds can pose difficult and expensive treatment and disposal problems. This is particularly true in countries such as the United States where land disposal of untreated liquid wastes has been banned (Wiles, 1987). In such circumstances, cheap and environmentally sound processes for stabilising and solidifying such wastes clearly have a major role to play in waste management strategies of the future.

This work has shown that a carefully selected, natural adsorbent can be chemically modified to adsorb a wide range of organic compounds from aqueous and waste solutions. Promising stabilisation/solidification materials can be produced by the use of the adsorbents, together with cement, to treat wastes which would otherwise be unacceptable for treatment by conventional cement-based stabilisation/solidification processes.

The solidified organic compounds were shown, by microstructural analysis, to be well bound in the cement matrix. Microstructrual techniques were also used to characterise the cement phases and show how the additives such as phenols and the clay affect the hydration of cement.

The modified clay, which had been developed for the solidification process, was also used to treat contaminated soils, with a view to the development of an in-situ soil treatment process. The clay/soil mixes contained the hazardous contaminants well and the clay reduced the permeability of the soil, slowing the flow of water. The use of the clay in the treatment of contaminated soil has great potential, particularly for large sites with minor contamination problems.

8.1 ADSORPTION OF ORGANIC COMPOUNDS BY EXCHANGED CLAYS

Work by MacBride et al. (1977) and Mortland et al. (1986) has shown that clay-organic complexes have widely varying adsorption properties for organic compounds. Mortland et al. suggested that organophilic clays would make ideal adsorbents for use in, for example, chromatographic separation from solvents or from the gas phase. This study has investigated the properties of organophilic clays as potential adsorbents for the separation of organic compounds from waste streams and as an interface between the organic components of the waste and the cement in the S/S process.

Sodium montmorillonite, when exchanged with quaternary ammonium compounds, has shown the ability to adsorb a wide range of organic compounds from aqueous solution and more importantly, the organic components of industrial waste streams.

Quaternary ammonium compounds can displace metal ions from the interlamellar space of the clay, resulting in the expansion of the silicate layers (Theng, 1974) and thereby providing sites for the adsorption of organic compounds. The adsorption of organic compounds by these exchanged clays has been found to be controlled by three major factors:

(i) The properties of the quaternary ammonium cation, in particular its size.

(ii) The interaction of the exchanged clay with organic molecules (the adsorbent-adsorbate interaction).

(iii) The interaction of the organic molecules with the solvent used (the adsorbate-solvent interaction).

The size of the quaternary ammonium cation is important, not only for producing a hydrophobic interlamellar environment, but also for expanding the lamellae of the clay to permit the penetration(and hence adsorption) of organic compounds. Thus, in general, the adsorption of organic molecules was increased by using exchanged clay with longer-chained quaternary ammonium compounds. These results are consistent with the work by Cowans and White (1962) who found that for a range of alkylammonium clays, dodecylammonium bentonite best adsorbed phenol from aqueous solution. The presence of a benzyl group in the quaternary ammonium cation increased the hydrophobicity of the quaternary ammonium compounds and this caused a slight improvement in the adsorption of organic compounds.

The work examined the adsorption of three phenols by a range of fourteen QAS-exchanged clays under varying conditions. The phenols chosen were phenol, 3-chlorophenol and 2,3-dichlorophenol, which increase in acidity and hydrophobicity as the molecular weight increases. Phenols are common organic pollutants in wastewaters from, for example, steelworks, the pharmaceutical industry and the electroplating industry (Patterson & Kadudala, 1981).

The QAS's chosen to be exchanged with the Wyoming bentonite varied in aliphatic chain length from C_1 to C_{18}. Tetramethylammonium montmorillonite (C_1) adsorbed the least of all three phenols, and unlike the other QAS-exchanged clays adsorbed a similar number of moles of each phenol (Figures 3.1 to 3.3).

Mortland et al. (1986) found that the tetramethylammonium cation was not sufficiently large to cover all of the silicate surface. Consequently, such a surface will possess both hydrophobic and hydrophilic properties, bestowed upon it by the ammonium cation and the silicate surface respectively. Such a surface would provide an additional source of attraction for small. polar molecules like phenol and give rise to its larger than expected adsorption.

As the aliphatic chain length of the QAS was increased from C_1 to C_{18}, there was only a slight increase in the adsorption of phenol itself (Figure 3.1). 3-Chlorophenol showed a greatly increased adsorption at longer chain lengths and was adsorbed best by TDTMAM which contained a C_{14} carbon chain (Figure 3.2). 2,3-Dichlorophenol was adsorbed well and in similar amounts by TDTMAM and HDTMAM (C_{16}), with the greatest adsorption occurring onto ODTMAM (C_{18}) (Figure 3.3). The different amounts of 3-chlorophenol and 2,3-dichlorophenol adsorbed by the longer chain QAS can be understood by correlating the aliphatic chain length of the QAS with the increased interlamellar spacing created by the QAS upon exchange. 2,3-Dichlorophenol, the largest molecule of the three phenols tested, required the greatest interlamellar space for maximum adsorption. 3-Chlorophenol required slightly less. Wolfe (1985) found that low concentrations of phenol formed mono-layer complexes with the phenol parallel to the silicate surface on dodecylammonium montmorillonite. At higher concentrations the phenol was found to crowd the interlamellar space causing the dodecylammonium cation to stand erect, perpendicular to the clay surface causing an interlamellar expansion. Mortland & Pinnavia (1971) suggested that the phenols would be tilted in the clays so giving larger basal spacings than expected.

The presence of a benzyl group in the QAS slightly enhanced the adsorption by the long chain QAS, by increasing hydrophobicity. At shorter chain lengths the size of the benzyl group (and in the case of TMPAM (C_1) the benzene ring) became the dominant feature, particularly in the adsorption of 2,3-dichlorophenol (Figure 3.3). The size of the QAS and their ability to increase the interlamellar space was of great importance in maximising the adsorption of larger molecules. For example, DODDMA-Br, a QAS with two C_{18} aliphatic chains, was thought to be able to form pillars between the silicate layers, so holding them apart (Weiss A, 1963) and increasing the interlamellar space. Adsorption by DODDMAM of 2,3-dichlorophenol and phenol was considerably reduced compared to the single chain QAS adsorption. In the case of phenol this was due to the layers being too far apart, thereby allowing the free movement of the phenol in and out of the interlamellar space. For 2,3-dichlorophenol, the QAS may crowd the interlamellar space so preventing the dichlorophenol from being adsorbed. This effect was magnified by the use of TODAM which had four C_{18} aliphatic chains which filled the interlamellar space and prevented any of the phenols from being adsorbed to any appreciable degree.

Adsorption of a range of common organic pollutants, chloroform, acetone, benzene, toluene, naphthalene, aniline and phthalic acid by the exchanged clay showed a wide range of variation in the amounts adsorbed (Figure 3.15). Acetone, adjusted for losses by evaporation, was well adsorbed. Cation-dipole interactions of an electrostatic nature were suggested by Bissada et al. (1967) as playing an important role in the adsorption of polar organic molecules. Bissada et al. found that acetone formed a double-layer complex with montmorillonite. Wolfe et al. (1986) found that greater than 50% acetone adsorption caused significant crowding in the interlamellar space which forced the QAS cations perpendicular to the clay surface and so increased the interlamellar spacing.

Benzene, toluene and naphthalene were adsorbed from aqueous solution but to a lesser extent than phenol. Wolfe et al. (1986) found that benzene and toluene adsorbed by dodecylammonium montmorillonite from water formed a single layer in the clay. The interlamellar spacing suggested that crowding by the aromatic molecules caused the cations to tilt at an angle to the silicate suface. Cadena (1989) found that benzene was adsorbed to a much greater extent than toluene onto TMA-bentonite. He concluded that the interlamellar space created by TMA^+ provided preferred access to benzene over toluene.

The presence of an hydroxy group on the organic adsorbates seemed to enhance adsorption from water. For example, phenol was adsorbed more strongly than benzene. It was thought that the hydroxy group might enhance adsorption of organics by forming hydrogen bonds with the aliphatic chain of the QAS and also by interaction with the silicate surface. Doner and Mortland (1969) demonstrated the existence of hydrogen bonding between the adsorbed organic and QAS by observing the shifts of the carbon-oxygen and nitrogen-hydrogen stretching frequencies in the infrared spectrum of the amide and alkylammonium ions. Four QAS exchanged clays were prepared using QAS which contained hydroxy and ethoxy groups attached to the aliphatic chains of the QAS in the hope that these compounds would provide additional sites for hydrogen bonding, particularly for molecules which contain no electronegative group capable of hydrogen bonding to the aliphatic chains of the QAS. Adsorption of the phenols, chlorobenzene and chloronaphthelene by these modified QAS-exchanged clays was, however found to be no greater than with the non-hydroxylated QAS-exchanged clays. This suggests that either hydrogen bonding did not occur or was unable to enhance adsorption of the organic compounds.

Exchanged clay-adsorbate and adsorbate-solvent interactions were found to be two extremely important interrelated factors controlling the adsorption of a particular organic molucule. If the interaction of a particular molecule with the solvent was weak (eg 2,3-dichlorophenol or benzene with water, or phenol with hexane) then there was a large partition in favour of the exchanged clay surface, with the amount adsorbed being largely determined by the hydrophobicity of the clay surface. On the other hand, where adsorbate-solvent interactions were strong (e.g. phenol in water, or 2,3-dichlorophenol or benzene in hexane) then adsorbate-solvent interactions predominated and adsorption was found to be poor. Thus exchanged clays would be most ideally suited to a situation in which organic compounds were present in a solvent in which they were only sparingly soluble.

Wolfe et al. (1986) examined the adsorption of eleven common organic pollutants from aqueous solution by alkylammonium montmorillonites. He found that the clays exhibited removal efficiencies from 10 to 50% of the efficiency expected for the adsorption on activated carbon. This work has shown that the adsorption of the aqueous phenols by activated carbon, specifically developed for wastewater treatment, was of a similar order of magnitude to the adsorption by BODDMAM at the concentrations tested. At higher phenol concentrations activated carbon performed better than the clay. The adsorption capacity of activated carbon is dependent upon the specific microporosity and surface activity of each activated carbon (Bansal et al., 1988).

Spectroscopic studies of the QAS-exchanged clays showed the presence of the QAS on the clay, but the interactions of the terminal methyl groups with the clay surface, reported by Gonzales-Carreño et al. (1977), could not be observed (Figure 3.10).

Adsorption of the phenols occurred rapidly, and the equilibrium of phenol between the clay and solution was reached in under 30 minutes. The very slow partial desorption of the phenols after 56 hours was probably due to the release of any phenol adhering to the outer surface of the clay, or to the loss of the loosely bound QAS adsorbed in excess of the cation exchange capacity of the clay (Figure 3.5). Adsorption of QAS by clays in excess of their exchange capacities has been shown by several workers (Cowans and White, 1958; Weiss, 1963; Theng et al., 1967; Johns and Sen Gupta, 1967). For the larger cations, Furukawa and Brindley (1973) found that the excess QAS was resistant to removal by washing with water or organic solvents.

As the three organics chosen were acidic, the pH of adsorption was expected to have a significant effect upon the amount of phenol adsorbed (Figure 3.7). 2,3-Dichlorophenol and 3-chlorophenol were adsorbed in high concentrations at pH's above 4 and below 9. Above pH 4 the phenols would be partially ionized, indicating that the phenoxide ion was well adsorbed onto the clay. Above pH 9 the base started to attack the QAS on the clay, causing it to be displaced from the clay surface and so reducing the uptake of the phenols. Phenol behaved in a very different way from 3-chlorophenol and 2,3-dichlorophenol, reaching its maximum adsorption at pH 10. This effect was due to the complete ionization of phenol only at high pH values (pk$_a$ = 1.28 x 10^{-10}). This increases adsorption was due to the more reactive phenolate ions (Jones 1988), the opposing effect being the attack on the adsorbed QAS by the base causing desorption.

Zinc, cadmium and mercury were adsorbed to a limited extent by BODDMAM and the results indicated that at high concentrations these metals might displace the quaternary ammonium compound, so reducing the adsorption of 3-chlorophenol (Figure 3.9). Netzer & Ghanayem

(1984) suggested that the metals were first precipitated by the increase in pH as the clay was introduced into the solution. The second process was the adsorption of metals on the montmorillonite. Inskeep & Bahan (1983) showed that the increased pH increased the negative surface charge of the clay, and for unexchanged bentonites less competition between the hydroxonium ions at high pH and the metal ions, increased metal sorption (Garcia-Miragaja & Page, 1978). This effect, although important, was found to have little effect on the adsorption of organics from the real mixed waste streams which contained high metal concentrations.

Wyoming bentonite exchanged with the BODDMA cation was found to be the most effective overall adsorbent. A series of commercial exchanged clays of similar structures to BODDMAM were surveyed for their ability to adsorb the phenols and Perchem 462 was found to be the best. The commercial exchanged clay, Perchem 462, was used in the solidification work because of the limitations of producing BODDMAM on a larger scale in the laboratory, and with a long term view to potential future scale industrial application.

8.2 PHYSICAL AND LEACHING CHARACTERISTICS OF SOLIDIFIED MATERIALS

Preliminary experiments were carried out to determine the amount of cement and water that needed to be added to the exchanged clay to give a sample with good structural integrity and high setting rate. The ratios of clay to OPC chosen were 0.5, with a 0.35 water/cement (w/c) ratio. Comparative studies of the cement and cement/clay mixes showed that the exchanged clay mixes had a lower compressive strength than the cement pastes alone. The exchanged clay mixed well with cement, producing an homogeneous solid. Unexchanged clays did not mix well with cement and greatly affected the strength of the matrix, because the water gelling properties of the clay caused it to form lumps of clay in the cement mix. The detrimental effect of clays on cement is well documented, but the reason for strength loss is unknown. Microstructural studies of the cement/clay mixes (discussed in Section 8.3 following) showed how the clay alters the cement hydration reaction.

The phenols were adsorbed onto the exchanged clays from dilute aqueous solutions. The latter acted in a dual role, as a solvent for the phenols allowing free access to the clay surface and also as a solvent to remove the excess QAS from the surface of the exchanged clay. The presence of phenol, adsorbed onto the exchanged clay, had no effect upon the strength of the cement/clay matrix. The setting rates of the phenol-loaded exchanged clay/cement samples were rapid (>4.8 x 10^3 kN/m^2 in 24 hours) and the unconfined compressive strengths exceeded 4.0 x 10^3 kN/m^2 after 28 days (Figure 4.4); this value is twelve times a value commonly used for regulatory purposes for solidification products (Wilkinson, 1988). The setting rate and strengths greatly exceeded those of the WB/OPC samples, which did not reach the required strength during the 28 day curing period, although the setting rate was slower than the OPC/phenolic controls.

The major problem with the use of the exchanged clays was that they had excess QAS adhering to the outer surface of the clay. This excess QAS, due to its surfactant properties, caused foaming of the OPC mix when water for the hydration of the OPC was added, particularly at high W/C ratios. The addition of antifoam to the mix had little effect upon the foam. The most effective method of controlling the problem was found to be washing the exchanged clay prior to solidification. The effect of washing the clays was shown by the increased strength of the matrices (Figure 4.3) and the reduction in water absorption (Figure 4.6).

Two separate equilibrium leach tests were carried out on the solidified samples, each used ground samples and seven day extraction times. The equilibrium leach test did not attempt to determine the pattern of leaching, as its sole aim was to predict the concentration of the solidified organic that could be released from the sample. The equilibrium leach test was carried out after the samples had cured for 28 days and then repeated on a duplicate set of samples after 56 days. The longer curing time greatly reduced the release of the phenols from all of the samples, suggesting that the continued hardening of the OPC improves the stability of the mix.

The dynamic leach test was carried out on whole samples, so more accurately represents the behaviour of the solidified sample. Leaching, in the sample, is dependent upon factors such as the rate of water penetration into the sample and upon the durability of the matrix. The dynamic leach test was carried out on 28 day-old solid samples, which during the course of the test age over a further 28 days. The test results reflected the physical characteristics of the samples such as the permeability, as well as showing the pattern of release. The leachate chosen for both of the leach tests was distilled water, since the use of commonly used inorganic leachates such as buffered acetic acid was considered inappropriate when studying the leaching of organic molecules.

Long term dynamic leach tests were carried out on the exchanged clay solidified with cement. The experiment showed the long term stability of the QAS in the clay in the highly alkaline environment of the cement. The results showed that the release of QAS fell rapidly after a high initial loss, due to excess QAS still retained on the clay. QAS are biocides (Spooner, 1984) so a slight loss from the solidified sample would act to reduce the potentially harmful biodegredation of the solidified material.

The percentage of phenols released by the exchanged clay samples in the dynamic leach test was similar to that released in the equilibrium leach tests, suggesting that the exchanged clays stabilised the phenols well (Figures 4.10 to 4.12). If the phenols had not been stabilised by the presence of the exchanged clay, a high release of the phenol from both leach tests, or from the equilibrium leach test compared to the dynamic leach test would be expected. The release of phenol from both leach tests was observed from the Wyoming bentonite/OPC samples. These samples gave very low strength solids that released high percentages of the phenols from both of the leach tests. The effect of the permeability of the matrix was demonstrated by the OPC control, since during the dynamic leach test only low percentages of phenols were released. The equilibrium leach tests however, gave significantly higher releases. The exchanged clay samples released very low percentages of the phenols during both leach tests, only slightly higher releases occurring at the high phenol loadings. The excess phenols released at the higher loading had not been adsorbed into the clay and so were not so well stabilised. The presence of the exchanged clay greatly increased the stabilisation of the phenols compared to both the OPC only and the WB/OPC mixes. Of the two exchange clays tested, Perchem 462 showed slightly enhanced stabilisation of all three phenols compared to Perchem 97, a result predicted from the adsorption studies.

At the end of the dynamic leach tests, the compressive strengths of the samples were determined in order to study the effect of the phenols and the leaching on their strength (Table 4.9). The exchanged clay samples were weaker than the cement-only samples but had a much higher strength than the unexchanged Wyoming bentonite and the unwashed exchanged clay samples. In general, there was little difference in strength between the samples containing each of the phenols or between the two different exchanged clays.

Solidification of aqueous 3-chlorophenol/zinc solution with OPC and the exchanged clay produced good strength solids which performed well in leach tests (Figures 4.14 to 4.16). In the leach tests the highest release of 3-chlorophenol was from the samples containing high concentrations of zinc. This was consistent with the effects found in the adsorption experiments, which suggested that the zinc was able to displace the chlorophenol from the clay to a small extent. The percentage release of zinc, highest from the low dosed sample, showed that chlorophenol was unable to have the same displacing effect on the zinc. The adsorption of zinc seemed to show a concentration effect, most zinc being adsorbed from the higher concentration solutions.

Solidification of the pure organic liquids, chlorobenzene and chloronaphthalene, using the exchange clay and cement was very successful (Figure 4.17). The organic liquids could not be solidified by the cement paste alone because of their immiscibility with the aqueous inorganic matrix, but with the clay to act as an interface solidification was achieved. Leaching from the solidified samples was less the 5% of the total present, indicating sucessful stabilisation of the organic compounds.

8.3 MICROSTRUCTURAL ASPECTS OF THE S/S PROCESS

The physical macrostructural tests of the setting rate, permeability and strength of the S/S samples gave an indication of the effect of the clay additives on the cement hydration process. Microstructural studies showed how the different phases of cement were influenced by the exchanged clay and, indeed, how the exchanged clay was influenced by the highly alkaline cement.

X-ray diffraction analysis was used to determine the crystal phases present in the S/S samples, to characterise cement hydration reactions and to measure the interaction of montmorillonite with the QAS and other organic compounds. SEM was used, in conjunction with XRD, to observe the distribution of the crystal phases throughout the sample and to show the non-crystalline products. EDS was used to analyse individual crystals in the SEM samples.

Analysis of Wyoming bentonite showed that the clay was composed of flaky particles of 3 to 10 µm diameter. Jenningen & McAtee (1975) suggested that montmorillonite clay, when immersed in an aqueous QAS solution, aggregated with overlapping sheets in order to reduce the surface area exposed to the solvent. Wolfe (1985) noticed similar flocculation of the suspension with sodium montmorillonite immersed in dodecylammonium chloride solution. In this work the exchanged clay closely resembled the Wyoming bentonite, with individual flaky particles and no signs of curling or aggregation (Figure 5.4).

X-ray analysis showed that the unexchanged clay's $d_{(001)}$ reflection, i.e. the interlamellar space was approximately 0.994 nm. Exchange of the interlamellar cations for QAS cations increased the interlamellar distance to 1.969 nm for BODDMAM. The interlamellar spacing was related to the length of the carbon chain and qualitative relationships have been found to exist between the layer charge of the silicate, the shape and cross-sectional area of the molecules and the interlamellar spacing (Weiss, 1963).

Adsorption of some organic molecules by the exchanged clay caused swelling. For example, the adsorption of chloronaphthalene by the clay increased the interlamellar spacing to 2.506 nm, conversely chlorophenol adsorption did not increase the spacing. When the interlamellar organic cations are capable of solvation, van der Waal's interactions are exhibited between the organophilic residues of these and the adsorbed molecules. Accommodation of the adsorbed molecules in the interlamellar space may affect the orientation of the organic cation such that swelling occurs (Farmer & Mortland, 1966). For aromatic hydrocarbons such as chloronaphthalene, the molecules become closely packed in the interlamellar space, forming quasi-crystalline structures (Lagaly et al., 1973). The ammonium nuclei of the organic cations remain in contact with the clay surfaces and the alkyl residues adapt themselves to the molecules of the chloronaphthalene by conformational changes around the C-C bonds (Raussell-Colom & Serratosa, 1987). In high concentrations of organic liquids such as chloronaphthalene, long chain alkylammonium derivatives of montmorillonite form thixotropic gel structures with high liquid contents (Weiss, 1963 and Grim, 1968). Swelling of the exchanged clay did not occur in the presence of chlorophenol, possibly because the nature of the chlorophenol enabled the molecule to fit in between the QAS chains without causing significant disruption.

When the exchanged clay was incorporated into the cement paste the clay was found to break down into small flaky particles and clumps of flocculated particles much smaller than 1 µm (Figure 5.11). XRD analysis of the clay showed a reduction in intensity, which would correspond to the observed reduction in crystal size (Figure 5.10). The XRD spectrum suggested that there was a slight increase in the interlamellar spacing. Adsorption by the exchanged clay at high pH seen in Section 3.6 indicated that breakdown of the clay probably occurred around pH 9 where the maximum release of QAS occurred. The SEM did not confirm the breakdown of the clay (Figure 5.13). Analysis of the clay showed the QAS was still present up to its maximum exchange capacity up to pH 11 (Table 3.5). Adsorption of organic species occurred up to pH 12, although the effect of the high pH on the organic molecules themselves had an effect upon the magnitude of adsorption (Figure 3.7).

Many organic compounds are widely known to have retarding effects upon cement hydration and to cause significant weakening of the cement matrix (Section 1.5.2(a)). This work has studied two contrasting organic compounds, 3-chlorophenol, a low melting point, polar organic solid and chloronaphthalene, a hydrophobic aromatic liquid.

The hydration of chlorophenol dosed cement paste was shown, by XRD analysis, to be inhibited compared to the undosed pastes after 28 days (Figure 5.5). The percentage of C_3S, originally present in the cement,which hydrates to give C-S-H gel and calcium hydroxide, was 42% greater in the high chlorophenol-dosed samples than in the undosed paste. Ettringite, a hydration product which forms in the early stages of hydration, slowly converts to monosulphate as the paste ages. In the chlorophenol dosed samples the ettringite was present in far higher amounts than in the undosed sample. By 28 days there appeared to be little conversion of ettringite to monosulphate, whilst in the undosed paste virtually no ettringite remained. The large amount of C_3S and the persistence of ettringite showed that the chlorophenol was interfering with cement hydration.

The mechanism of set retardation in Portland cement paste containing organic admixtures was most extensively reviewed by Young (1972) and Jones (1988). Their observations agree well with the results of this work. Young concluded that, although experimental data was scarce, the probable mechanisms of retardation would include two distinct phases. Initially, the organic admixture would be concentrated on to the aluminate component, which would increase the reactivity and hence the formation of aluminate products (e.g. ettringite). Subsequently, after the period of initial reactivity, retardation of C_3S hydration occurred which would lead to a dormant period, the length of which would be determined by the effect of the admixtures on the nucleation of calcium hydroxide.

The SEM micrographs of OPC paste showed the effects of increasing chlorophenol concentrations on hydration. At the highest chlorophenol concentrations large needle-crystals, over 30 µm long, appeared in the paste. EDS analysis showed these crystals were composed of the calcium salt of chlorophenol (Figure 5.7). Roy et al. (1986) and Skipper et al. (1987) have examined the effect of parachlorophenol and parabromophenol on cement pastes. Using SEM and backscatter imaging they showed that parachlorophenol was evenly distributed throughout the cement matrix, whilst parabromophenol was inhomogeneous. It is possible that the parachlorophenol was able to form phenolate salts in a similar way to the observations in this work, and so became spread throughout the matrix, whilst parabromophenol remained concentrated in the pore solutions.

Chloronaphthalene did not mix with cement paste but formed a layer on top of the sample. The chloronaphthalene had no observable effect on cement hydration.

The addition of the exchanged clay to the cement paste had a weakening effect upon the macrostructrual strength of the matrix compared to the cement-only paste (Section 4.3.2(a)). The use of unexchanged Wyoming bentonite with cement had an even greater effect on the strength of the mix. This was partially due to the swelling properties of the clay in water, which removed the water required for hydration of the cement, and partially due to the effect on the clay itself on cement hydration. Microstructurally the clay strongly affected the hydration phases of the cement modifying the final hydration products.

Over a curing period of 7 to 28 days, cement paste showed the expected decrease in the ettringite peaks and increase in the final hydration product, calcium hydroxide. The cement/exchanged clay mix had almost double the percentage of C_3S remaining after 28 days compared to the OPC paste. The ettringite peak was initially absent in the cement/clay mix, but developed between 7 and 14 days, to eventually be 144% larger than the corresponding peaks in the cement paste after 28 days (Figure 5.17). The increased ettringite levels, formed between 7 and 14 days, were probably one of the main causes of the reduction in the strength of the cement/clay paste; Wieldeman (1982) suggested that the late formation of ettringite would disrupt the cement matrix if it formed after the initial set of the mix had taken place.

The SEM micrographs of the exchanged clay/cement mix showed that the surface of the cement paste was covered with fine needle-crystals less than 1 µm long (Figure 5.20). The composition of the crystals is unknown, but it is possible that they either consist of (i) the excess ettringite, (ii) the clay, after it had been peptized in the alkaline cement paste and recrystalised as the paste cured,or (iii) due to the interaction of the clay and ettringite phases.

Stabilisation of aqueous chlorophenol solutions by exchanged clays and solidification of the clay/organic mixes with cement produced a solid which performed well in macrostructural tests. Microstructurally the solidified clay samples, with chlorophenol adsorbed up to the maximum exchange capacity of the clay, had no effect upon the hydration of the cement compared to the undosed exchanged clay/cement samples (Figure 5.22). High chlorophenol concentrations, above the exchanged capacity of the clay, strongly inhibited the hydration of the cement. The sample had a low strength, similar to the chlorophenol/cement mix. These results showed that, once the clay had become saturated with the organic compound, it was unable to adsorb further chlorophenol, but before that point the clay was able to prevent the chlorophenol from interfering with the cement hydration.

Chloronaphthalene could not be incorporated into the cement matrix alone, but formed a layer on the surface. Mixed with clay however, it formed a thixotropic gel which could be dispersed in the cement matrix. The microstructural studies of the chloronaphthalene solidified product showed that, even at concentrations in excess of the exchange capacity of the clay, the chloronaphthalene was incorporated into the cement matrix and did not inhibit cement hydration.

These results were particularly encouraging for future work on development of clays as adsorbents of organic compounds from mixed inorganic/organic wastes. The clays enable the organic constituents to be incorporated into the cement S/S mix and adsorption of the organic constituents prevents inhibition of cement hydration and hence allows the setting of the cement matrix.

8.4 THE ABILITY OF EXCHANGED CLAYS TO TREAT INDUSTRIAL WASTES

The use of Perchem 462 has been found to be a very effective pre-solidification adsorbent for the organic components of three mixed industrial wastes. The industrial wastes contained organic components in excess of 4% and for this reason could not be treated by conventional cement-based stabilisation/solidification processes.

In the mixes which were made up, an inert filler (calcium carbonate) was used to reduce the cement content to as low as 12% and thereby more accurately simulate a commercial solidification mix. This could only be achieved, however, by (i) pre-adsorbing the waste onto the clay and (ii) washing the clay to remove residues of the waste remaining when the adsorption capacity of the clay had been saturated. If this was not done, hydration of the mixes was found to be inhibited and setting delayed or prevented altogether. The work with the three wastes indicated that there was, in all cases, a residual organic element which was not adsorbed, and this was presumed to be the cause of delayed hydration in the mixes with unwashed clays. These compounds would probably comprise the more hydrophilic, water soluble, waste components.

The setting rates and unconfined compressive strengths observed were encouraging (Tables 6.4 & 6.7). In all cases, where the waste was properly solidified and water alone was used for cement hydration, a penetration strength in excess of 4.8 x 10^3 kN/m^2 was obtained after 7 days and a compressive strength (after 28 days) of >540 kN/m^2. The strengths were, in fact, higher than current working values and therefore there exists some scope for the reduction in the amount of cement (26% in most mixes) used. Leaching tests indicated that the amount of TOC leached from a unit weight of solidified waste could in some cases be as low as 1% of that present in an equivalent weight of unsolidified raw waste (Figure 6.8). This was considered to be an extremely encouraging result for the three wastes, which would be impossible to solidify satisfactorily using present commercial formulations.

The porosimetry studies described in Section 4.3.2 showed that the solidified matrix contained small amounts of entrapped air. Jones (1988) found that 0.05 to 1% entrapped air significantly reduced the degredation of the cement matric after freeze/thaw testing. This suggests that the presence of air caused by the excess QAS may have an advantageous effect upon the durability of the solidified samples.

The use of adsorbents for the organic components in mixed industrial waste streams extends the potential use of cement-based stabilisation/solidification processes to a wider range of industrial wastes. Factors influencing the use of exchanged clays in a cement-based process would include the cost of the raw materials, especiallly the exchanged clay adsorbent and the content of the waste eg. pH. Additionally, some modifications in the present methods of solidifying inorganic wastes would be required, which would include mixing the exchanged clays with the waste to allow the adsorption of waste components. The clay plus adsorbed waste would then be amenable to recovery by filtering and washing to remove poorly adsorbed waste components. The washed clay plus adsorbed waste could then, probably, be combined with cement, inorganic inert wastes and water (or inorganic aqueous wastes) to form the final mix.

Of the limited number of alternative treatment options for this kind of waste, incineration would probably represent the most likely competitor to stabilisation/solidification. For the industrial wastes containing low organic content, technical factors would require that the calorific value of the waste stream entering the incinerator be increased by the addition of fuels etc., which inevitably increases costs. In general terms, the cost of incineration could be up to ten times greater than the S/S methods described in this thesis and, while under proper conditions it can be shown that incineration will completely destroy organic components, the flyash produced by this process may require further treatment before disposal. Thus, while incineration has an advantage over stabilisation/solidification in that organic compounds are usually completely destroyed, the high costs of incineration and toxic inorganic by-products would suggest that stabilisation/solidification could be an inexpensive and effective alternative. Since the toxic components within a cementitious matrix in a stabilisation /solidification process are not destroyed, however, validation through, for example, field trials, are required so that the long term effects of weathering can be addessed.

8.5 TREATMENT OF CONTAMINATED SOIL BY EXCHANGED CLAY

The treatment of contaminated land has become an important environmental problem, as the potentially harmful consequences for man, plants, animals and the abiotic environment are realised (Rörsch, 1985). Contaminated soils occur at mining, industrial or waste disposal sites; for example, disused town gas production sites, railway sidings, oil refineries and landfill sites. The type of contamination in the soil varies widely depending upon the previous uses of the site. Treatment of contaminated soil usually involves either incineration of the soil, solvent or steam extraction or removal to a hazardous waste landfill site. These treatments are expensive and only suitable for highly contaminated soils which occur on valuable sites. The development of cheaper, in-situ treatment methods for contaminated soils would allow the development of less valuable derelict sites and the treatment of soils, rather than the removal of the problems to a landfill site elsewhere.

Exchanged clays have been shown to adsorb a wide range of organic molecules from aqueous solution and from industrial wastes. Their possible application to stabilise soils and their potential use in the S/S process as dry fillers were therefore examined.

The first soils that were tested were soils which had been dosed with phenol, 3-chlorophenol and 2,3-dichlorophenol. Batch tests on the soil/exchanged clay mixes indicated that the phenols were well retained by the clays and, as shown by Boyd (1982) for natural clay soils, the increasing degree of chlorination increased the adsorption. Boyd also showed that the introduction of a substituent on to the phenol increased the adsorption by the clay soils. Meta- or para substituted phenols were better adsorbed than the ortho-substituted, due to steric hindrance of potential hydrogen bonding between the phenol and the clay in the latter. These results were reflected in the trends from the batch and column tests for the phenol dosed soil, in which phenols were adsorbed in the order 2,3-dichlorophenol > 3-chlorophenol > phenol (Figures 7.1 and 7.2). The column tests gave greater than 95% retention for all three phenols over the extraction period. This was very encouraging as the leachate was made strongly alkaline to facilitate maximum release from the acidic phenols..

Stabilisation and solidification of the phenol dosed soil by the exchanged clay/cement mix produced acceptable solid products, unlike the soil/cement controls which had no strength after 28 days (Table 7.8). Leach tests on the dosed soils showed that chlorophenol and 2,3-dichlorophenol were well stabilised (Figures 7.3 and 7.4). Phenol required twice the amount of clay in the solidification mix to produce reasonable retention values.

The results from the phenol dosed soils suggested that stabilisation of contaminated soils by the exchanged clay may provide a suitable method for containment of the hazardous constituents. The potential of the clays for the treatment of common contaminants in soils was confirmed by the use of the clays to stabilise soil from a derelict gas works site. The soil was heavily contaminated with coal tar and had PAH concentrations in excess of 1.8 g/kg dry soil.

Batch tests on the gasworks soil stabilised with the exchanged clay showed that 1 g of the exchanged clay per 10 g soil could reduce the release of PAH to 10% of that of the unstabilised soil (Figure 7.5). The release of individual PAH was halved by the use of 10% exchanged clay in the soil. This is particularly important for PAH's such as Benzo(a)pyrene which are highly carcinogenic and have been shown by Hosler et al. (1988) to be poorly removed from the soil by biodegredation. Column tests on the soil showed that the presence of the clay significantly reduced the release of PAH (Figure 7.6).

This exploratory study into the use of the exchanged clays for the in-situ treatment of contaminated soils has shown that the clays are well able to adsorb the hazardous constituents from the soil. The clays are also able to physically stabilise the soil, especially if it has a high fraction of sand, and to reduce the percolation of water through the soil.

8.6 FUTURE WORK

This study has shown that QAS-exchanged clays are able to adsorb a wide range of organic compounds from aqueous solution or pure liquids. Cement-based S/S of organic compounds using the exchanged clay has been shown to produce a durable solid product with low releases of the organic compounds during leach testing. Microstructural studies of the S/S products have shown that the presence of the clay reduced the detrimental effects of 3-chlorophenol on cement hydration, however the clay itself altered the cement hydration reaction. Studies on wastes have shown that the clays adsorbed most of the organic components of the waste and after washing could be solidified to produce solid products. The application of the exchanged clays to stabilisation of contaminated soils has shown that there is potential for their use, either as stabilisation additives on their own, or as part of a cement-based S/S process.

During the course of these studies it has become clear that the whole area of cement-based stabilisation/solidification of hazardous wastes requires continued scientific investigation in order to fully optimise the processes for a wide range of hazardous wastes and to enable the prediction of the long-term behaviour of the product in the environment.

Areas which warrant investigation in the future include:-

1. An in-depth study into the characteristics of organic contaminants in industrial wastes, which would include a survey of the frequency of occurrence of the individual organic compounds and the inorganic compounds commonly associated with them.

2. To extend the development work for industrial wastes to produce a broad-spectrum clay-based or mixed clay/activated carbon adsorbent for treatment of organic-contaminated wastes without the need for a filtering or post-adsorption washing stage.

3. Detailed macro- and microstructural studies of the effects of mixed metal/organic solutions on cement hydration and the effect of these co-adsorbed onto clays and other adsorbents.

4. Work is required to develop testing procedures for S/S processes to give a clear idea of their behaviour over long time periods in the field. Tests which require development include:-
   (a) Strength tests, which more accurately reflect the confined pressure exerted on the S/S product in the field.
   (b) Leaching tests which would give a realistic idea of the potential release of stabilised contaminants, and from these results the development of a model to predict release over a longer time period.

(c) Correlation between gas and water permeability so that gas permeability could be used to assess permeability of S/S samples rapidly and with great accuracy.

5. Pilot scale studies of the exchanged clay/cement S/S process to fully assess the technical and economic aspects of the process on a larger scale.

6. Long-term field trials of S/S processes to assess the behaviour of a number of adsorbents with hazardous wastes .

7. Pilot scale studies and field trials on the use of the exchanged clay for the in-situ treatment of contaminated soils.

9. SUMMARY AND CONCLUSIONS

1. The major deficiencies of cement-based stabilisation /solidification (S/S) processes are their inability to treat inorganic wastes contaminated with organic material or organic wastes. This work has shown that this deficiency can be successfully remedied by the use of organophilic clays as adsorbents prior to cement-based S/S.

2. A range of organophilic clays were produced by the exchange of quaternary ammonium cations with the interlamellar sodium cations of Wyoming bentonite. This caused an expansion of the clay's silicate layers. For example, exchange of benzyloctadecyldimethylammonium cation led to an expansion of 0.975 nm. This created a hydrophobic environment in the interlamellar space which facilitated the adsorption of organic molecules and decreased the influence of the charged silicate layers. In general, the longer-chain QAS-exchanged clays adsorbed the organic compounds best, due to the chains increasing the interlamellar spacing. The exchanged clays prepared by this process were shown to adsorb a wide range of organic compounds from a number of solvents. The compounds chosen for this work were typical of those which commonly occur in industrial waste streams.

3. From the fourteen QAS-exchanged clays examined Wyoming bentonite exchanged with the benzyloctadecylammonium cation was the best overall adsorbent. In contrast, tetraoctadecylammonium montmorillonite (TODAM), with four C_{18} aliphatic chains, was a poor adsorbent, probably because the aliphatic chains of the QAS completely filled the interlamellar space preventing penetration of the potential adsorbates.

4. The organic compounds that were best adsorbed were those which had the least affinity for their solvent. For example, the experimental data has shown that 2,3-dichlorophenol, a fairly

hydrophobic molecule, was adsorbed well from aqueous solution but to a lesser extent from hexane, in which it was more soluble.

Many industrial wastes have high aqueous contents, but the organic compounds present are frequently only sparingly soluble and hydrophobic, so they can be present in emulsion or colloidal form or absorbed onto suspended particulate material. The interlamellar space of an exchanged clay provides a hydrophobic environment for the adsorption of these compounds.

Adsorption of hydrophilic molecules from non-polar solvents, for example, phenol from hexane, was facilitated by the charged clay surface and polar head of the QAS.

5. For the treatment of organic wastes it is important to show the difference between (i) bonding interactions, (ii) adsorption and (iii) physical absorption of the organic components of the wastes. This is because for the successful S/S of wastes the components must be firmly held either by chemical bonding or adsorption to ensure long term stability. Detailed analysis by Fourier Transform Infrared Spectroscopy (FTIR) showed no evidence of bonding interactions between the adsorbed organics and the aliphatic chain of the QAS. This technique was unable, however, to give further information on the adsorption mechanisms.

6. Adsorption of chloronaphthalene by benzyloctadecyldimethylammonium montmorillonite (BODDMAM) caused an expansion of the interlamellar space to 2.506 nm. The expansion was caused by the accommodation of the chloronaphthalene in the interlamellar space which may have caused re-orientation of the QAS-cations such that swelling would occur. Adsorption of 3-chlorophenol by BODDMAM caused no expansion of the interlamellar spacing.

7. The long term stability of the quaternary ammonium cations and the organic compounds adsorbed onto the clay was assessed by a series of rigorous extended adsorption experiments in water. The results showed that the adsorbed species, QAS and other

organic compounds, remained on the clay even after 56 days testing.

8. Due to the high alkalinity of cement paste, the adsorption capacity of the exchanged clay over a range of pH was studied in detail. pH affected the adsorption of the organic compounds onto the exchanged clay, particularly the acidic phenols. 3-Chlorophenol and 2,3-dichlorophenol were adsorbed best in the pH range 4 to 9, whereas the maximum adsorption of phenol occurred at pH 10. Neither the adsorbed organic compounds nor the QAS were desorbed when the clay was washed with high pH solutions (pH 11), similar to the pH of hydrating cement paste. From scanning electron microscopy (SEM) studies of clay/cement mixtures, high pH values, similar to those found in hydrating cement paste, caused the clay to break down into smaller crystallites. As indicated in the studies of pH effects on adsorption, however, this effect did not appear to lead to loss of the adsorbed organics.

9. The behaviour of the clays in the presence of metal ions was considered important, in view of the potential use of the clays for the treatment of inorganic waste streams contaminated with organic compounds. Studies were undertaken to address the degree of competition between organics and metals for adsorption sites on BODDMAM. The results showed that Group IIB metal cations displaced 3-chlorophenol from the clay to a small extent. This was considered to be caused by either back-exchange of metal cations with the QAS, or because of displacement of the 3-chlorophenol from the interlamellar space by the metal cations.

10. In order to scale up the experimental work to use the QAS-exchanged clays in cement-based S/S processes, commercially produced exchanged clays were surveyed to determine if they could be substituted for BODDMAM. Perchem 462, a QAS-exchanged montmorillonite with one aliphatic carbon chain between C_{14} and C_{18}, was found to be suitable.

The use of the commercial exchanged clay in a cement-based S/S mix caused foaming in the cement matrix due to the excess QAS present on the clay. This effect decreased the strength and increased the permeability and porosity of the matrix compared to cement paste alone. The amount of entrapped air could be greatly reduced by washing the clay prior to use. The presence of some entrapped air in the cement could, however, be advantageous in reducing the effects of freeze-thaw on the matrix when exposed to field conditions.

11. A widely accepted method for assessing the intergrity of solidified materals is exposure to potential leachants under laboratory conditions. The suitability of the QAS-exchanged clay for cement-based S/S applications was first assessed by testing a series of clay/cement mixes. The long-term stability of the exchanged clay in the cement matrix was shown by extended leaching tests to be good. Release of excess QAS was slight and, with respect to future waste disposal applications, the biocidal properties of the QAS released may be beneficial in reducing biodegredation of the solidified matrix.

12. The presence of exchanged clay in the cement matrix was found to greatly affect the microstructure of cement, causing initial inhibition of tricalcium silicate (C_3S) hydration and increasing ettringite formation to 144% of that in the cement paste alone after 28 days. The excess ettringite was thought to contribute significantly to the poor macrostructural strength of the clay/cement matrix. SEM micrographs of the clay/cement matrix showed that the surfaces were covered with mats of fine needle crystals, the composition of which was not known.

13. Phenolic compounds in aqueous solution could be solidified, in low concentrations, by the cement paste without the use of exchanged clay. Equilibrium leach tests, which involved crushed samples shaken in aqueous leachate for 7 days, showed however, that the phenols were not stabilised as they were readily released during testing. In contrast, phenols could be

solidified with the exchanged clay at weights up to one hundred times that in the cement-only controls. Even at the highest loading, the clay/cement mix retained the phenols well under equilibrium leaching conditions.

Dynamic leach tests, using monolithic samples in stirred aqueous leachate, indicated that phenol retention by the cement-only control matrix was comparable with that of the exchanged clay/cement matrix, over the duration of the test, for samples containing low concentrations of the phenols. For higher concentrations, however, fully analogous cement-only controls could not be prepared due to the phenols' solubility limitations. At low phenol concentrations the comparable results of the cement-only controls and the cement/clay mixes in the dynamic leach test were due to the nature of the test, in which the permeability of the sample was an important factor in governing the amount released. The low permeability of the cement matrix reduced the contact time between the aqueous leachate and phenol entrapped in the cement matrix.

14. Mixtures of zinc and 3-chlorophenol were solidified by the exchanged clay/cement mix. The release of 3-chlorophenol was slightly enhanced in the presence of high concentrations of zinc in both dynamic and equilibrium leach tests, but the release was less than that expected in the light of the results from the adsorption studies.

15. Chlorobenzene and chloronaphthalene could not be solidified by cement alone as both were highly immiscible with the inorganic cement paste. The exchanged clay/cement mix allowed chlorobenzene and chloronaphthalene to be incorporated into the cement matrix and to be retained during leach testing.

16. Phenols were found to inhibit the hydration of cement. X-ray diffraction (XRD) analysis showed that significant levels of C_3S were still present after 28 days. The presence of phenol in the cement matrix was also found to stabilise ettringite, slowing its conversion to monosulphate. SEM analysis of the 3-

chlorophenol/cement mix showed the presence of large crystals that were found, by energy dispersive spectroscopy (EDS), to contain the calcium salt of 3-chlorophenol. S/S of 3-chlorophenol with the exchanged clay/cement mix, up to the maximum capacity of the clay, reduced the microstructural effect of 3-chlorophenol on the cement. Above the capacity of the clay, the inhibiting effects of 3-chlorophenol were observed.

17. Chloronaphthalene had no effect upon the hydration of cement as it was immiscible with the cement paste. Chloronaphthalene could be incorporated into the cement matrix in the presence of clay, but still had no effect on the microstructure of the cement, even in excess of the maximum chloronaphthalene capacity of the clay.

18. Three industrial wastes which were mainly inorganic but contaminated with up to 12% organics were used to test the application of the exchanged clays in the S/S process. The organic components of three wastes were adsorbed well by the exchanged clays and the metals present were also partially adsorbed. In each case, however, a small proportion of the organic component could not be adsorbed, even with excess clay present. This effect was of importance in subsequent solidification experiments, since it was shown that exchanged clays loaded with adsorbed organics required washing with water before a reasonable set of any mix could be achieved.

19. Following the clay washing stage, all three industrial wastes were successfully solidified using the exchanged clay and a model commercial mix of cement and inert filler (calcium carbonate). Strength and setting rates of the solidified wastes met commercially acceptable criteria. In the absence of the clay no set was obtained. Leaching tests on the solidified wastes showed up to a 99% reduction in the total organic carbon (TOC) leached, compared with the untreated waste. A preliminary economic assessment of the S/S mix showed that it was a

potentially viable alternative to the incineration of low organic content (low calorific value) inorganic wastes.

20. Stabilisation of phenol-dosed soils by the exchanged clay was shown to have potential for in-situ contaminated soil treatment. In column tests >95% retention of all three phenols was achieved. S/S of the phenol-dosed soil produced a mix with acceptable strength and leaching characteristics.

21. Contaminated soil from a derelict gas works site, stabilised with the exchanged clay, showed a 90% reduction in the release of PAH during leach tests compared to the undosed soil.

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APPENDIX

Paper 1: Cement-based solidification for the safe disposal of heavy metal contaminated sewage sludge.
Waste Management and Research, *6*, 217-226. (1988).

Paper 2: Organophilic clays for the successful stabilisation/solidification of problematic industrial wastes.
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CEMENT-BASED SOLIDIFICATION FOR THE SAFE DISPOSAL OF HEAVY METAL CONTAMINATED SEWAGE SLUDGE

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Cement-based solidification processes for the safe disposal of metal contaminated sewage sludges in landfill have been evaluated as a possible alternative to conventional methods, such as disposal to agricultural land or sea dumping. The treatments evaluated were based on ordinary Portland cement (OPC) alone and OPC containing soluble sodium silicate as an additive. The abilities of the systems to stabilize the metal contaminants present in the sludge were determined by extensive leaching tests, using water or buffered acetic acid over a 9 day cycle, designed to simulate the most severe conditions likely to be met in a landfill. For both the OPC/sludge mix and the OPC/silicate/sludge mix, these tests indicated that the release of metals from the cement matrix was low and the patterns of release could be divided into two distinct groups. The first group, comprising zinc, lead and cadmium, gave pH-dependent releases under equilibrium (crushed block) test conditions, suggesting that the metals are bound up in the cement matrix as the insoluble hydroxides at high pH. The second group, consisting of copper and nickel, were released throughout the test, suggesting that the metals were complexed by ligands present in the sludge and were, therefore, soluble under alkaline, as well as acid, leaching conditions.

Key Words—Solidification, sludge disposal, cement, sodium silicate, heavy metals, leaching, landfill.

1. Introduction

In the UK, approximately 1.2 million dry tonnes of sewage sludge are produced annually (Department of the Environment/NWC, 1983) of which about 18% are disposed of to landfill, usually in conjunction with domestic refuse. In the future, competition for space with other wastes and concern over possible odour, groundwater or surface-water pollution problems may restrict sludge disposal to landfills. Solidification or stabilization of sewage sludge prior to landfilling may, however, enable the operation to be carried out in a more environmentally acceptable manner, particularly when sludges contain industrial wastes such as heavy metals. The feasibility and implications of using these techniques, therefore, needs to be examined in greater detail.

Stabilization is a treatment process that induces chemical change in a waste to form insoluble compounds that entrap toxic elements or compounds in an impervious polymer or stable crystal lattice. Solidification is a treatment process that produces a solid monolithic or soil-like mass from a liquid waste (although this may not necessarily involve chemical stabilization) and leads to a product with improved structural integrity and physical characteristics. This allows the material to be readily handled or transported, and the solidified material has sufficient strength to allow for land reclamation. Furthermore, the modified structure significantly reduces the leachability by decreasing

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the mobility and exposed surface area of the waste, thereby minimizing the possibility of groundwater and surface-water contamination. This has always been a major consideration in the safe disposal of toxic wastes to land.

Cement-based stabilization/solidification processes incorporate the waste as part of a rigid inorganic cement matrix. The cement most widely used in many stabilization/solidification processes is ordinary Portland cement (OPC), which is very similar in composition to ASTM specification Type 1 (Bye 1983). The key constituents are calcium aluminosilicates. In OPC these may comprise up to 92% of the total weight, as shown in typical composition data given by Lee (1970). Extensive studies of the hydration mechanism of cement (Jennings & Pratt 1979; Birchall *et al.* 1980) indicate that the process of Portland cement hydration involves an osmotic pressure gradient drawing water across an initially formed semipermeable membrane around the calcium silicate particle. Lead nitrate was found by Thomas *et al.* (1981) to inhibit cement hydration by forming an impermeable coating around the calcium silicate grains. A similar mechanism was suggested to occur with metal cations (Cu, Zn, Cd) which give highly insoluble hydroxy compounds in alkaline solution (Stepanova 1981). The precipitation of the hydroxides onto the cement grains would provide a viable explanation for metal fixation in the cement matrix.

It has been suggested (Poon *et al.* 1985*a*,*b*) that a similar process can occur between waste sludges containing metallic cations and cement during the fixation process. Evidence for this has been put forward by Falcone *et al.* (1984), who added sodium silicate to lime precipitated plating wastes heavily contaminated with zinc and chromium. This was found to reduce the leachability of these metals, especially when the samples were solidified with an OPC/PFA (pulverised fly ash) mix. Côté & Bridle (1987), Edwards & Duedall (1985) and others have also reported on the leaching of metal ions from cement solidified wastes. Silicate addition is the basis of several proprietary stabilization/solidification processes (Clements & Griffiths 1985) and an example of this approach to solidification has been investigated in the work presented here.

Alternative mechanisms suggested for metal ion fixation by cement involve absorption by cement hydrates, substitution and solid solution in hydrate structure, or formation of metal complexes (Tashiro *et al.* 1977). Other mechanisms based on crystal capture (Schofield 1979) and the formation of a three-dimensional polymer matrix (Salas 1979) have also been suggested. However, many claims relate to semiquantitative observations and interpretations leaving many of the fundamentals to be resolved, and only recently have proper scientific evaluations of the physicochemical mechanisms involved in some commercial stabilization/solidification processes been undertaken (Poon *et al.* 1985*a*,*b*; 1986*a*,*b*).

With respect to the specific problems of stabilization/solidification of sewage sludge, Tittlebaum *et al.* (1985), in their comprehensive review of stabilisation techniques for organic wastes, noted that only a very limited amount of work had been carried out on this aspect. They reported that a reduction of COD from 100 000 mg l^{-1} to 400 mg l^{-1} had been achieved for leachate from a cement-stabilized activated sewage sludge from Michigan. In separate acid-leaching tests on a stabilized municipal sludge from Indiana, phenol concentrations of 71 mg l^{-1} in raw sludge leachate were reduced to less than 0.75 mg l^{-1} in leachate from the stabilized product.

More recently, Malone & Jones (1985) reported experiments on the solidification of anaerobic digester sludge containing high concentrations of Cu, Cd, Pb and Zn and sludge incinerator ash contaminated by Cr, Cu, Pb and Zn using processes based on OPC/silicate, lime and gypsum, respectively. The lime-based process produced the hardest, most durable material and was considered the most cost-effective method of the three, although the final product did not withstand the cycle of durability tests used by the authors. In overall terms, however, the present state of scientific knowledge on stabilization of organic wastes, including sewage sludge, using cement and lime-based processes is very limited.

For this study, a silicate/cement treatment based on OPC and a soluble silicate additive was evaluated for its applicability to a sludge contaminated with heavy metals. Evaluation was based on a leaching test protocol and physical hardness measurements, and comparisons made with a cement-only stabilized product and unstabilized sludge.

2. Materials and methods

2.1. *Sewage sludge solidification*

Primary sewage sludge was obtained from a treatment works in the north of England. The concentrations of heavy metals in the sludge are shown in Table 1. Between 40 g and 200 g of sludge were solidified using (a) 40 g of OPC, and (b) 40 g of OPC and 10 ml of 40% sodium silicate (Na_2SiO_3), to give the mixes shown in Table 2. Control

TABLE 1

Total concentrations of metals in primary sewage sludge (results supplied by Water Research Centre, U.K.)

Metal	Weight in dry solid (mg kg^{-1})	Weight in 40 g of sludge* (mg)
Copper	440	1.06
Nickel	390	0.94
Zinc	1700	4.10
Cadmium	48	0.12
Lead	460	1.10
Chromium	1100	2.65
Iron	3000	7.23
Manganese	670	1.61

* Dry solids content = 6%.

TABLE 2

Mix ratios and setting measurements for cement-only and silicate-modified samples

Sample	Ratio cement:liquid†:silicate	Penetration strength ($\times 10^6$ N m^{-2})			
		3 days	7 days	14 days	28 days
A* Cement/water	1:1 : 0	>4.80	>4.80	>4.80	>4.80
B* Cement/sludge	1:1 : 0	>4.80	>4.80	>4.80	>4.80
C Cement/sludge	1:2.5: 0	NS	NS	4.11	4.80
D Cement/sludge	1:5 : 0	NS	NS	NS	NS
E* Cement/water/silicate	1:5 :0.5	0.69	1.03	1.44	2.06
F* Cement/sludge/silicate	1:5 :0.5	0.48	0.69	0.82	0.96

NS. not set.

* Samples used in leaching tests.

† liquid = water or sludge.

samples were made by substituting an equivalent weight of water for the sludge. The mix ratios chosen are based upon those used by previous workers (Poon *et al.* 1985*a*) and reflect the range found in commercial processes.

Subsamples of each mix were transferred into 14.3 cm^3 moulds in preparation for dynamic leaching tests, and allowed to set for 24 h before demoulding. The remainder of each mix was transferred to plastic containers, to be used for equilibrium leaching tests, and allowed to set. Both sets of samples were cured for a total of 28 days at 20°C and 58% relative humidity.

2.2. *Setting rates*

The setting rate was determined by measuring hardness values with a pocket concrete penetrometer at 2.5 cm penetration after 2, 7, 14 and 28 days.

2.3. *Dynamic* (*whole block*) *leaching test*

The 14.3 cm^3 blocks were suspended in 100 ml of extractant (either deionized water or buffered 0.5 M acid (pH 4.5–4.6), and gently stirred by means of magnetic stirrers for 24 h. The leachates were filtered through 0.45 μm membranes and 27 ml aliquots preserved for analysis. Fresh portions of extractant (deionized water or buffered acetic acid) were added and the process repeated for a further 8 days.

2.4. *Equilibrium* (*crushed block*) *leaching test*

The samples were crushed to a particle size of less than 2 mm and 40 g portions transferred to plastic containers. Extractant (deionized water or buffered 0.5 M acetic acid) was added to each container and the samples agitated using a rotational shaker. After 24 h, the slurries were filtered through 0.45 μm membranes and 27 ml aliquots preserved for analysis. Fresh portions of extractant were used to resuspend the filter cake and the leaching tests were repeated for a further eight days. Extactions for comparative purposes were carried out on unstabilized sludge using a 40 g sample with leaching, filtration, etc., being performed in an identical manner as for stabilized samples.

2.5. *Sample analysis*

The filtrates were preserved in 1% nitric acid solution and analysed in duplicate for Cu, Zn, Ni, Cd and Pb by atomic absorption spectroscopy (AAS).

3. Results and discussion

3.1. *Setting rates*

The setting rates of the stabilized samples are shown in Table 2. The primary sludge used in this work contained 6% dry solids by weight, the composition being fibrous organic material contaminated with inorganic and organic residues. Increasing the sludge/cement ratio from 1:1 to 5:1 clearly had a detrimental effect upon setting rates and, in view of the substantial water content of the sludge, this can be partially ascribed to an increasing water/cement ratio effect commonly observed in construction practice

(Neville 1981). This effect may also be partially due to the effects of the membrane/osmosis model of cement hydration previously referred to (Jennings & Pratt 1979; Birchall *et al.* 1980). Metal contaminants in the sludge probably form insoluble metal hydroxides which are precipitated onto the cement grains, thus reducing the permeability of the membrane coating and inhibiting the hydration process. The final sample strength may also be reduced by the fibrous constituents in the sludge.

In contrast, the silicate/sludge and silicate/water samples indicated improved setting characteristics compared with the analogous non-silicate samples, reflecting the acceleration effect of silicate on the hydration process. Significantly, however, the silicate/sludge setting rate was slower than the silicate/water sample, and this may again reflect the hydration-inhibiting effect of insoluble hydroxide formation by metals in the sludge.

3.2. *Leaching behaviour*

Leaching tests were carried out on mixes B and F, which had the highest setting rates of the cement/sludge mixes (Table 2) and on mixes A and E which were the silicate-free control samples. Figures 1 and 2 show the daily release of zinc and copper, respectively, from samples under both equilibrium (crushed block) and dynamic (whole block) leaching test conditions. The equilibrium test results are given as the concentration of metal (mg l^{-1}) in 100 ml leachate following extraction of a 40 g crushed sample. The dynamic leach test results are given as the concentration of metal (mg l^{-1}) in 100 ml leachate following extraction from a sample block of volume 14.3 cm^3. It should be noted that in both Figs 1 and 2 the concentration scale for water-leached data is an order of magnitude smaller than for acid-leached data. Accompanying pH profiles for equilibrium (crushed block) leach tests are given in Fig. 3.

Extraction efficiencies of the leaching procedures is given by the cumulative weight of each metal released expressed as a percentage of the metal originally present in the sample (Jackson *et al.* 1984), and Fig. 4 presents extraction efficiency data for equilibrium (crushed block) tests over a 9 day period.

The use of acetic acid as an extractant provides a severe test for the samples and is expected to predict the metal release over many years in landfill conditions (Boyle *et al.* 1983). Use of both acetic acid and water as extractants in the present work demonstrated considerable contrasts in sample behaviour.

In terms of visual appearance, the dynamic leaching test blocks leached by water showed very little sign of disintegration, whereas the acid leached samples had started to break up after eight days. It should be noted that the silicate/cement acid-leached sample broke down after five days and subsequent leaching tests were performed under quasi-equilibrium conditions. The cement/water and cement/sludge samples showed few effects of disintegration until the end of the tests, when they were allowed to dry out slightly. The silicate/cement/sludge sample remained almost intact in both water and acetic acid, possibly due to the binding properties of the fibrous matter in the sludge.

With respect to metal release under acid leaching, in equilibrium (crushed block) conditions, the silicate-modified samples released only low concentrations of Cu, Zn, Pb and Cd for the first four days. On days 5 to 6, however, a sudden increase in metal release occurred which coincided with the point at which the pH of the leachate fell below 7 (Fig. 3). Figure 1 clearly illustrates this for Zn. In the analogous cement samples the pH remained above 11 for the first eight days of the test, and the release of the same four metals was gradual, showing no clear maxima. Nickel showed a maximum release after 1–2 days for both silicate-modified and cement-only samples. In the

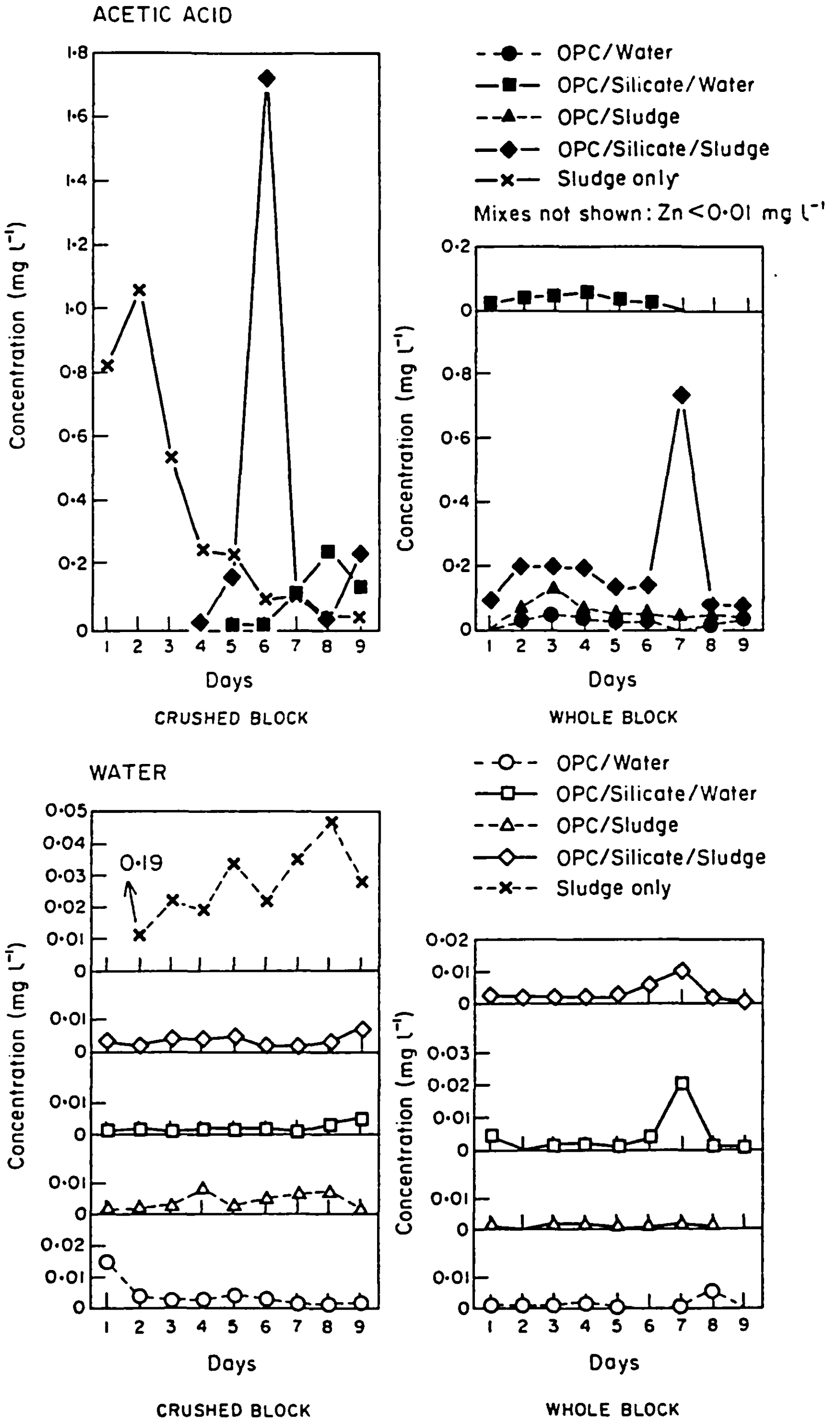

Fig. 1. Leach test daily concentration profiles for zinc.

dynamic (whole block) leaching tests under acid conditions, the pH values of the acid leached samples fell below 7 from day 1 onwards, but nonetheless for Cu, Zn and Cd release from the silicate-modified samples, a similar pattern of release to that demonstrated in the equilibrium leaching tests was observed (Montgomery *et al.* 1987).

Results from both dynamic and equilibrium (Fig. 3) leaching tests using water showed that the pH remained between 11 and 12 throughout, reflecting the dominant alkalinity of the solidified matrices in this leaching medium. Concentrations were, in general,

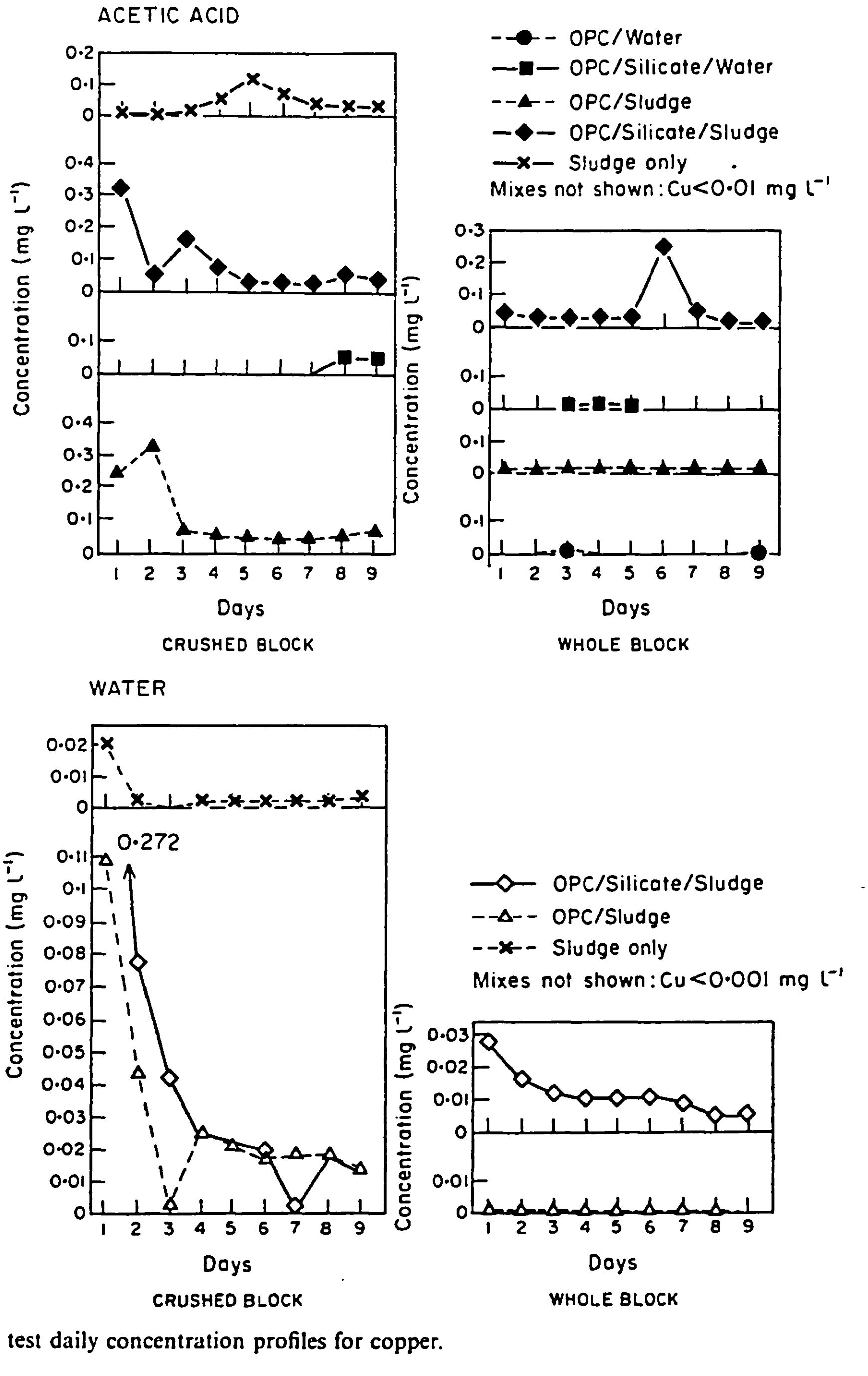

Fig. 2. Leach test daily concentration profiles for copper.

much lower than for acid-leached conditions, but Cu (Fig. 2) and Ni demonstrated an exponential-type removal pattern from both cement-only and silicate-modified samples. Zinc removal from cement-only and silicate-modified samples showed a maximum after 7–8 days, as with acid-leached conditions, but at much lower concentrations (Fig. 1).

A clearer overall pattern of behaviour for the five metals is evident from consideration of the extraction efficiency data. This is summarized for equilibrium leaching tests in Fig. 4; data for dynamic leaching conditions were broadly similar. The main trends observed show that when water was used as an extractant on the cement samples, Cu and Ni demonstrated significant extraction efficiencies, whilst Zn, Pb and Cd showed negligible values. For silicate-modified samples, substantially higher extraction

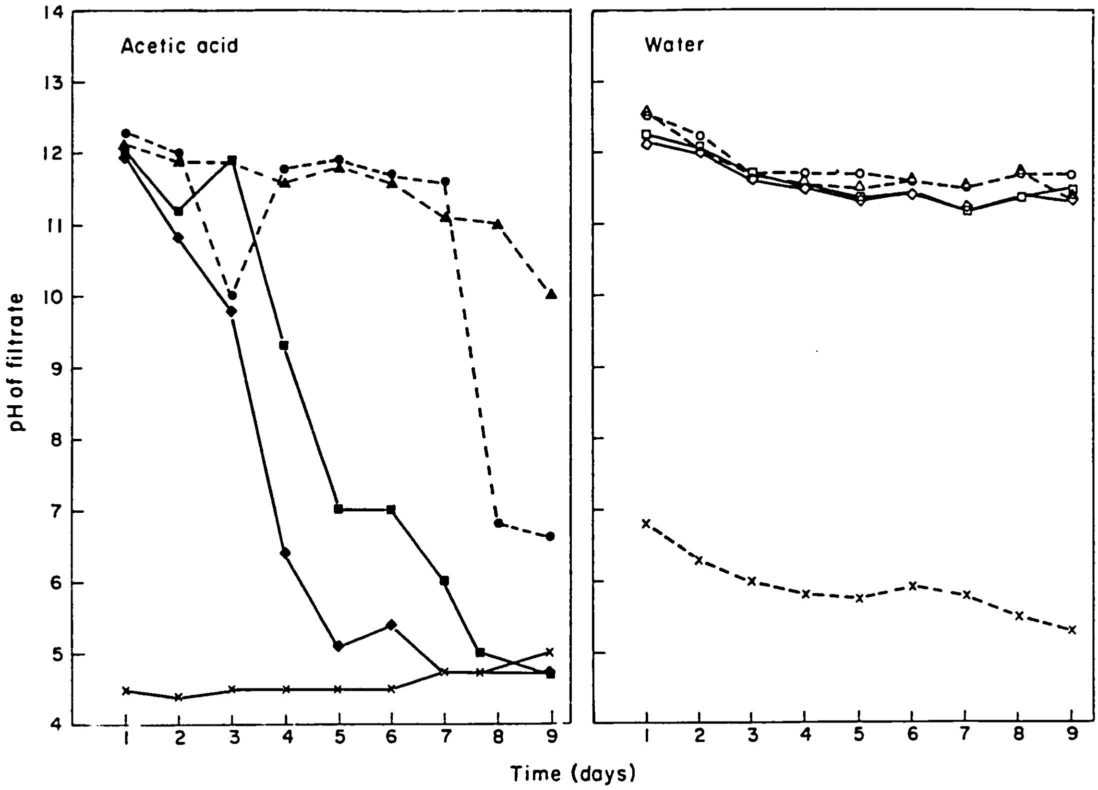

Fig. 3. Changes in pH during equilibrium (crushed block) leach tests. ●, ○, OPC/water; ■, □, OPC/silicate water; ▲, △, OPC/sludge; ◆, ◇, OPC/silicate/sludge; ×, sludge only.

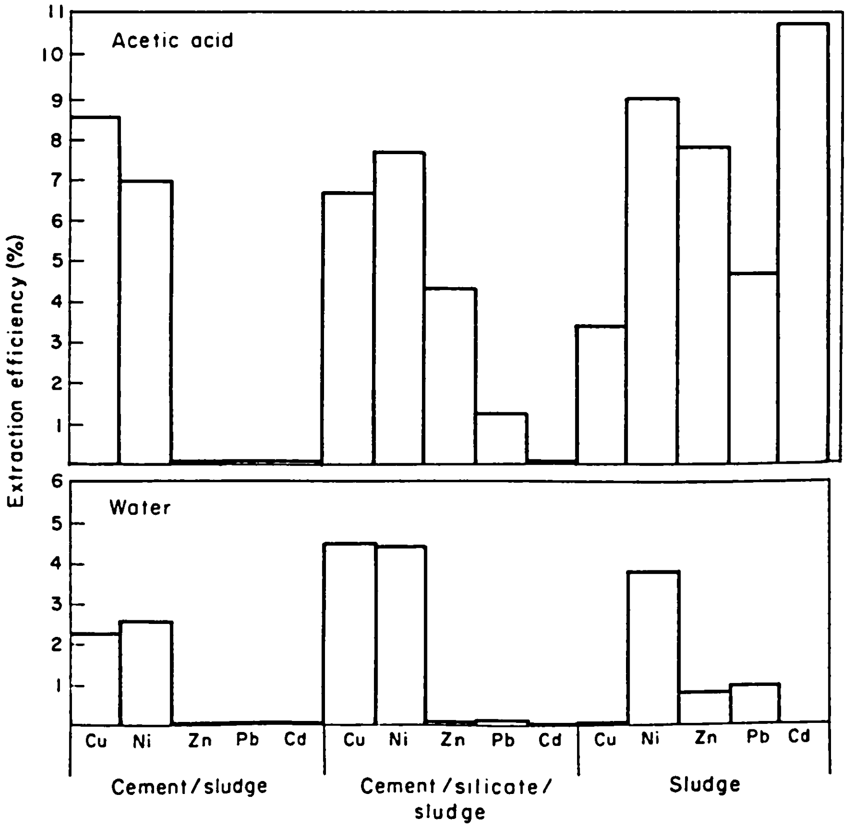

Fig. 4. Metal extraction efficiencies for solidified samples in equilibrium (crushed block) leach tests.

efficiencies for Cu and Ni were clearly evident, while Zn, Pb and Cd again showed negligible release. Use of acetic acid as an extractant clearly give rise to enhanced extractability for most metals, but the anomalous release pattern for Cu and Ni from stabilized samples is again evident. Particularly noticeable, however, is that Cu and Ni extraction efficiencies from unstabilized sludge samples are often comparable to or less than the corresponding values for stabilized samples. The behaviour of Cu and Ni may be explained by noting that the pH was generally high for all equilibrium leach tests on cement-containing samples and that therefore some Cu and Ni may have been released as anionic complex ions. Further release occurred under acid conditions when the pH fell below 7 and structure of the cement began to break down.

4. Conclusions

This study has shown that both cement and silicate-modified cement solidify concentrated primary sewage sludge. At a high sludge/cement ratio, a high setting rate solid can be obtained with very favourable leaching properties for some metals.

The leaching test results show that the metals tested were generally released only in low concentrations and their patterns of behaviour could be broadly divided into two distinct groups. Metals in the first group comprising Zn, Pb and Cd, were effectively stabilized in both silicate-modified and cement-only samples, and results indicated that they formed insoluble metal hydroxides in the alkaline matrix. Metals in the second group, comprising Cu and Ni, were released more readily from solidified sludge than from the unsolidified counterpart, suggesting that these metals exist as pH dependent metal complexes in the sludge itself. Overall, however, the results indicate that stabilization/solidification has the potential to become a viable alternative disposal route for sewage sludge which has a heavy metal content unsuitable for direct disposal to land or sea.

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ORGANOPHILIC CLAYS FOR THE SUCCESSFUL STABILISATION/SOLIDIFICATION OF PROBLEMATIC INDUSTRIAL WASTES

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ABSTRACT

Cement-based stabilisation/solidification has been used for treatment of inorganic industrial waste for a number of years. An urgent need now exists to expand the use of this technique to inorganic wastes containing a significant level (up to ~15%) of organic contaminants. Application of organophilic clays to this problem is reported and the successful retention of the organic component of some problematic industrial wastes is demonstrated.

INTRODUCTION

The safe disposal of hazardous liquid and solid wastes is forming a rapidly expanding field of environmental research and technology as direct disposal to landfill becomes more tightly controlled or even prohibited in many countries, particularly the USA. Cement-based stabilisation/solidification is one technique used successfully for about 20 years for the disposal of purely inorganic wastes as a pre-landfill treatment (1). This technique employs cheap, readily available materials (e.g. cement and PFA), has a low energy requirement and produces a monolithic, leach-resistant solid. The technique is, however, unsuitable for wastes containing organic compounds (>1-2%). Enhancement of this technique using suitable additives to allow the treatment of inorganic wastes with organic components up to 15% by volume would provide a significant alternative to expensive existing treatment options such as incineration.

This paper addresses the stabilisation/solidification of problematic inorganic wastes containing up to 12% organic content. The work investigates the use of modified clays as pre- solidification adsorbents and shows their promising application in the treatment of two industrial wastes.

EXPERIMENTAL

Materials

Wyoming Bentonite was supplied by Laporte Industries, Widnes, UK. The ten quaternary ammonium salts (QAS) used are detailed in Table 1. Perchem 462®, a commercial exchanged clay, was supplied by Perchem Ltd, UK. Ordinary Portland cement (OPC) was supplied by Blue Circle, UK. Phenol, 3-chlorophenol 2,3-dichlorophenol (AnalaR) and calcium carbonate (GPR) were supplied by BDH Chemicals, UK. The two industrial wastes used in these experiments were essentially inorganic (Table 2) but contained up to 12% organic compounds.

Table 1 : Structure of quaternary ammonium salts (QAS) exchanged onto Wyoming Bentonite.

Chain Length	Structural Formula of Cation	Name of Cation	Acronym of QAS
1	$(CH_3)_4N^+$	Tetramethylammonium	TMA
1	$(CH_3)_3N^+C_6H_5$	Trimethylphenyl -ammonium	TMPA
8	$(CH_3)_3N^+(CH_2)_7CH_3$	Octyltrimethyl -ammonium	OTMA
14	$(CH_3)_3N^+(CH_2)_{13}CH_3$	Tetradecyltrimethyl -ammonium	TDTMA
14	$(CH_3)_2C_6H_5CH_2N^+(CH_2)_{13}CH_3$	Benzyldimethyltetra -decylammonium	BDMTDA
16	$(CH_3)_3N^+(CH_2)_{15}CH_3$	Hexadecyltrimethyl -ammonium	HDTMA
18	$(CH_3)_3N^+(CH_2)_{17}CH_3$	Octadecyltrimethyl -ammonium	ODTMA
18	$(CH_3)_2C_6H_5CH_2N^+(CH_2)_{17}CH_3$	Benzyloctadecyl -dimethylammonium	BODDMA
18	$(CH_3)_2N^+((CH_2)_{17}CH_3)_2$	Dioctadecyldimethyl -ammonium	DODDMA
18	$N^+((CH_2)_{17}CH_3)_4$	Tetraoctadecyl -ammonium	TODA

Table 2 : Properties of the industrial wastes.

	Waste A	Waste B
Origin	Process effluent from glycid ether production	Mixed inorganic/organic effluent
Appearance	Brown/red sludge containing chlorinated solvents	Black 'oily' sludge containing solvents amines and latex products
Odour	Solvents	Organic nitrogen compounds
pH	9.94	7.64
TOC (mgl^{-1})	37140	123150
Inorganic Carbon (mgl^{-1})	81	68
Zinc (mgl^{-1})	48.3	216
Copper	24.3	8
Nickel	15.4	<0.2
Cadmium	2.0	<0.05
Lead	<0.5	<0.5

Preparation of Exchanged Clays

Unexchanged Wyoming Bentonite (100g) was ground and sieved to a particle size of < 200 microns, dried (105°C/24 hours) and cooled in a desiccator. A sample (75g) of the clay was suspended in 1.5l of a stirred solution of 0.1 M QAS for 48 hours. Higher chain length QAS solutions required heating to 60°±2°C to allow them to dissolve. The clay suspensions were filtered under vacuum, care being taken to exclude the heavy insoluble impurities. The filter cake was washed and re-filtered three times, to remove excess QAS, then dried (105°C/48 hours), ground and sieved (<500 microns). TODAM and DODDMAM were dried over silica gel in a vacuum desiccator (7 days) due to their heat sensitivity.

Adsorption Studies

The adsorbent (clay or exchanged clay, 1.0g) was mixed with aliquots (100ml) of the aqueous phenol solutions (1.0 mM) and shaken by end-over-end rotation for 3 hours. The industrial wastes were diluted to give a range of organic concentrations and mixed with the exchanged clay for 24 hours. The suspensions were then filtered and the filtrate analysed for the phenol using a colourimetric method (2) or by total organic carbon (TOC) analysis for organic content in the case of the industrial waste.

Solidification of Exchanged Clays containing (i) Phenols and (ii) Waste

Due to the difficulty in preparing large quantities of exchanged clay in the laboratory, Perchem 462® was used in all solidification experiments. The organic cations of this clay consisted of predominantly ODTMA. The production of samples of this clay loaded with phenol or waste was based on the results of the adsorption experiments. Samples of clay with 'high' and 'medium' and loadings of each phenol and 'low' loadings of dichlorophenol were solidified, together with suitable controls as detailed in Table 3. The mixes were prepared and cast in cylindrical moulds (60mm x 60mm) for subsequent dynamic leach-tests and unconfined compressive strength (UCS) tests. The remainder of each mix was retained for equilibrium leach testing.

Table 3 : Phenol solidification mixes.

	Type of Phenol (%)					
Clay/phenol Load	Phenol	3-chloro phenol	2,3-dichloro phenol	Mix Make-up	Water/Cement Ratio	Water/Clay Ratio
Perchem 462®						
High	1.08	2.06	2.00	46% OPC	0.35	0.67
Medium	0.10	0.14	0.29	23% clay		
Low	-	-	0.03	31% water		
Wyoming Bentonite						
High	0.36	0.77	-	43% OPC	0.35	1.0
Medium	0.03	0.07	0.09	21% clay		
Low	-	-	0.01	36% water		
OPC						
High	0.57	-	-	74% OPC	0.35	-
Medium	-	0.11	-	0% clay		
Low	-	-	0.01	26% water		

A sample of each industrial waste (2l) was stirred with Perchem 462® (200g) for 24 hours and then filtered under vacuum until no free liquid was visible. The filter cake was weighed and the waste:clay ratio determined to be 1.25. The filter cake was then washed with water and re-filtered; a liquid:clay ratio of 1.25 being maintained. Solidification samples were prepared by mixing the filter cake with OPC and calcium carbonate. Water was then added to hydrate the OPC and mixing continued until a homogeneous mix was achieved. (The role of calcium carbonate was to act as a bulking agent; in existing cement based solidification processes solid wastes fulfil this function). Table 4 shows the composition of the solidification mixes produced. Cylindrical moulds of solidified waste were prepared for the determination of unconfined compressive strength and also for use in an equilibrium leach test.

Table 4 : Industrial waste solidification mixes.

Sample	Clay % wt	OPC % wt	Calcium carbonate % wt	Liquid % wt	TIS[1] %	l:c[2]	TOC in leach sample mg
1	9	26	20	45	55	1.5	229
2a	9	26	20	45	55	1.5	3092
2b	9	12	33	45	55	1.5	2480

Note: [1] Total Insoluble Solids
[2] Liquid (available for hydration): OPC ratio
Sample 1 : contained Waste A
Sample 2a,b: contained Waste B

Leach Tests and Compressive Strength Tests

The test procedures for both dynamic and equilibrium leach-tests were adapted from those developed by Environment Canada (3). Dynamic leach test samples were suspended in distilled water (1l at 20°C). The water was stirred gently and analysed at regular intervals between 1 and 28 days. The blocks were resuspended in fresh distilled water (1l) after each analysis and phenol determinations were carried out as before (2). Equilibrium leach-tests were performed on 28 and 56 day samples (7 and 28 days for the wastes). Approximately 40g of crushed sample plus four times the weight of distilled water were shaken end-over-end for 7 days. The solids were allowed to settle and the supernates were filtered through membrane filters (0.45 μm). After suitable dilution, analysis for phenols and TOC was carried out as before. Compressive strength measurements were carried out after 28 days curing at 20 ± 2°C and 100% relative humidity.

RESULTS AND DISCUSSION

Adsorption Studies

The results of adsorption studies are shown in Figure 1 and illustrate very clearly the improved adsorption of phenols onto the exchanged montmorillonite over unexchanged Wyoming Bentonite. The magnitude of the adsorption of both 3-chlorophenol and 2,3-dichlorophenol by the best QAS-exchanged clay, BODDMAM, was approximately 90% of the initial phenol in solution; however only 45% of the corresponding unsubstituted phenol was adsorbed.

The general trend of phenol adsorption demonstrated by these QAS-exchanged montmorillonites is increased adsorption with increasing chain length, i.e. ODTMAM > HDTMAM >>OTMAM >> TMAM. The only exception to this trend occurs if the quaternary ammonium cation contains a benzyl group, which results in a slightly improved adsorption ability; thus BODDMAM adsorbs the phenols more strongly than ODTMAM even though they have the same aliphatic chain length. Perchem 462® showed similar adsorption capacities to ODTMAM, and this is reasonable in view of its similar structures.

The TOC adsorption isotherms for the adsorption of the industrial wastes by Perchem 462® (Figure 2) shows that the organic component of the waste was well adsorbed. As the concentration of the waste increased the amount of the TOC adsorbed also increased, and no maximum was reached even using undiluted wastes.

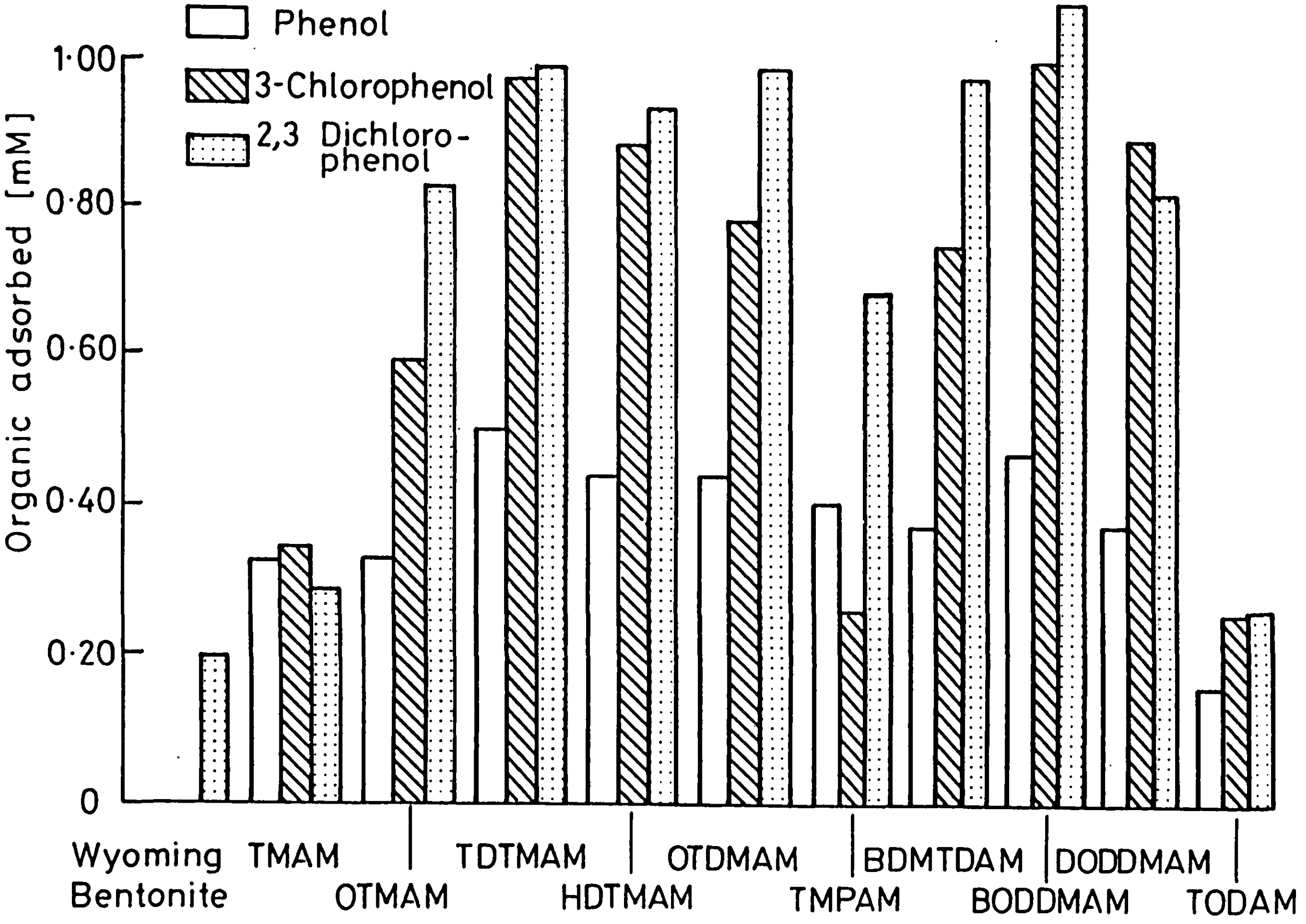

Figure 1 : Phenol adsorption by exchanged clays

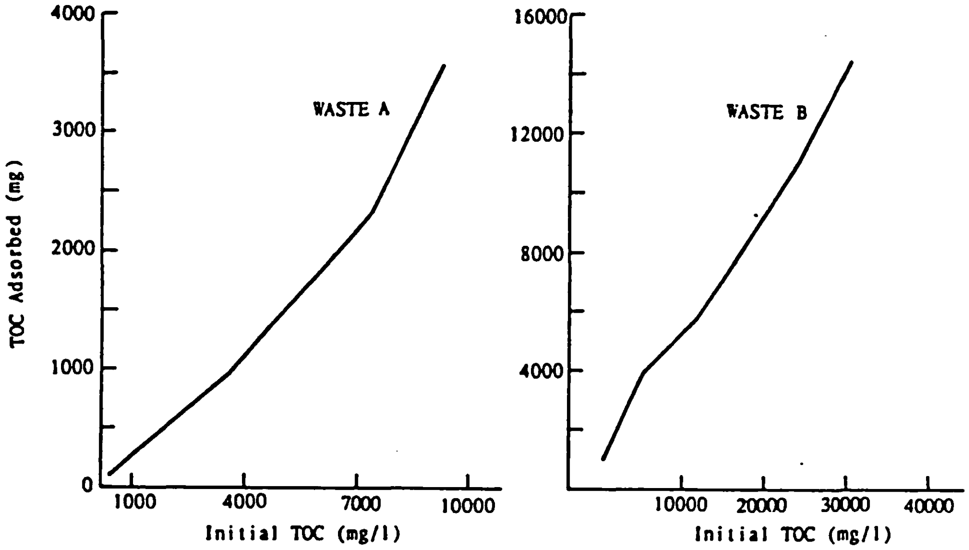

Figure 2 : Adsorption of TOC from industrial wastes A and B

Dynamic Leach Tests

The results of the dynamic leach-tests for the solidified phenols are shown in Figure 3a. The results show the total weight of each phenol released over the 28 day period, expressed as a percentage of the total weight of phenol originally present in the sample. In practice it was found that the actual concentration of the phenols in the leachate varied considerably between day 1 and day 28 of the test, the maximum release occurring within the first few days of the test. It should be emphasized that although similar percentages of phenol were released from clays loaded with different concentrations of the phenols, the leachate concentrations were several orders of magnitude different. The general trends, demonstrated at all three concentrations of the different phenols, were that the unexchanged Wyoming Bentonite/OPC mix does not stabilize any of the phenols, and by increasing the permeability of the matrix the clay causes greatly increased leaching compared to the OPC/water mix. In contrast, the exchanged clay stabilized the phenols well, particularly as the degree of chlorination, and hence hydrophobicity of the phenols, increases. For example, the Perchem 462® mix containing a high phenol load releases only 12% while the medium- and low-loaded samples all released less than 5%.

An interesting feature of these results was the very low releases recorded for the OPC-only mixes, which appears able to stabilize phenols as effectively as the exchanged clay mix. For example, in the case of the high loading of phenol, the release from the OPC-only mix is about half that of the Perchem 462®/OPC mix. Separate permeability studies in this laboratory which are at present being completed have shown that the permeability of the OPC-only sample is low compared to the other samples. Consequently in the 28 days leaching period the leachate would not penetrate the OPC sample to the same extent as the other samples and so less phenol would presumably be exposed to the leachate.

Equilibrium Leach-Tests

In general it would be expected that the equilibrium leach-tests (Figure 3b) would show higher releases of the phenols compared with a dynamic leach-test results, since the samples are ground and subjected to severe leaching conditions. However, if the phenols are well bound in the matrix the release will be small and only unbound molecules will be lost. From Figure 3b it can be seen that almost 100% of the phenols are released from the unexchanged Wyoming Bentonite mix and that the OPC-only sample released about 40% of the phenol present. This indicates that the stabilizing effect seen in the

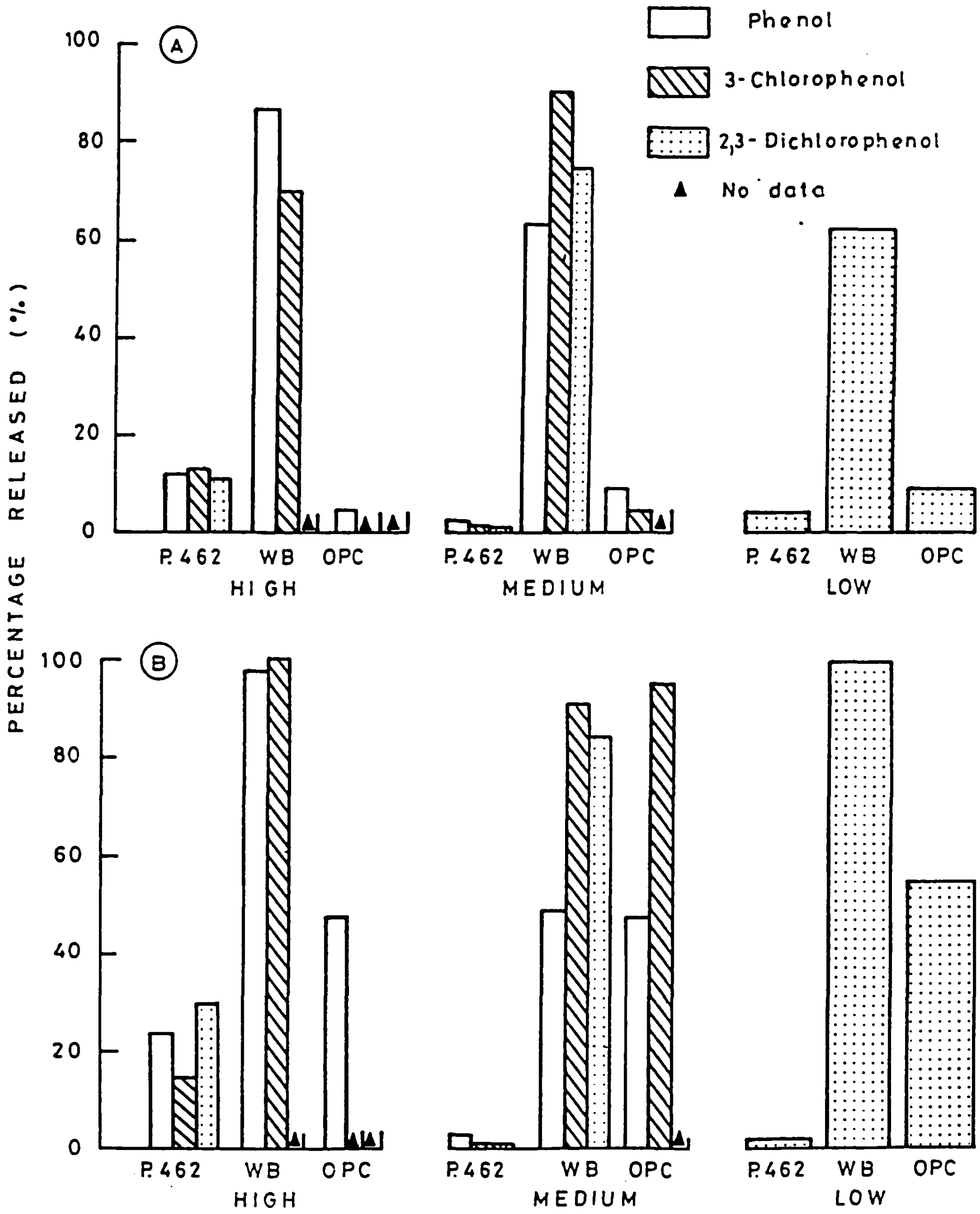

Figure 3 : Results of (A) dynamic and (B) equilibrium leach tests

dynamic leach-tests of the OPC-only mixes is due to the inability of the leachate to penetrate the cement samples. In the high loading situation, the Perchem 462® mix shows the expected higher release than in the dynamic leach test, but this amount in the case of phenol is still significantly less than the OPC-only mix. The medium and low loading of the samples clearly demonstrates the ability of the exchanged clay mixes to stabilize the phenols present compared to the OPC-only mix - the releases of the phenols being in all cases less than 5%.

When the samples were allowed to cure for a longer period (56 days) a gradual hardening of the matrix would be expected, with a corresponding reduction in phenols released, and this was found to be the case. The releases of 3-chlorophenol and 2,3-dichlorophenol (not shown) were found to almost negligible under these conditions.

Figure 4 shows the leach-test results for the industrial waste. Retention of the TOC content by both of the solidified wastes was very good. After 7 days the sample containing Waste 1 retained over 65% of the original TOC and after 28 days, when the sample had reached its full hardness, it was able to retain 78% of the TOC. Waste 2 was retained even more successfully. After only 7 days 98% of the original TOC was retained.

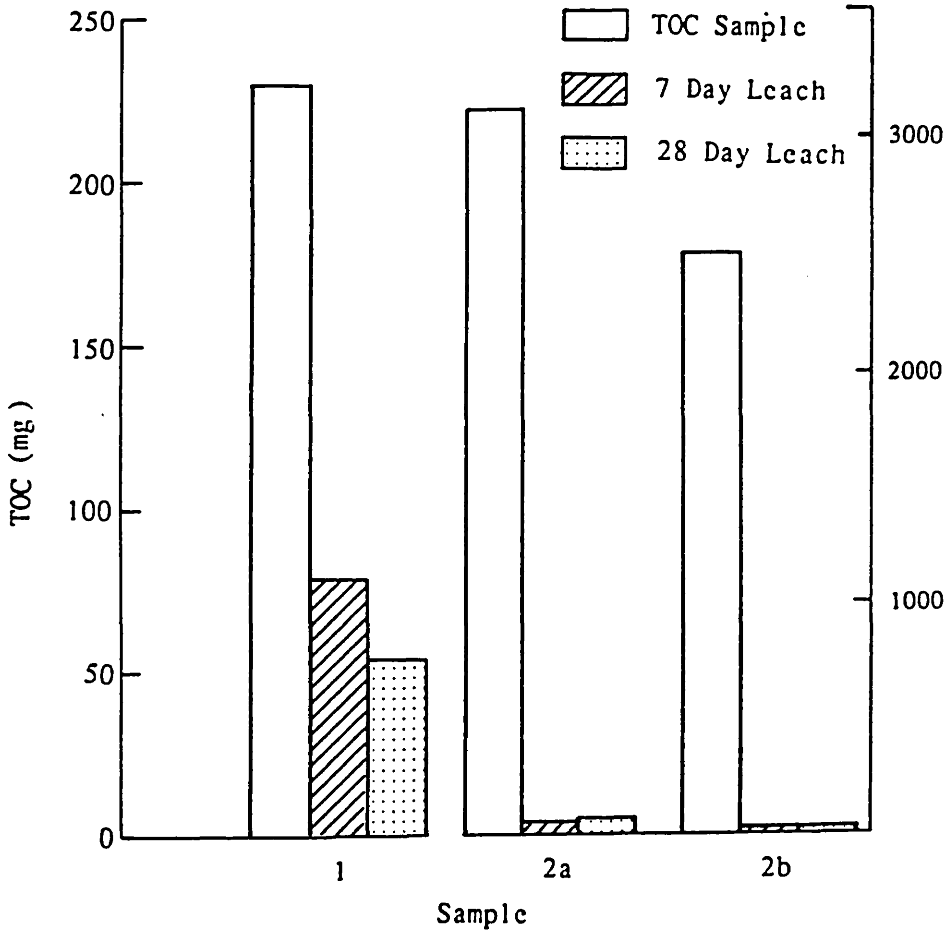

Figure 4 : TOC leaching from raw wastes and solidified mixes (for each sample, data refers to the same weight of waste)

Compressive Strengths

The unconfined compressive strengths of the solidified mixes are shown in Table 5. The Perchem 462®/OPC mixes give strengths (in all cases > 4×10^6 Nm^{-2}) which are substantially greater than the Wyoming Bentonite/OPC mixes, indicating another beneficial effect of the QAS-clay on the integrity of the solidified product.

Table 6 shows the unconfined compressive strength of the solidified industrial wastes. All of the solidified products reached a satisfactory strength after the 7 day curing period.

Table 5 : Compressive strengths of the phenol-containing solidified mixes at 28 days (units = $10^6 Nm^{-2}$).

Clay/Load	Phenol	3-Chloro-phenol	2,3-Dichloro-phenol
Perchem 462®			
High	9.2	7.5	4..6
Medium	7.4	8.4	6.9
Low	-	-	12.6
Wyoming Bentonite			
High	0.9	0.9	-
Medium	0.6	0.8	0.5
Low	-	-	0.3
OPC Control			
High	48.7	-	-
Medium	50.4	41.6	-
Low	-	-	65.9

Table 6 : Compressive strength data (7 and 28 day) for solidified industrial wastes.

	Unconfined Compressive Strength ($\times 10^6 Nm^{-2}$)	
Sample	7 day	28 day
1	2.46	2.85
2a	1.54	2.56
2b	0.35	0.60

CONCLUSION

Industrial wastes in solid or slurry form which are mainly inorganic in character but which contain significant organic content can pose especially difficult and expensive treatment and disposal problems. This is particularly true in countries such as West Germany and the United States where, notably in the latter, land disposal of untreated wastes has either been banned completely or at best is becoming an increasingly limited option (4). In such circumstances, cheaper and environmentally sound processes for stabilising and solidifying such wastes clearly have a major role to play in waste management strategies of the future. This work has shown that, with the use of readily available additives, promising stabilised and solidified materials can be produced from wastes which would otherwise be quite unacceptable for treatment by existing conventional stabilisation/solidification systems. It is anticipated that further modification and refinement of this type of approach will lead to a continually expanding range of mixed inorganic/organic wastes which can be successfully treated.

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