ERRATA

Page	Location	Correction
13	insert	all ratios in weight/weight
47	line 4	Fe_2O_3
66	Figure 4.14	XRD pattern of anhydrous OPC (upper) and OPC hydrated in water (lower) for 1 day
67	Figure 4.15	XRD pattern of anhydrous PFA (upper) and PFA hydrated in water (lower) for 1 day
81-94	Figures 4.22 - 4.31	X axis - relative absorption Y axis - energy (eV)
163	line 24	silicic
177	line 21	$\frac{1}{2}Ba^{2+}$, $\frac{1}{2}Co^{2+}$
180	Eq (16)	$SrCl_2 + Ca(OH)_2 + CO_2 =$ $SrCO_3 + CaCl_2 + H_2O$

CEMENT-BASED STABILISATION AND SOLIDIFICATION TECHNIQUES FOR HAZARDOUS WASTE DISPOSAL

A dissertation submitted in partial fulfilment
of the requirements of the University of London
for the Degree of Doctor of Philosophy in
Public Health Engineering
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by

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ABSTRACT

This report presents an extensive study into the use of cement based stabilisation/solidification processes for the disposal of toxic heavy metals. The group IIB elements (zinc, cadmium and mercury) were used as (model) waste compounds due to their importance in industrial applications. Immobilisation mechanisms of these metals by two different commercially available processes which are based on Ordinary Portland Cement/sodium silicate (Chemfix) and Ordinary Portland Cement/pulverised fuel ash (Sealosafe) formulations were studied using several macro and micro analytical techniques. The macro analysis was based on leaching tests, compressive strength and permeability measurements, while scanning electron microscopy, x-ray diffraction, mercury intrusion porosimetry and extended x-ray absorption fine structure analysis were utilised to study the micro-structure of the solidified products. A good correlation was obtained from these two studies and two principal mechanisms were identified for the immobilisation of heavy metals, namely chemical fixation and physical encapsulation. Zinc and cadmium were demonstrated to be adequately immobilised by the chemical means but mercury required a strong physical barrier in order to minimise leaching. A similar mechanism was shown to be in operation for the immobilisation of metals by the two different stabilisation/solidification processes. The effect of adding different additives such as sodium silicate and pulverised fuel ash to the cement matrix was quantified in terms of the physical and chemical properties.

The leaching mechanism of the solidified material has also been studied and the importance of micro-structure on the leach rate was demonstrated by extended leaching tests and electron microscopy. As a result of this study, a method has been formulated to provide a time based prediction of the long term leaching characteristics of the solidified material.

Several critical factors in affecting the successful use of the stabilisation/solidification processes were identified and an alternative processing procedure was formulated to provide a rational, cost effective approach to process design and operation. Based on the understanding of the fixation and leaching mechanisms, a quality control test procedure has been devised to provide a simple method to assess the physical and chemical qualities of the solidified material.

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NOTATION

C_3S = Tricalcium silicate
C_2S = Dicalcium silicate
C_3A = Tricalcium aluminate
C_4AF = Calcium aluminoferrite
AFt = Ettringite
AFm = Monosulphate
C-S-H = Calcium silicate hydrates
C-H = Calcium hydroxide
PFA = Pulverised fuel ash
OPC = Ordinary Portland Cement
W/C = water/cement ratio
Si/C = silicate/cement ratio
S = PFA + OPC
W/S = water/solid ratio

1. INTRODUCTION

There is a growing interest among the waste disposal industry and controlling bodies in the utilisation of stabilisation/solidification processes for the disposal of hazardous wastes. This is because of the recent stringent regulations introduced requiring alternative methods to mono-or co-disposal of hazardous wastes direct to land which has caused major environmental concern.

The United States Environmental Protection Agency and the British Department of Environment have shown considerable interest in developing these processes. A few reports have been published to describe and quantify these processes in economic terms. In the technical research area, however, except for empirical leaching tests and physical properties studies, little attention has been paid to the possible mechanisms of stabilisation/solidification of hazardous components by these processes. The reason is that while the chemistry of cement, pulverised fuel ash and associated materials is a complex science on its own, the addition of hazardous components to these matrices makes the system more difficult to study. However, without a thorough understanding of the mechanisms, the waste disposer, and especially the waste disposal controlling agencies do not have the technical understanding to issue guidelines and licensing for such disposal practices.

Recently in the UK, the stabilisation/solidification of hazardous wastes has decreased partly due to their relatively high operating cost, but principally because of the lack of technical understanding and credibility. This has resulted in reluctance by the waste producers and waste disposal controlling bodies to use these processes.

1.1 Legislation on hazardous waste disposal

In the UK there has been progressive implementation of legislation on the control of hazardous waste disposal since the 1970s, after an outcry at the discovery of cyanide wastes dumped near the Midlands. The Deposit of Poisonous Waste Act (1) was introduced in 1972 as an emergency measure to remedy the situation. The Act made it an offence to remove or deposit waste which is poisonous, noxious or polluting and liable to give rise to an environmental hazard to land without giving three days pre-notification to the local authority and regional water authority. This Act approached the hazardous waste problem by drawing up an exclusive list of waste which presented no personal or environmental hazards. Although the 1972 Act was superseded by the implementation of Section 17 of Part I of the Control of Pollution Act 1974 (2) and its associated regulations, this former definition of hazardous (notifiable) waste is still generally adopted in the waste disposal industry. The Control of Pollution (Special Waste) Regulations 1980 (under review) uses an inclusive list approach to waste and defines a special waste as: (3)

- a waste which is a prescription only medicine;

- wastes which contain a substance listed in Schedule 1 of the Regulation and which by reason of the presence of such substance is either dangerous to life or has a flash-point of less than 21°C.

The listed substances are presented in Appendix A.

It also provides for a consignment note system providing disposal authorities with documentary evidence that the waste covered by the Regulations has been properly disposed of. The Regulations make the waste producer responsible for determining whether his waste is "special", for ensuring that the carrier he employs is fully aware of the nature of the waste and of any special precautionary measures he should take, also for ensuring that the intended

disposal site is properly licensed and for providing pre-notification of the details of his intent to dispose of the waste to the appropriate waste disposal authority (4).

Comprehensive reviews and discussions on the development and application of this Act, its implication on waste producers and disposal bodies can be found in Holmes (5), Wilson (6), House of Lord's Report (7), Waste Management Papers (8) and a recent report published by the Hazardous Waste Inspectorate (9).

Another important piece of legislation which plays an important role in controlling waste disposal is the Dumping at Sea Act 1974. This Act implements the Oslo and London Dumping Convention, making it an offence to dump any material at sea without a licence from the relevant licensing authority. The licensing body is required to protect the marine environment and the living resources which it supports from any adverse consequence of dumping and seek alternative ways of dealing with wastes for which a sea dumping license is being sought.

The British Government has set up various committees and working parties to review the problem of hazardous waste disposal. The House of Lords Select Committee on Science and Technology conducted an extensive enquiry in 1980 to review the organisation and methods of hazardous waste disposal in the UK. Their report (7), generally known as the Gregson Report, has received widespread attention among central and local governments and the waste disposal industry. The Government has recently published their response to the Committee's findings (10) which suggests a genuine determination to build up a satisfactory regime for hazardous waste disposal in the country. Following the recommendation of the Gregson Report the Government set up the Hazardous Waste Inspectorate in 1983 to examine the management of hazardous waste in this country at all stages from the point of arising to that of final disposal by visiting facilities being used to handle, store, treat, process and dispose of such waste. The first report of the Hazardous Waste Inspectorate was published recently (9) and they

commented that "all is not well" with hazardous waste management in the UK. They revealed widely disparate attitudes among the waste management circles ranging from "thoroughly professional" to the "downright neglectful" especially in the aspect of landfill disposal. They identified two principal reasons for such malpractice. Firstly, the waste disposal authority had failed to specify and enforce adequate standards. Secondly, severe competition among waste disposal contractors forced price cuts and subsequent lowering in standards and led to incompatible waste being disposed of at unsuitable sites. Although landfill disposal is still regarded as the least expensive sound means of disposal it is accepted that in order to withold the principle of "Best Practicable Means" for hazardous waste management, alternate methods of treatment and disposal should be developed that are both safe and effective.

1.2 Waste Arising In The UK and Europe

There are conflicting data available for the total amount of hazardous waste produced in the UK. This is due to the practical difficulties in classifying a waste as hazardous and because most of the hazardous waste produced in this country is handled by the private sector.

The House of Lord's Select Committee Report (7) stated the following figures for hazardous waste arising in the country.

England	4.4 m	tonnes/a
Wales	435000	tonnes/a
Scotland and Northern Ireland	710000	tonnes/a
TOTAL	5.5 m	tonnes/a

The Department of the Environment (9) estimated a figure of 4.4 million tonnes of hazardous waste arised in England and Wales during 1983. Of these totals special waste arisings were estimated at 1.6 million tonnes. The total amount of hazardous waste arising in western Europe was estimated to be 40 million tonnes per annum. The National hazardous waste arising in Europe on a comparable basis is presented in Table 1.1. Given this huge quantity of waste, the disposal problem is high on the priority list of environmental issues throughout Europe.

Table 1.1 Hazardous waste arising in western Europe (11)

	tonne y^{-1}
Austria	350,000
Belgium	1,100,000
Denmark	100,000
West Germany	18,000,000
France	2,000,000
Ireland	100,000
Italy	4,900,000
Netherlands	500,000
Norway	127,000
Portugal	2,800,000
Sweden	520,000
Switzerland	114,000

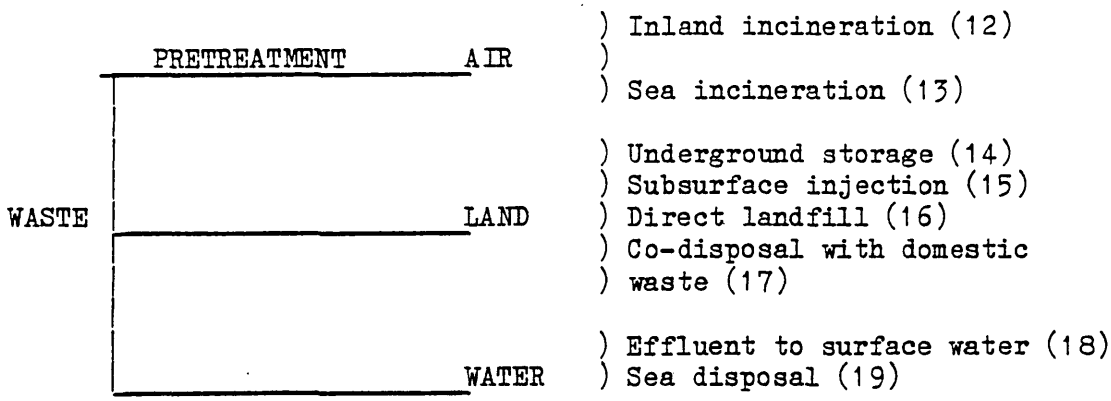
1.3 Disposal options

The first option to be considered in waste management should be waste reduction and recovery. The Department of the Environment has issued a code of practice (6) giving guidance to reduce water consumption in industry. In addition, various waste streams can be utilised for the recovery of metals, oils, solvents and fuel.

For non-recoverable waste there are only three options available for their ultimate disposal, i.e. to air, to land and to water (sea and surface water).

This is illustrated in Figure 1.1

Figure 1.1 Disposal Options



A brief summary of the advantages and disadvantages of the disposal practices is given in Table 1.2.

With proper management landfill disposal of hazardous wastes has, in the UK, been regarded as the least expensive, environmentally sound means of ultimate disposal (17). This is reflected by the proportion of waste that goes to landfill as illustrated in Figure 1.2.

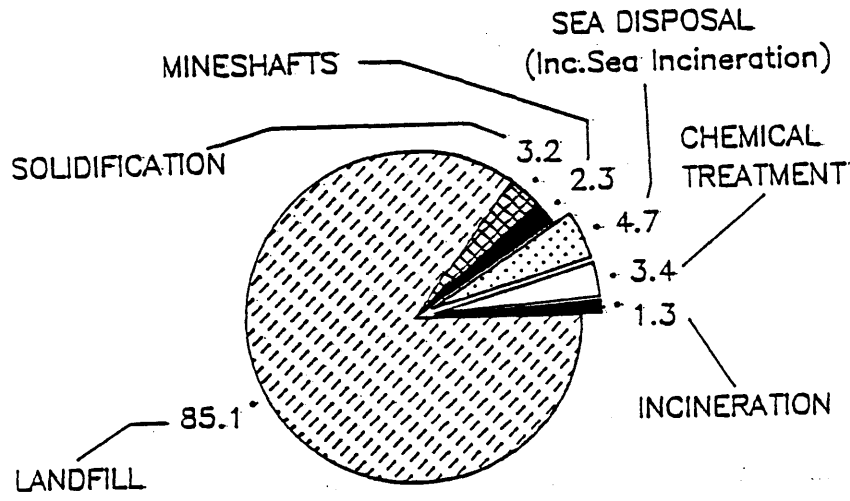


Figure 1.2 Alternate disposal routes and their amount as percentage of total (9)

TABLE 1.2 Advantages and disadvantages of different waste storage and disposal methods (20)

Disposal	1	Relatively inexpensive	1	Demonstrated potential for significant environmental degradation of ocean and coastal areas if performed in uncontrolled manner
	2	Does not require continental land acreage	2	Not economically feasible for wastes generated in non-coastal areas
Effluent to Surface Waters	1	Relatively inexpensive	1	Demonstrated potential for significant environmental degradation of rivers and lakes if performed in uncontrolled fashion
	2	Does not require land acreage	2	Not economically feasible for wastes generated far from river or lake
Subsurface Injection	1	Does not require extensive surface land acreage	1	Requires suitable site-specific geological conditions
			2	May provide long-term potential for uncontrollable groundwater contamination
Incineration	1	Effective at detoxifying certain compound classes, eg PCB	1	Relatively expensive
	2	Does not require land acreage	2	Requires combustible feed or fuel addition
			3	Many produce residues that must be stored or disposed of
			4	Frequently requires pollution control devices that can produce additional wastes
Incineration at Sea	1	Prevent air pollution and aerial fall out	1	Very expensive
			2	Inadequate supervision may lead to illegal discharge at sea

TABLE 1.2 (Continued)

Landfill (Lagooning)	1	Relatively inexpensive	1	Requires significant land acreage
			2	Typically physically unstable; therefore land cannot be reused
			3	Demonstrated potential for groundwater contamination if lagoon unlined or liner deteriorates
			4	Demonstrated potential for surface water contamination if lagoon uncapped and heavy rainfall occurs
			5	Many available liners have limited lifetimes and require replacement to avoid contamination
Co-disposal with Domestic Refuse	1	Relatively inexpensive	1	Limited to certain categories of waste
	2	Capitalize attenuation and degradation potential of biomass	2	Concentrated waste not applicable
			3	Potential groundwater contamination

However, for some specific types of waste, more stringent regulations have been introduced requiring alternative disposal methods, or treatment prior to mono or co-disposal of hazardous waste to land. These pretreatment methods can be classified in three categories: volume reduction (a), detoxification/degradation (b), and stabilisation/solidification (c).

(a) Volume Reduction

Volume reduction can be achieved by

1 Thickening : sedimentation
flotation

2 Dewatering : centrifugation
filtration

(b) Detoxification/Degradation

The object of this treatment is to yield non/less hazardous by-products before disposal. These methods include:

1 Chlorinelysis
2 Oxidation
3 Neutralisation
4 Biological degradation
5 Catalysis
6 Ion Exchange
7 Activated carbon absorption
8 Biochemical processing

Listed in Table 1.3 are some of the treatment facilities available in the UK, with their capacities.

More detailed accounts of these pretreatment methods can be found in Landreth (21), and a study conducted by NATO's Committee on the Challenges of Modern Society (22).

TABLE 1.3 Installed treatment capacity and current throughput of UK hazardous waste treatment facilties (23)

Operator	Location	Types of wastes processed	Capacity t/year	Current throughput t/year	Spare capacity t/year	%
DP Effluents	Runcorn, Cheshire	Acid treatment and liquid wastes	3000	15000	15000	50
Polymeric Treatments Ltd	Killmarsh, North Derbyshire	Dewatering of sludges	5000	Due to commence end of 1980	5000	100
Hargreaves Clearwaste Services Ltd	Wakefield, West Yorkshire	Most inorganic waste	10000	2000	8000	80
Re-Chem International Ltd	Fawley, Hampshire	Most inorganic wastes	20000	11000	9000	45
Re-Chem International Ltd	Pontypool, Gwent	Most inorganic wastes	20000	11000	9000	45
Re-Chem International Ltd	Roughmute, Stirlingshire	Most inorganic wastes	20000	1000	1900	95
Safeway Sludge Disposal	Garrets Green, Birmingham	Acid treatment and sludge dewatering	30000	12000	18000	60
Totals			135000	52000	83000	61
'Solidification' plants (mainly for treatment of inorganic wastes)						
Polymeric Treatments Ltd	Aldridge, West Midlands		250000	150000	100000	40
Stablex	Thurrock, Essex		300000	25000	272000	92
Totals			550000	175000	375000	68

(c) Stabilisation/Solidification

Stabilisation, solidification or chemical fixation are general terms used to describe processes that immobilise, isolate, or contain industrial waste material.

The ultimate disposal options available for hazardous wastes include incineration and disposal to land and sea. Incineration especially incineration aboard an ocean going ship (to allow dispersion of any unpleasant gases produced) is a very attractive option to reduce bulk and toxicity of waste but the application is limited by high costs. The environmental and ecological damage caused by sea disposal is causing increasing concern and international regulations have greatly reduced the amount of hazardous material which can be disposed of to sea. Disposal to land therefore seems to be the most likely option to be used in future. Environmental pollution, especially contamination of ground water resource and consequent legislation, has forced industry to look for improved landfill disposal methods. Chemical pretreatment methods such as detoxification/degradation and stabilisation/solidification are increasingly used prior to ultimate land disposal. Detoxification/degradation processes are generally waste specific and therefore cannot be widely applied. Although there are limitations associated with the presently available stabilisation/solidification processes, the improved leaching characteristics, reduced permeability and improved compressive strength of the treated waste make these disposal methods attractive.

1.4 Stabilisation/Solidification processes

Stabilistion is a pre-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, on the other hand, is a pre-treatment process that produces a solid monolithic mass from a liquid waste

with improved structural integrity and physical characteristics, allowing the material to be readily handled or transported.

Stabilisation/solidification methods claim to offer several advantages including improvement in the handling characteristics of the waste whilst producing a solidified material with sufficient strength to allow for land reclamation. Furthermore, the modified structure significantly reduces the leachability by decreasing the mobility and surface area of the waste exposed. The mobilisation of wastes into water has always been a major consideration in containing hazardous waste, as such, much of the emphasis on stabilisation/solidification processes has been placed on preventing the waste from coming into contact with water and controlling the chemical conditions of the aqueous environment in order to minimise solubility.

Stabilisation/solidification processes can be classified as inorganic fixation processes based on cement, lime, silicates and clay and encapsulation techniques that use specific organic polymers. A general classification of these processes is presented in Figure 1.3.

The United States Environmental Protection Agency lists processes currently available in the following categories: (24)

i) Cement based processes

ii) Lime based pozzolanic processes

iii) Thermoplastic techniques

iv) Organic polymer techniques

v) Surface encapsulation

vi) Glassification

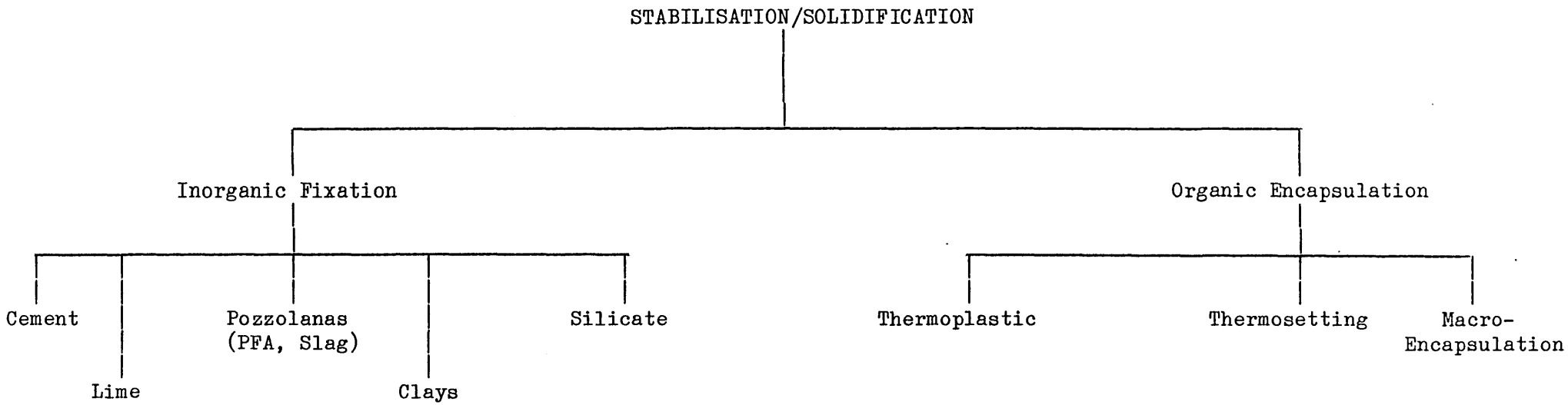


FIGURE 1.3 General classification of stabilisation/solidification processes

Cement based processes (25, 26)

Cement is an anhydrous clinker containing tricalcium aluminate and tricalcium silicate and other components. When mixed together with water a hydration reaction occurs forming a rigid matrix. In the solidification process the waste is mixed with the cement to form a slurry and additives can be included to improve the setting reaction.

Pozzolana based processes (27)

Pozzolanas contain constitutents which combine with lime in the presence of water to produce cementitious matrices. The most commonly used pozzolanas in chemical fixation processes are fly ash and cement kiln dust although there are a number of other natural and artificial pozzolanas. The pozzolanic or lime based processes are similar in their application to cement based processes.

Thermoplastic processes (28)

Thermoplastic materials are organic polymers which soften and harden reversibly on heating and cooling. The most commonly used materials for waste disposal are asphalt and bitumen. The waste is dried, heated and dispersed through the heated plastic matrix. The mixture is then cooled, solidified and usually disposed of in a secondary container.

Organic polymer techniques (29)

The organic polymers are thermosetting plastics which form hardened cross-linked polymers in-situ on the addition of a catalyst. The urea-formaldehyde process is the most common organic polymer technique, with polyester and polybutadiene processes also in use.

Surface encapsulation (30)

An inert material provides a seal between the waste and the environment. Materials such as polyurethane epoxide or fibreglass resins or a mixture of these are brushed or sprayed onto either the waste particles or a container of waste.

Self-cementing techniques (31)

Portions of certain waste sludges containing calcium sulphate or calcium sulphite can be calcined to produce a partially dehydrated cementitious material on mixing with the original waste sludge.

Glassification (32)

Waste materials can be fused with silica to form glass or a crystalline silicate material or fused with other materials to form ceramics.

A summary of method, resource use and possible environmental impact for each process is presented in Table 1.4. A summary of advantages and disadvantages of these techniques is presented in Tables 1.5 and 1.6, and a comparision of their costs is given in Table 1.7.

A wide variety of wastes have been treated by these processes including metal finishing waste, plating and lead smelting acid waste, mine tailings, effluent treatment sludges and flue gas emission control waste. Available data suggest that success is limited and that the processes are more favourable to inorganic wastes especially those containing cations. Organic wastes and inorganic anionic wastes are more suitable for organic encapsulation processes. Table 1.8 lists some of the experience gained with a few selected waste categories. However frequent

TABLE 1.4

Summary of method, resource use and possible environmental impact of the various stabilisation/solidification processes

Process	Method	Resources	Environmental Impact Considerations
Cement-based	(Possible pre-treatment) Mixture to form a slurry which solidifies - using simple technology. Landfill disposal.	Portland cement Silicate additives Fly ash Blast furnace slag Cement kiln dust. (Water) Process energy requirement relatively low.	Add to weight and bulk for landfill disposal. Dust hazard. Requires landfill Site Transportation of hazardous materials.
Pozzolanic	(Pretreatment) Mixing to form a slurry which solidifies - non-specialised technology. Landfill disposal.	Fly ash cement kiln dust Lime (Water) Process energy requirements are relatively low.	Add to weight and bulk for landfill disposal. Dust hazard. Transportation of wastes
Thermoplastic	Waste dried, heated 130-230° and dispersed through heated plastic matrix Mixture cooled and disposed in secondary containment form	Energy Specialised equip-ment and labour. Secondary container Polymers eg, Bitumen Asphalt Polyethylene	Air pollution Volume reduced Fire

TABLE 1.4 (Continued)

Process	Method	Resources	Environmental Impact Considerations
Thermosetting organic polymers	Usually batch process. Waste is blended with polymer then a catalyst added and dispersed. Possible drying of polymer mass, disposal may be in secondary container.	Specialist equipment Monomer-catalyst system, eg urea-formaldehyde Vinyl ester styrene Polyester Epoxy resins Possible energy use.	Weep water for disposal. Air Pollution (hazardous) fumes)
Surface encapsulation	Waste dried, mixed or coated with binder moulded or bonded and heated (up to 200°C) Coated with jacket by fusion	Binder and jacket materials, eg polybutadiene, polyethylene Energy Specialist equipment.	Waste volume reduction Fire hazards. Ultimate disposal route required.
Glassification	Spray drying and heating of waste Fusion with minerals at temperatures of 1000 to 3000°C	Very high energy use Specialist equipment	Volume reduction Possible air pollution from toxic emissions

TABLE 1.5 Summary of advantages and disadvantages of inorganic fixation processes

ADVANTAGES	DISADVANTAGES
Low capital investment of equipment and running costs.	Large amount of raw materials are required.
Materials required are relatively cheap and plentiful	Raw materials (especially cement) are energy intensive.
Techniques for processing are relatively well established	Certain wastes, such as those containing organic compounds may cause some difficulties in curing.
Natural alkalinity of material helps to neutralise acidity in waste solution.	Weight and volume of treated product is considerably increased.
Extensive dewatering is not required because materials incorporate water and can be adopted to wide range of water content.	Treated waste may be vulnerable to leaching, especially mild acids and therefore additional sealant may be required.
Physical properties of treated waste can be varied from soft clay to a monolithic material by selectively varying the ratio of reagent.	Mechanism of stabilisation not well established.
Selected additives can be used to improve retention for certain organic wastes.	

TABLE 1.6 Summary of advantages and disadvantages of organic encapsulation processes

ADVANTAGES	DISADVANTAGES
Contamination migration rates are generally lower than with inorganic processes.	Materials used are expensive.
Less fixative is required when compared with inorganic processes.	Large expenditure of energy in drying, fusing and polymerisation.
Treated materials are of lower density thus reducing transportation costs.	Some organic polymers are flammable.
Organic materials form an impermeable boundary between waste and leaching solution	Processes require skilled labour and expensive equipment.
Processes can encapsulate a wider range of wastes.	Some raw materials are biodegradable and liable to attack by organic solvents.
	Incomplete polymerisation of some of these materials could itself cause pollution.

TABLE 1.7 Economic considerations for waste stabilisation/solidification systems (33)

Type of treatment System	Major materials required	Unit cost of Materials (1980)	Amount of material required to treat 100 lbs of raw waste	Trends in price	Equipment Costs	Energy Requirements
Cement-based	Portland cement	$0.03/lb	100 lb	Stable	Low	Low
Pozzolanic	Lime flyash	$0.03/lb	100 lb	Stable	Low	Low
Thermoplastic (bitumen-based)	Bitumen drums	$0.05/lb $27/drum	100 lb 0.8 drum	Related to oil prices	Very high	High
Organic polymer (polyester system)	Polymer catalyst drums	$0.45/lb $1.11/lb $17/drum	43 lb of polyester catalyst mix	Related to oil prices	Very high	High

TABLE 1.8 Compatibility of selected waste categories with different waste stabilisation/solidification techniques (32)

Waste Component	Cement Based	Pozzolanic/ Lime Based	Thermoplastic Encapsulation	Organic Polymer Techniques	Surface Encapsulation	Glassification
Organics						
Organic solvent and oils	May impede setting, may escape as vapour, may weaken matrix	May impede setting, may escape as vapour	Organics may vaporise on heating, or may decompose	May retard setting of polymers	Must first be absorbed on solid matrix subject to solvent attack	May volatilise or decompose
Solid Organics (eg, plastics, resins, tars)	Good - often increases durability	Good - often increases durability	Possible use as binding agent	May retard setting of polymers	Compatible - many encapsulation materials are plastics	Some solids retard setting
Inorganics						
Acid wastes	Cement will neutralise acids to a limited extent	Compatible	Can be neutralised before incorporation otherwise slow deterioration of matrix, fire or possible violent reactions	Compatible	Can be neutralised before incorporation	Interfere with process unless neutralised
Oxidisers	Compatible	Compatible	May dehydrate and rehydrate causing splitting	May cause matrix breakdown	May cause deterioration of encapsulation materials	Violent reaction at process temperatures

TABLE 1.8 (Continued)

Waste Component	Cement Based	Pozzolanic/ Lime Based	Thermoplastic Encapsulation	Organic Polymer Techniques	Surface Encapsulation	Glassification
Sulphates	May retard setting and cause splitting unless special cement is used	Compatible	May dehydrate	Compatible	Compatible	Compatible in many cases
Halides	Easily leached from cement, may retard setting	May retard setting, most are easily leached	Compatible	Compatible	Compatible	Compatible in many cases
Heavy Metals	Compatible but may require pretreatment	Compatible	Compatible	Acid pH solubilises metal hydroxides	Compatible	May volatilise
Radioactive materials	Compatible	Compatible	Compatible but highly radioactive	Compatible	Compatible	Compatible
Other materials	Ammonium driven off as ammonia gas. Silt, clay lignite and coal may retard setting and curing		Arsenic waste compatibility	Strong alkaline wastes may hinder curing	Compatible with asbestos wastes	

technical problems have not been adequately studied scientifically and there is a need to quantify retention in mechanistic terms.

While many of these materials are not totally retained by these processes their release to the environment by leaching is considerably retarded. Therefore while a process may not be totally adequate for a concentrate-and-contain philosophy it may well be suitable for a dilute-and-disperse policy.

1.5 Cement based stabilisation and solidification processes

Cement based fixation systems are the most commonly employed stabilisation/solidification techniques because of the relatively low capital and running costs and the relatively simple processing technique when compared with organic encapsulation systems.

Chemfix and Sealosafe are both cement based stabilisation/solidification processes which have been operated in the UK. British patents No 1,337,301 and 1,418,215 describe the Chemfix processes. Basically, Chemfix is an inorganic process based on an Ordinary Portland Cement (OPC) and sodium silicate formulation. The stabilisation/solidification process involves mixing a predetermined amount of cement with a contaminated liquid, followed by the addition of the setting agent, sodium silicate. The resulting slurry is transferred or pumped to a nearby lagoon to set and cure. The reagent levels added are related to the required strengths of the final solid - either soft and clay-like or hard and rock-like. The process is claimed (25) to be based on three phases of reaction: an initial rapid reaction between the soluble silicate and all polyvalent metal ions to form insoluble metal silicates, followed by a slower reaction between the silicate and reagent to form a gel, and lastly the hydration of cement. The final product is thought to be built on tetrahedrally coordinated silicon atoms alternating with oxygen atoms along the backbone of a linear chain (25). The pollutant metal ions are ionic bonded

between adjacent chains to form a cross-linked, three-dimensional, polymer matrix similar to the pyroxene mineral.

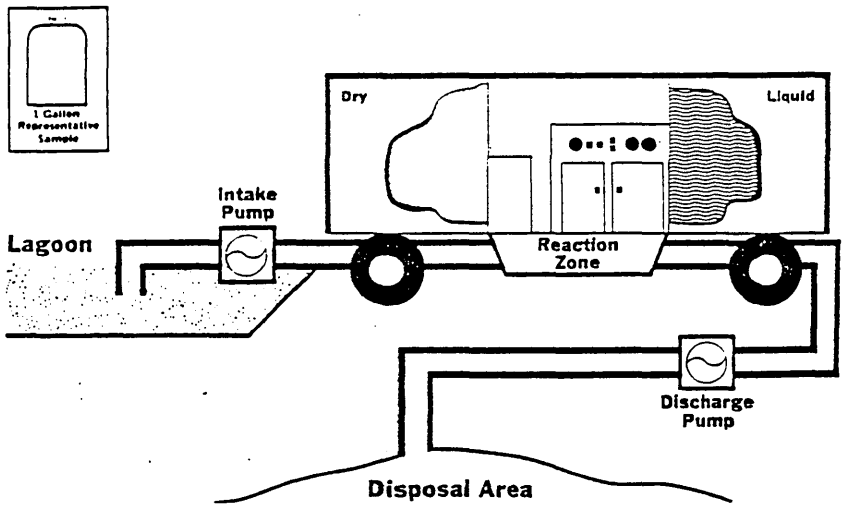


Figure 1.4 Schematic of the Chemfix Process (25)

The Chemfix process has been operated using a mobile plant on individual sites. A schematic flow diagram of the Chemifx process is illustrated in Figure 1.4. Figure 1.5 shows the actual process in operation. Sealosafe, on the other hand is a process based on cement and pulverised fuel ash (PFA) and is described in British patent 1,485,625. This process involves the stepwise addition of predetermined quantities of cement and PFA to the slurried waste. The slurry is then discharged and/or transported to a lagoon to set and cure. The final product is claimed to be leach free with a rock-like feature. The mechanism of such a stabilisation/ solidification process is claimed (26) to be based on "crystal capture" which is a combination of two interdependent reaction mechanisms: pollutants present in pollution form as ions and react with the OPC/PFA forming strong bonds and the pollutants present in insoluble form are dispersed and trapped within the polymer matrix (Fig 1.6).

Figure 1.5 The Chemfix operation using a mobile treatment plant

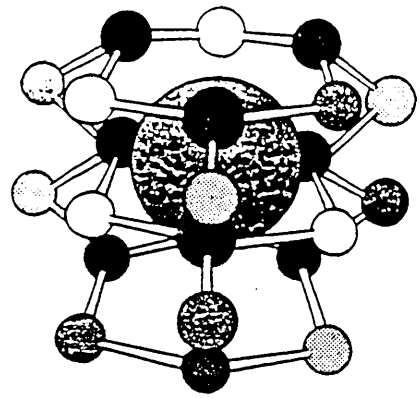


Figure 1.6 The crystal capture mechanism claimed for Sealosafe (26)

Three solidification plants are in operation in the UK. The process is said to be dividied into five unit stages. These are: (26)

1 Reception.

2 Disintegration, during which the waste is dispersed into suitable form for treatment.

3 Pretreatment to convert certain wastes into a chemical form suitable for stabilisation (e.g. for arsenic, chromium and cyanide wastes).

4 Stabilisation: Mixing of stabilisation agent with waste to form a slurry.

5 Disposal: Slurry is transported away to land disposal site to set and cure.

Materials that have been processed by these two processes are listed in Tables 1.9 and 1.10

Most additives used by the processors are proprietary and patented. Because of commercial competition, companies are reluctant to

discuss additives to their particular processes, neither will they discuss their techniques and rates of mixing. Many techniques however are based on empirical formulation between types of waste and additives. Because of this, little data of scientific value is available and consequently waste disposers are frequently not aware of the process most suited to their needs. There is a need for a thorough evaluation of the various commercially available processes so that sufficient information is available for a sensible decision to be taken on type of treatment with regard to economic considerations and protection of the environment.

TABLE 1.9 Chemfix process current industrial applications (34)

Industry	Waste category or source	Physical form of waste
Automobile	Automobile Assembly Wastes	Liquid-Sludge
	Foundry Plant Wastes	Sludge-Solid
Chemical	Activated Sludges	Sludge
	Dissolved Metals	Liquid
	Mineral/Metal By-Products	Sludge
	Neutralised Acids	Liquid-Sludge
	Toxic Metal Containing Sludges	Sludge
Chemical Cleaning	Waste Cleaning Solutions	Liquid-Sludge
Electronic	Mineral/Metal By-Products	Sludge
Fibre	Activated Sludges	Sludge
	Polymer Wastes	Sludge
Metal Finishing & Major Appliance	Dissolved Metals	Liquid
	Ion-Exchange Regeneration	Liquid
Food Processing	Activated Sludges	Sludge
	Processing Wastes	Liquid-Sludge-Solid
Mining	Culm or Tailings	Sludge-Solid
	Neutralisation Plant Wastes	Sludge
Municipal	Sewage Treatment Plants	Liquid-Sludge
	Water Treatment Plants	Liquid-Sludge-Solid
Non-Ferrous Metals	Acid Regeneration Wastes	Soluble Solid
	Fly Ashes	Solid
	Lime/Limestones Wet Scrubbers	Sludge-Solid
	Metal Fines	Solid
Paint & Painting	Conversion Coating Wastes	Liquid-Sludge
	Paint Sludges	Sludge
Pesticide	Toxic Metal-Containing Wastes	Sludge
Plastic	Activated Sludges	Sludge
	Polymer By-Products	Sludge

TABLE 1.10 Typical list of industrial wastes processed through a Sealosafe plant (26)

Source	Pollutants
Liquids	
Adhesive Manufacture	Mercury
Gas Purification Plant	Arsenic
Gas Purification Process	Alkaline sulfides
Paint Spray Booth	Cadmium, lead, tin
Plating Waste	Acid, tin
Plating Liquor	Acid, chromium
Plating Solution	Acid, cadmium
Metal Processing	Cyanide
Solids	
Catalyst Residues	Vanadium
Heat Treatment Residues	Cyanide, barium
Petrochemical Catalyst	Cobalt, molybdenum, nickel
Spent Catalyst	Chromium
Metal Refining Dust	Lead
Metal Smelting Dust	Fluoride
Fire Extinguisher Manufacture	Alkaline, cadmium
Metal Refining	Antimony
Metal Recovery Plant	Copper, nickel, zinc
Gas Purification	Sulphides, cyanide
Furnace Residues	Vanadium
Sludges and Filter Cakes	
Plating Industry	Cadmium, zinc, cyanide
Metal Smelting	Alkaline, arsenic
Tannery	Sulphide, chromium
Acid Pickling	Acid, chromium, zinc
Electrical Component Manufacture	Carbon, cyanide
Railway Washings	Alkaline
Effluent Treatment	Copper, tin
Printing Trade	Copper, zinc
Chemical Manufacture	Barium
Pharmaceutical Manufacture	Zinc
Electroplating Plant	Chromium, lead, copper, nickel
Chloralkali Plant	Mercury
Metal Finishing	Cyanide, zinc, lead, tin
Aluminium Finishing	Alkali, heavy metals

2 OBJECTIVE

2.1 Aim of research

(i) To identify the actual mechanisms operative in the immobilisation of heavy metal waste by cement based stabilisation/solidification processes.

(ii) To improve the mix design criteria of the existing stabilisation/solidification processes and to quantify their merits and short comings.

(iii) To provide the fundamental knowledge to formulate an improved alternative process.

2.2 Experimental approach

The approach adopted was to evaluate the micro and macro properties of various stabilised/solidified materials using:

I) micro-analysis
- (a) X-ray diffraction (XRD)
- (b) electron micropscopy (EM)
- (c) mercury intrusion porosimetry (MIP)
- (d) extended x-ray absorption fine structure (EXAFS)

(a) The XRD technique is useful in studying the changes in the crystalline phases of OPC and PFA upon the addition of waste material. Any new crystalline phase formed between the waste component and the cementitious matrices would be detected by this method. The intensity of the diffraction peaks relates to the quantity of the crystalline phases and can be used to assess the degree of hydration of the cementitious matrices.

(b) Microstructural studies using the Scanning Electron Microscope enable the morphology of the hydrated matrices with and without metal addition to be studied. When fitted with an

x-ray analytical device, the location of the added metal in the matrix can be identified, facilitating an understanding of the fixation mechanism.

(c) Porosity studies using the Mercury Intrusion Porosimeter allow the pore structure of the solidified waste to be studied. This property relates both to the microstructure of the matrix and macro-properties such as permeability and compressive strength.

(d) The EXAFS study is an experiment-sponsored by the Science and Engineering Research Council (SERC) - which uses a high energy synchrotron x-ray source to study the local environment of the metal in the cementitious matrix.

II) macro-analysis
- (a) leaching tests
- (b) compressive strength
- (c) permeability tests

(a) Two leaching test procedures were used to evaluate the leaching characteristics of the solidified waste in two different conditions. The tests are designed to study the long term behaviour and the leaching mechanisms of the solidified material.

(b) Compressive strength measurements on specially prepared cubes give a simple indication of the physical quality of the solidified product.

(c) Permeability studies are performed on the solidified waste using an oxygen permeator. This method is chosen to provide a quick and reproducible assessment of the permeability of the solidified material.

The group IIB elements in the periodic table (i.e. Zn, Cd, Hg) were chosen as model waste compounds because of their importance in industrial practice and their known difference in behaviour in the stabilisation/solidification system.

The correlation between macro and micro properties enables certain critical parameters governing the effectiveness of cement based stabilisation/solidification processes to be identified.

3 MATERIALS

3.1 Simulated heavy metal waste and stabilising materials

Group IIB elements, zinc (Zn), cadmium (Cd) and mercury (Hg) were chosen as simulated pollutants, based on their industrial significance. Chemically, although these three elements appear in the same group in the periodic table their behaviour differs considerably (35). The hydroxide $Cd(OH)_2$ is more basic than the amphoteric $Zn(OH)_2$, whilst $Hg(OH)_2$ is an extremely weak base. The chlorides of Zn and Cd are essentially ionic, whereas $HgCl_2$ has a molecular lattice. Zn and Cd are electropositive metals, but Hg has a high positive standard potential. All the M^{2+} ions readily form complexes but those of Hg^{2+} have formation constants greater by orders of magnitude than those of Zn^{2+} and Cd^{2+}.

The soluble salts of the metals were used as simulated wastes to avoid any imhomogenity in making up trial mixes. The nitrates of Zn and Cd were used because of their high solubility. However, because of the great weakness of $Hg(OH)_2$, an aqueous solution of $Hg(NO_3)_2$ tends to hydrolyse extensively giving a red precipitate of HgO. Thus a further salt of Hg ($HgCl_2$ which also has a fairly high solubility in water) was added to the list of the simulated wastes.

Chemicals used were all Analytical grade supplied by BDH (London, UK).

Stabilising materials

Cement: The cement used was an Ordinary Portland Cement supplied by Blue Circle plc (London, UK) specially made for research purposes. The chemical composition is presented in Table 3.1.

Pulverised Fuel Ash: To minimise the variability of materials, the fuel ash used was a commercially graded Pozzolana supplied by Pozzolanic Ltd (Hemel Hempstead, UK). The chemical composition is presented in Table 3.1.

Table 3.1 Oxide content (%) of OPC and PFA

	OPC	PFA
SiO_2	20.1	47.1
Al_2O_3	5.3	29.8
Te_2O_3	3.5	11.6
CaO	64.6	2.3
MgO	1.3	1.6
SO_3	2.8	0.7
Na_2O	0.13	1.3
K_2O	0.77	3.6
LOI	0.8	4.4

Sodium Silicate: The sodium silicate solution used was 40% aqueous viscous liquid with $NaO:SiO_2$ = 1.0 supplied by Imperial Chemical Industries (Runcorn, UK).

3.2 Basic Composition of Ordinary Portland Cement (OPC) and Pulverised Fuel Ash (PFA)

The main constituents of anhydrous OPC are tricalcium silicate (C_3S about 50% by mass), dicalcium silicate (C_2S ca. 25%), tricalcium aluminate (C_3A, ca. 10%) and an aluminoferrite phase approximately to the formula C_4AF (ca. 10%) (36). The hydration chemistry is dominated by the calcium silicate phases and these provide the main sources of strength development in the cement paste. Other minor constitutents include free lime and gypsum: the latter is added as a setting retarder.

Pulverised fuel ash , on the other hand is a pozzolanic material, possessing no cementitious properties of its own but able to react with the lime liberated during the hydration of calcium silicate in

cement to produce calcium silicate hydrates (C-S-H). Glassy particles in PFA are responsible for most of the chemical reaction. The quantity is probably closely related to the sum of (SiO_2 + Al_2O_3 + Fe_2O_3) in the ash (37). X-ray diffraction analysis has identified some crystalline phases, mainly quartz, mullite, hematite and magnetite. It has been suggested that as far as the pozzolanic reaction is concerned, the mineralogical composition of PFA is more important than its chemical composition (38). Unburnt carbon may constitute up to a few percent of the ash. This is accounted for by the loss of ignition (LOI). The PFA largely comprises insoluble compounds with less than 2% W/W of readily soluble material (39). Most PFA has a thin outer layer of acid sulphate surrounding an alkaline core that contains some free lime. Most soluble matter would finally appear in water as sodium, potassium and calcium sulphate.

It should be noted that the characteristics of PFA vary with its source. Even from a single source, these characteristics may be quite variable, depending on factors such as the source of coal, degree of pulverisation, age of plant, operating conditions and PFA collection and processing methods (37).

3.3 Basic chemistry of OPC

When OPC is allowed to mix with water chemical reactions occur. Generally, the aqueous environment of an OPC/water system becomes very alkaline, with a pH≃12.5, after the initial mixing (40). Calcium and SO_4^{2-} concentrations rise gradually, resulting from the dissolution of cement, mainly due to the presence of lime and gypsum. Concentrations of silica and alumina are much lower than that of Ca, this effect is generally accounted for by the induction mechanism.

These reactions are accompanied by the liberation of heat and the hydration reaction can be followed by calorimetric methods. A typical exotherm is given in Figure 3.1.

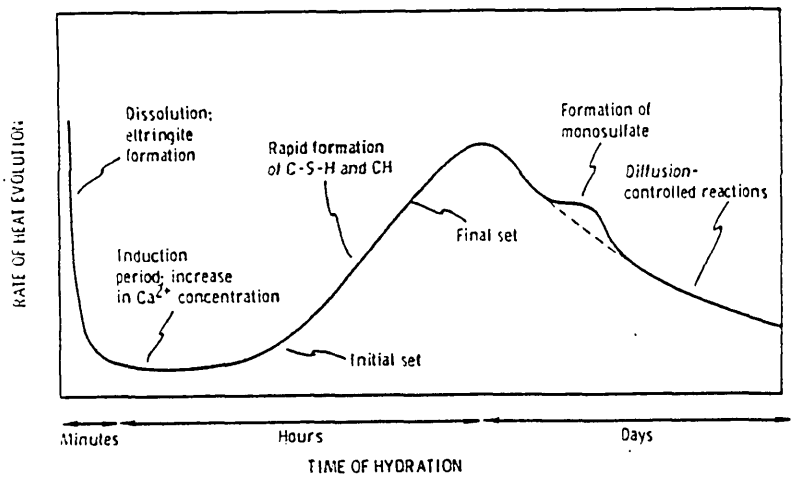


Figure 3.1 Typical exotherm of hydrating cement paste (42)

The hydration reaction occurs in a number of distinct stages. These are characterised by an initial evolution of heat with a later more gradual peak reaching a maximum after about 8-10 hours, decreasing slowly thereafter. The peaks are separated by an "induction period" when the rate of heat evolution drops to a very low value (41). The reasons for such a dormant period are not clear but there are various explanations including the formation of a gelatinous product of hydration forming a coating around the cement grain, or delayed nucleation of $Ca(OH)_2$ crystals affecting the chemical equilibrium for hydration (42).

All four major phases in OPC react with water to form hydration products. These reactions are illustrated in Figure 3.2.

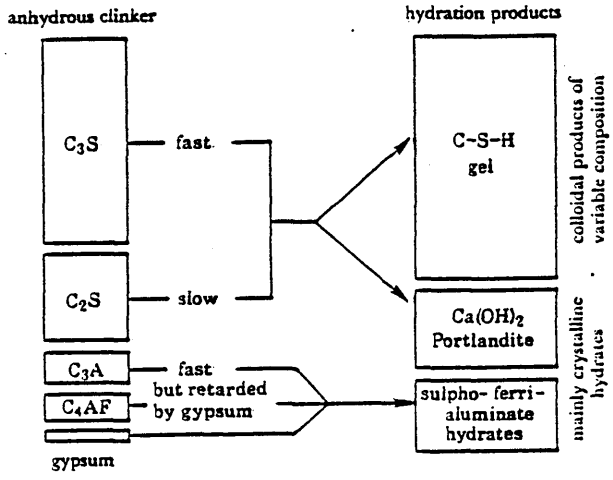


Figure 3.2 Schematic showing hydration reactions of Portland Cement (36).

These four phases do not react independently and there is a complex interaction between each phase.

3.4 Base chemistry of PFA and PFA/OPC systems

The solution chemistry of the PFA/water system is different from that of OPC. When water is first added to the anhydrous PFA, the more acid layer dissolves first and the water becomes temporarily slightly acidic (39). The alkaline core then reacts with the other material in solution the water becoming alkaline. Typical concentrations of the main parameters are presented in Figure 3.3. The exact nature of the curve, the time taken to reach neutrality and the final pH depend on the source and particle size of the PFA and on the water/PFA ratio.

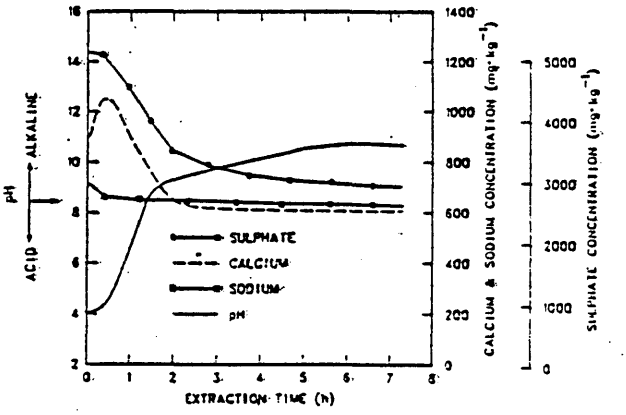


Figure 3.3 Initial aqueous environment of PFA/water system (39)

As previously mentioned, PFA is a pozzolanic material and does not possess a cementitious/hydraulic ability. Cabrera and Plowman (43) identified three mechanisms by which PFA interacts with OPC in the blended cement system.

(i) A physical effect: lubrication of the mix by the mainly spherical PFA particles allows the water demand of the mix to be reduced, with no loss of workability.

(ii) A rapid chemical reaction: soluble ions from PFA react with the calcium aluminates in the cement and retard their hydration.

(iii) A longer term pozzolanic reaction: silica and alumina from the PFA react with calcium hydroxide produced by the hydration of the calcium silicates in the cement.

The first two reactions are important in the first phase of the reaction, affecting the workability and setting of the blended cement. The third pozzolanic reaction - is the major reaction as far as stabilisation is concerned.

The amorphous particles in PFA are probably the most important pozzolanic constituents partaking in the pozzolanic reaction. Some of the possible reactions are: (44)

$$Ca(OH)_2 + SiO_2 + H_2O \longrightarrow xCaO.ySiO_2.zH_2O \quad (1)$$

$$Ca(OH)_2 + Al_2O_3 + H_2O \longrightarrow xCaO.yAl_2O_3.zH_2O \quad (2)$$

$$Ca(OH)_2 + SiO_2 + Al_2O_3 + H_2O \longrightarrow xCaO.yAl_2O_3.zSiO_2.wH_2O \quad (3)$$

$$Ca(OH)_2 + SO_4^{2-} + Al_2O_3 + H_2O \longrightarrow xCaO.yAl_2O_3.zCaSO4.wH_2O \quad (4)$$

At normal temperatures the lime-pozzolanic reaction is slow (45), the rate of reaction being dependent on the reactivity of the glassy materials present. This in turn depends on the surface area and degree of amorphousness of the material (PFA has a relatively low surface area ($< 1\ m^2g^{-1}$ (45)). Although lime from the hydration of OPC is available soon after the addition of water, it is due to the low surface area of the PFA that the pozzolanic reaction is not significant until several weeks hydration have taken place.

For most structural applications the pozzolanic content of a PFA/OPC blended cement is limited to 20 - 25 percent (45). This is because of the required early strength; for instance at stages 3 and 7 days, is generally reduced in direct proportion to the amount of pozzolana present in the cement. Another disadvantage of blended cement is the prolonged moist curing needed for the pozzolanic reaction without which the potential benefits of high ultimate strength and superior chemical durability cannot be realised.

3.5 Basic chemistry of sodium silicate

Soluble silicates have been used as additives in the stabilisation/solidification process (e.g. in Chemfix); the most widely used silicate is aqueous sodium silicate. The various types of sodium silicate normally marketed are listed in Table 3.2.

Table 3.2 Types of sodium silicate

SiO_2 : Na_2O	NAME	FORMULA
1 : 2	Sodium orthosilicate	Na_4SiO_4
2 : 3	Sodium sesquisilicate	$Na_6Si_2O_7$
1 : 1	Sodium metasilicate	Na_2SiO_3
2 : 1	Sodium disilicate	$Na_2Si_2O_5$

Sodium silicate solution is alkaline in nature: the pH value of the available silicates lies in the range of about 11 to 13 (46). The solution is strongly buffered by soluble silica in solution. Hence, within limits, the silicate solutions will maintain a fairly constant pH despite the additions of acid and the high pH of the solutions is maintained as acids are added until the alkali is almost completely neutralised.

Several classes of materials react with sodium silicate to form sols or gels. These materials include acids, acid forming materials such as chloride and bicarbonates, some organics and most importantly, as far as stabilisation processes are concerned, salts of heavy metals such as calcium, copper and lead.

When a polyvalent metal salt is mixed with a sodium silicate solution two specific reactions will take place. First the insoluble metal silicate will be precipitated, second the increase in pH in the environment of the metal ion at some point causes the

formation of a colloidal metal hydroxide. This may be visualised as an absorption of metal ions on gelatinous silica during mutual coagulation of the positively charged colloidal metal hydroxide and negatively charged colloidal silica (47). This suggests that no definite compounds are formed and that the hydroxides are precipitated along with the insoluble metal silicate.

Structurally, the precipitated gel of hydroxide and silicate is essentially amorphous in nature. In soluble silicate, the silicate ions are polymerised to form a mixture of polysilicate ions of non-uniform size. Upon precipitation, they cannot arrange themselves along with the metal ions into a regular crystal lattice. The mutual coagulation of silicate and hydroxide further inhibits the formation of regular crystal structure and therefore the insoluble precipitate is always amorphous.

Such a precipitate consists of three-dimensional network made up of a chain of particles that may range in size from polysilic acid units each containing only a few silicon atoms, to colloidal silica particles containing thousands of silicon atoms. The particles are bonded together into chains, probably by hydrogen bonding. However, with the surface SiOH group the Si-O-Si bond could be formed when these particles come together upon consolidation (46).

Thus it can be concluded that such a gel formed between polyvalent ions and a soluble silicate has a very unstable mix composition. The properties of such a gel, i.e. strength, durability and permeability, may vary greatly depending on factors such as concentration of the solution, Na_2O : SiO_2 ratio, temperature and the kind of salt with which it reacts (46). Frequently, these gels have a high specific surface area and are capable of acting as selective absorbents. On ageing the gel shrinks, becomes opalescent, cracks and dissolves readily in a caustic solution. Shrinkage is the most important process leading to the deterioration of the gel. Shrinkage may be caused by syneresis (i.e. spontaneous expulsion of water after the gel has been formed), desiccation and solution or erosion by groundwater. Thus the life of such a gel is limited, especially when it is exposed to air or basic groundwater.

4 MICRO ANALYSIS

4.1 Scanning electron microscopy, x-ray diffraction and porosimetry

4.1.1 Method

The samples that were prepared for analysis by SEM, XRD and MIP analysis are listed in Table 4.1.

Table 4.1 Mixes prepared for micro analysis

I	Cement	water/OPC = 0.6
II	Chemfix	(OPC + sodium silicate solution) solution/OPC = 1 silicate/OPC = 0.1 a) distilled water b) 2% Zn c) 2% $HgCl_2$ d) 2% $Hg(NO_3)_2$ e) 2% Cd
III	Flyash	solution/PFA = 1.0 a) distilled water b) 2% Zn c) 2% $HgCl_2$ d) 2% $Hg(NO_3)_2$ e) 2% Cd

Table 4.1 Mixes prepared for micro analysis cont'd

IV	Sealosafe	(OPC + PFA)	
		PFA/OPC	= 3.0
		solution/solid*	= 0.5

a) distilled water
b) 2% Zn
c) 2% $HgCl_2$
d) 2% $Hg(NO_3)_2$
e) 2% Cd

* solid = OPC + PFA

SEM and XRD examinations were performed on 1 day samples. The MIP study was performed on 7 day samples.

Electron Microscopy analyses were performed with a Jeol 35 CF (London, UK) Scanning Electron Microscope (SEM) fitted with an EDAX system manufactured by Pye Unicam (Cambridge, UK). The X-ray diffraction analyses were made on powdered samples, using a Philips X-ray powder diffractrometer with a CuKα radiation source (Cambridge, UK). Specimens for SEM and XRD examinations were prepared by stopping the hydration of the cementitious matrices by soaking in acetone. After drying, fracture surfaces of the specimens were mounted onto examination stubs using adhesive and subjected to electrical conductivity coating with either carbon or gold. Silver coating paint was applied judiciously to assure conduction to ground.

Powder specimens or specimens too weak to yield a fracture surface were examined without pre-grinding by mounting on the stubs using double sided adhesive tape, and coated as above.

The pore volume as a function of the pore radius was determined according to the following equation (for cylindrical pores) (48).

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

where P = applied pressure
d = pore diameter
γ = surface tension
θ = contact angle of the mercury on the pore wall.

A commercial mercury porosimeter manufacturered by Carlo Erba (Series 200) was employed.

4.1.1.1 Basic morphology of hydrated OPC and OPC/PFA pastes

In the hydration of cementitious matrices readily identifiable hydration products can be summarised as follows: (49)

i) Unhydrated cement grains : roughly of equal measurement and up to 20 and 40 μm in size. The surface may show signs of etching or of hydrolysis reaction with water.

ii) Calcium hydroxide crystals, C-H* : at early stages these appear as thin hexagonal plates up to tens of μm across. Sequential deposition causes these crystals to grow vast and form mass crystals with easily recognisable parallel planes.

iii) The AFm phases typified by monosulphate : AFm stands for Al-Fe-mono and is a low sulphate form of calcium aluminate sulphate hydrate. The phases are easily recognisable under SEM by their hexagonal plating structure, though much smaller than the C-H ($\triangleq$ 1 μm across and 0.1 μm thickness). They tend to show a characteristic edge-to-face contact at the fracture surface.

*Cement chemistry notations are used.

iv) The AFt phase, typified by ettringite: AFt stands for Al-Fe-tri which is a high sulphate form of calcium aluminate sulphate hydrate. These are unbranched crystals of hexagonal prisms, or needles up to a few μm long.

v) Calcium silicate hydrate (C-S-H): produced from the hydration of C_3S and C_2S. According to Diamond (50) four varieties of C-S-H can be distinguished by the SEM.

a) Type I. Fibrous particles typically 0.5 to 2 μm in length, sometimes branched. These have occasionally been described as tubular, but more often as solid, lath-like or rolled sheets. This phase provides the predominant structure in the early stages of hydration.

b) Type II. They are seen in the SEM as a honeycomb reticular network similar in scale to Type I. They occur universally in hardened cement paste and may also appear in the early stages of hydration.

c) Type III. They are equant or flattened grains, often below 0.3 μm across and common in hardened cement pastes.

d) Type IV. These are a compact material laid down within the initial outlines of the cement grains often called the inner product. They are similar in morphology to Type III C-S-H.

Two types of structure commonly found in OPC and OPC/PFA matrices are:

Hadley grain (51)

A robust shell of the hydration product between 0.5 and 1 μm in thickness formed around unhydrated particles, and shells joined

together with sufficient cohesive strength for many of them to rupture during fracture. This exposes the unhydrated particles, and reveals features often referred to as Hadley grains. The formation of these grains has been associated with particles emptying out from within the initial skeletal network. Hadley grain formation illustrates the weak bond developed within the network of interconnected thickening shells.

Duplex film

Often found in the hydrating OPC/PFA blended matrix is the Duplex film (52). This film is made up of a uniform continuous layer of calcium hydroxide deposited on the exposed surface, plus a thin layer of C-S-H gel particles. This gel is usually of the Type I variety. The film is thought to be developed from the deposition of C-H and C-S-H out of solution onto the surface of the grain rather than from the reaction product of the chemically inactive flyash particle surface. As hydration proceeds the duplex films may eventually become tied to bulk cement paste by deposition of additional calcium hydroxide, ettringite or other hydration products.

4.1.2 Results

4.1.2.1 SEM

The hydrated structures of the pure OPC/water system are shown in Figure 4.1 Appropriate to the high water/cement (W/C) ratios used, these structures were present with fibrils of calcium silicate hydrate (C-S-H), rods of ettringite and massive deposits of calcium hydroxide (C-H) crystals. Common features of C-S-H fibrils penetrating C-H crystals and ettringite crystals embedded in a cluster of C-S-H were visible. The structure was porous, this being a consequence of the high W/C ratio (i.e. 1 initially and - 0.6 finally).

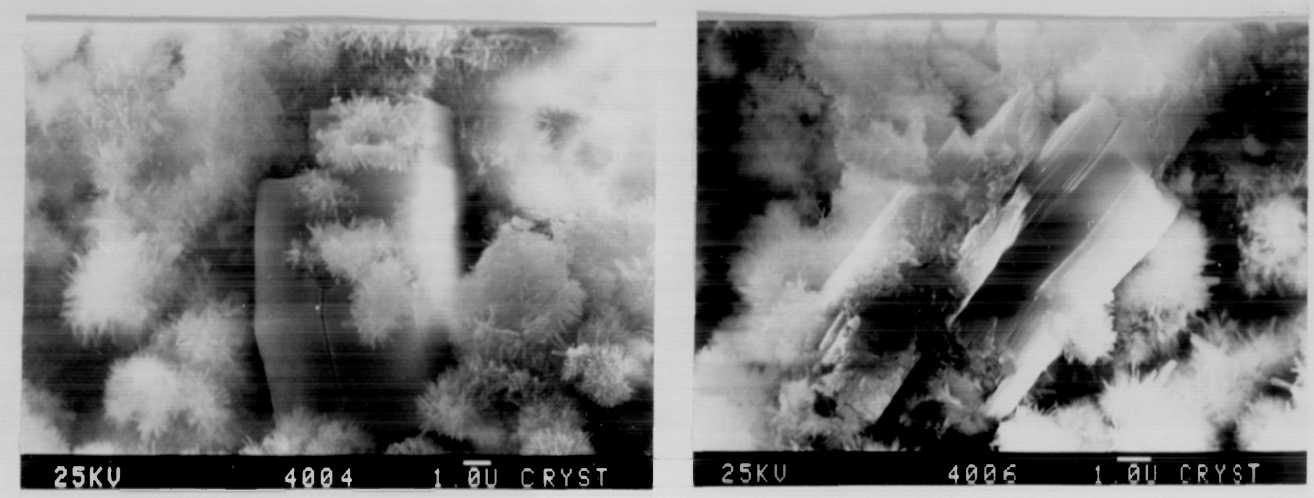


Figure 4.1 Micrographs of the cement sample showing large crystals of C-H, cluster of fibrous Type I C-S-H with some penetrating the C-H crystal.

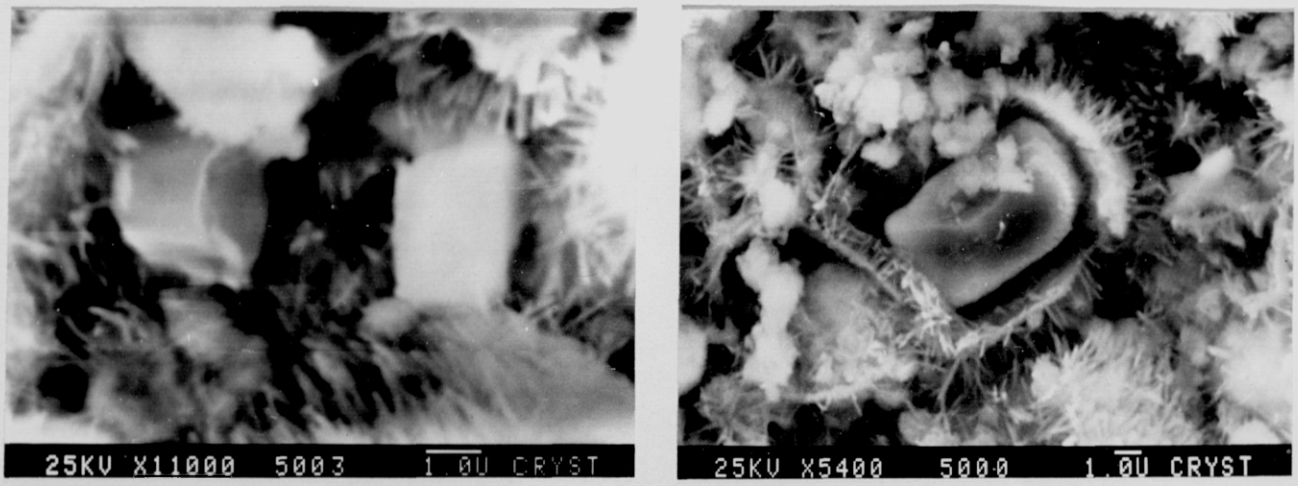


Figure 4.2 Micrographs of the Chemfix sample showing cement hydration products typified by Hadley grain with fibrous C-S-H. C-H crystals are smaller. Also observable are gel of Ca-Silicate.

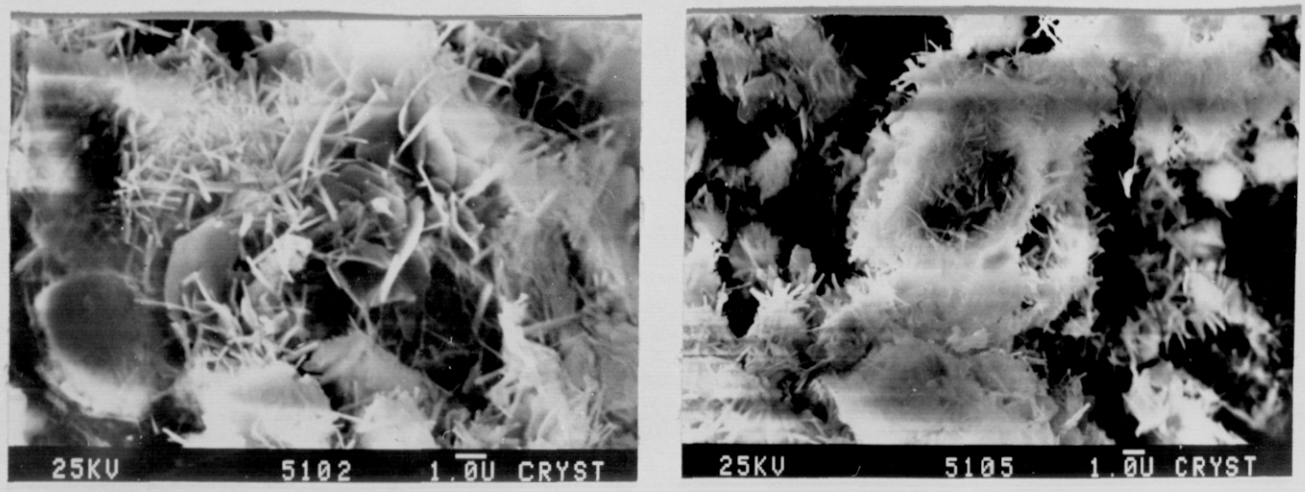


Figure 4.3 Micrographs of the Zn dosed Chemfix sample showing ettringite crystals and hexagonal AFm phase. Cement grains are covered by layer of amorphous gel.

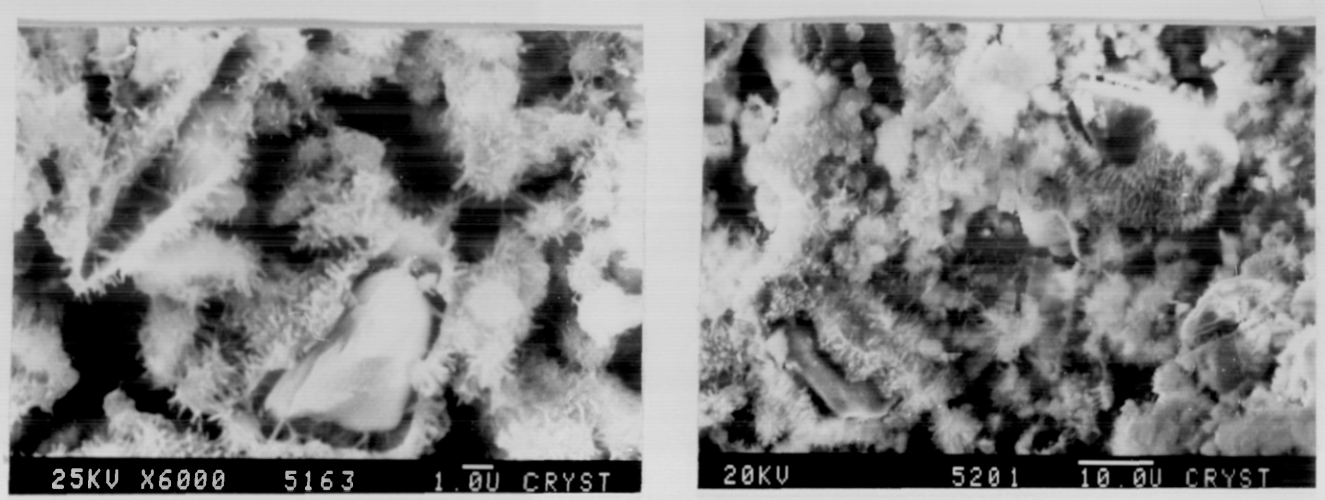


Figure 4.4 Micrographs of the $HgCl_2$ dosed Chemfix sample showing normal cement hydration products with Hadley grains and fibrous Type I C-S-H.

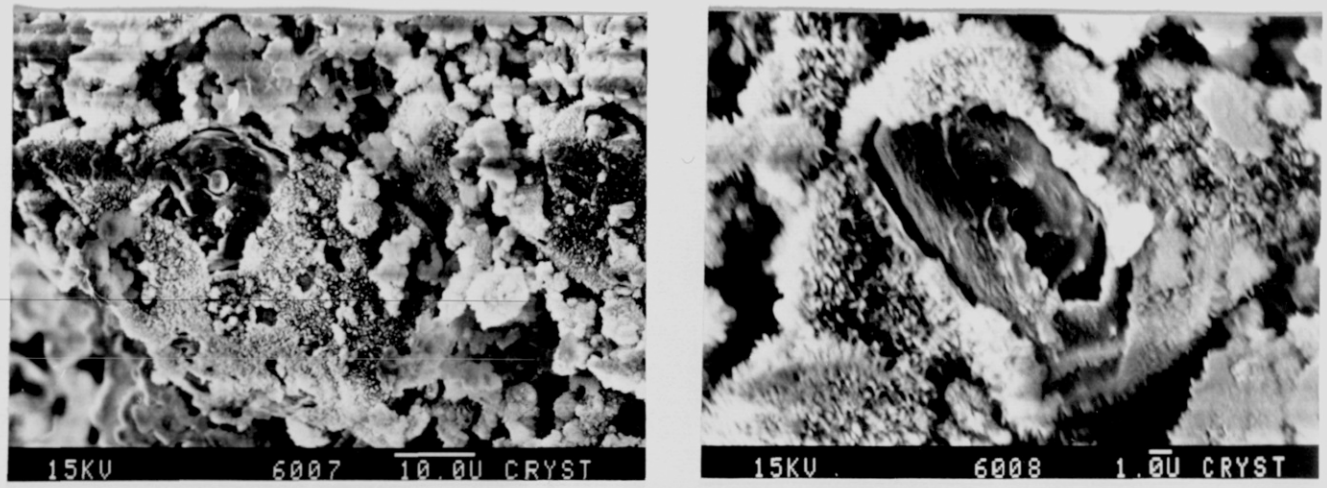


Figure 4.5 Micrographs of the $Hg(NO_3)_2$ dosed Chemfix sample showing Hadley grains but C-S-H formed are predominantly Type II with denser texture.

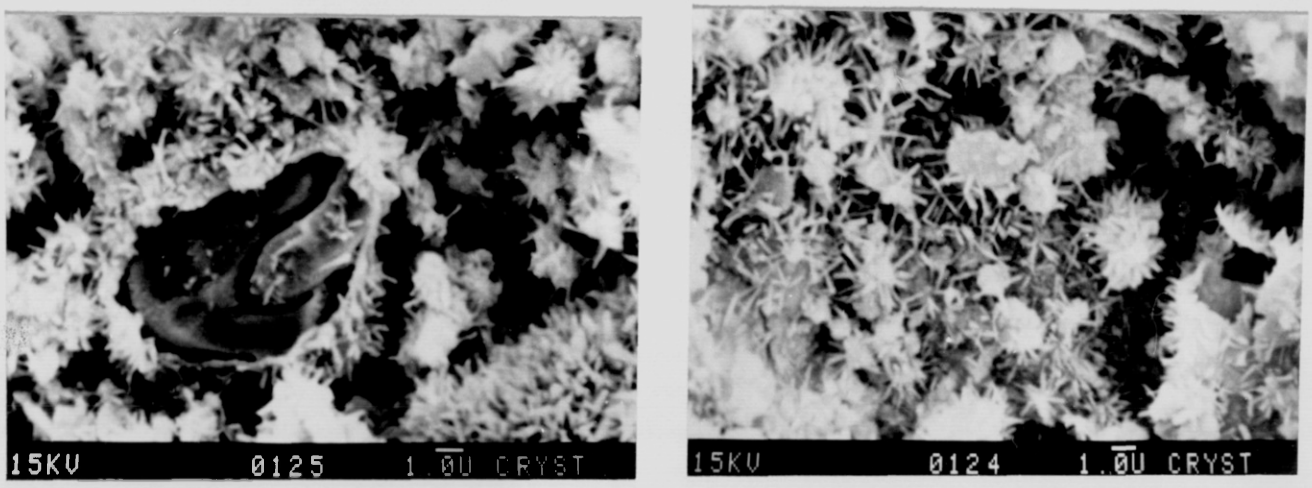


Figure 4.6 Micrographs of the Cd dosed Chemfix sample showing Hadley grain but with large amount of ettringite and monosulphate crystals.

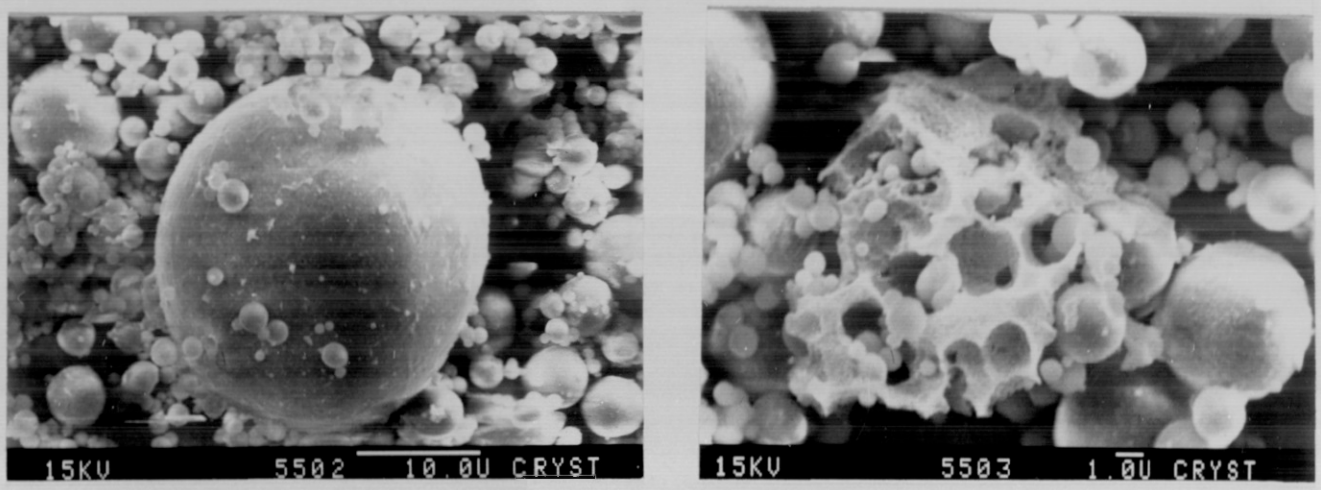


Figure 4.7 Micrograph of the as received pulverised fuel ash. Particles are spherical in shape with smooth surface. There are also areas of carbon residue showing a honeycomb embedding the smaller particles.

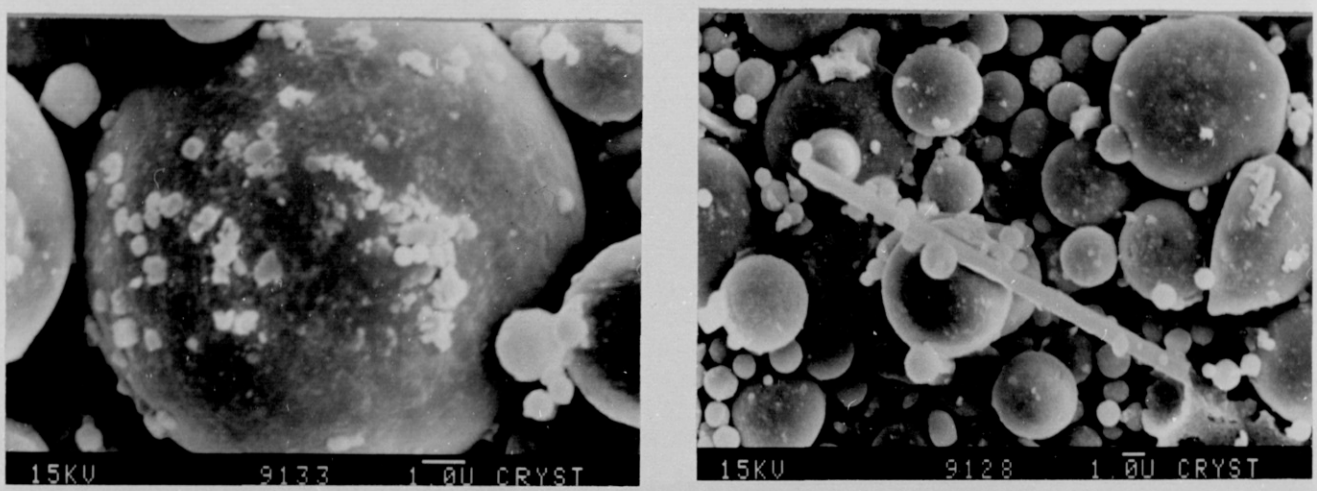


Figure 4.8 Micrographs of the hydrolysed PFA particles showing etched surface and long rods of gypsum crystals deposit between the particles.

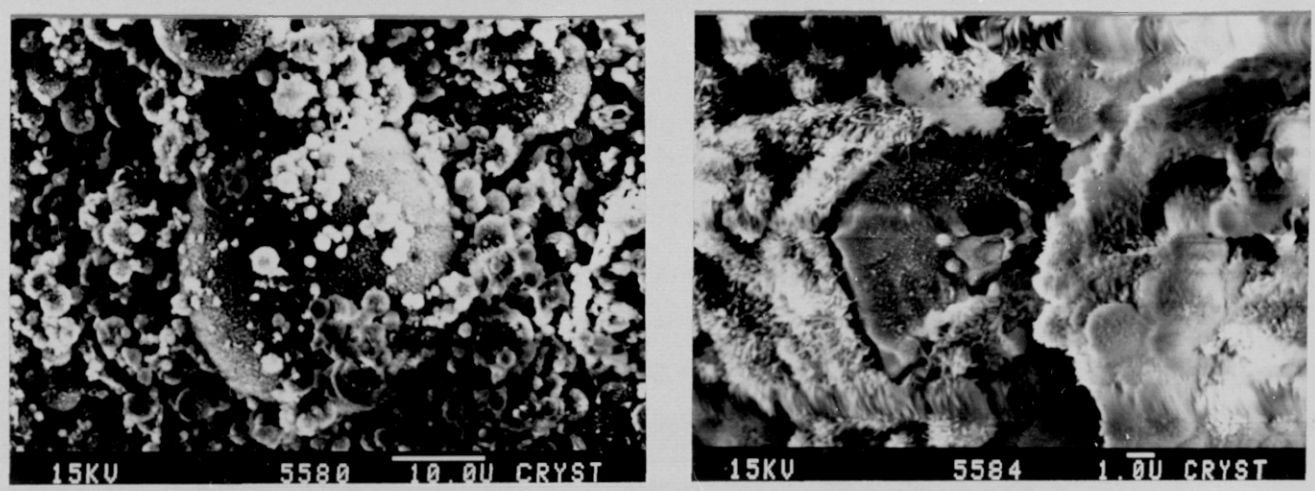
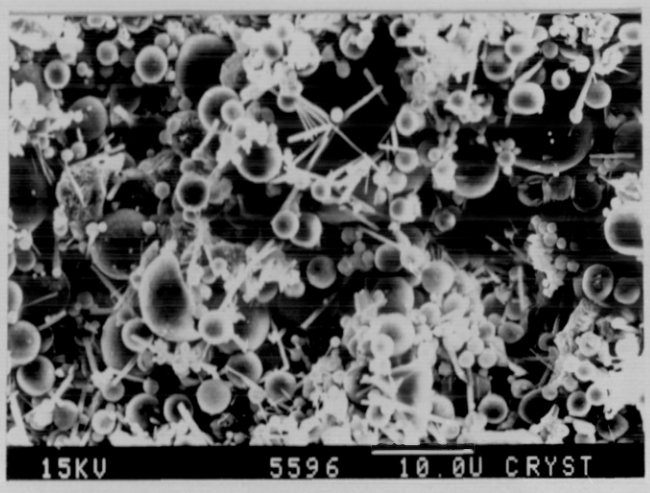


Figure 4.9 Micrographs of the Sealosafe sample showing deposition of hydration products on the PFA particle. Hadley grains are produced from cement particles.



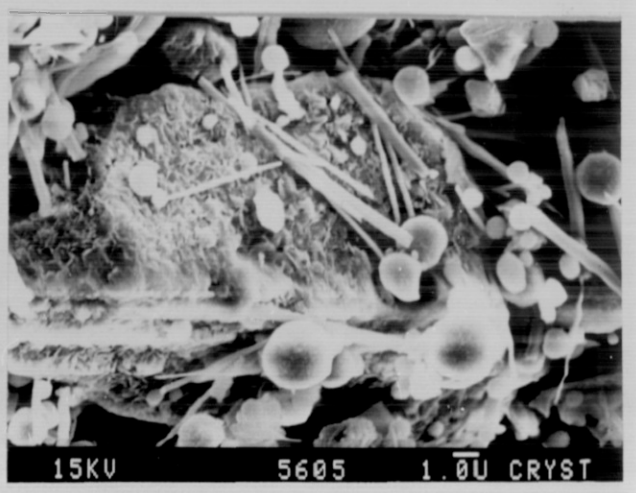
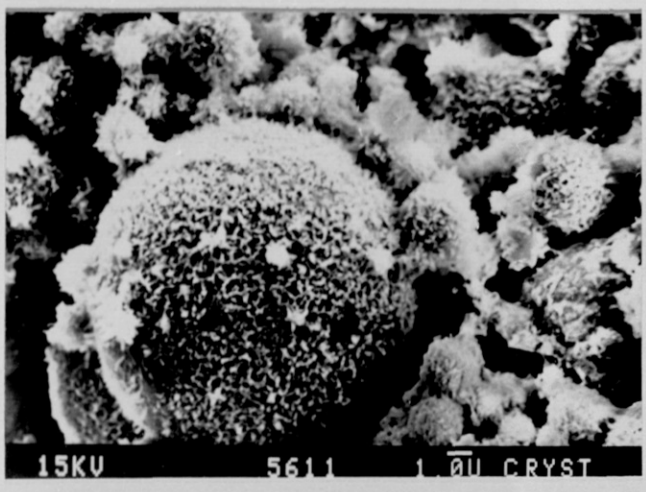


Figure 4.10 Micrographs of the Zn dosed Sealosafe sample showing long and large rods of ettringite crystals. PFA particles are smooth and little hydration took place on the cement particle.



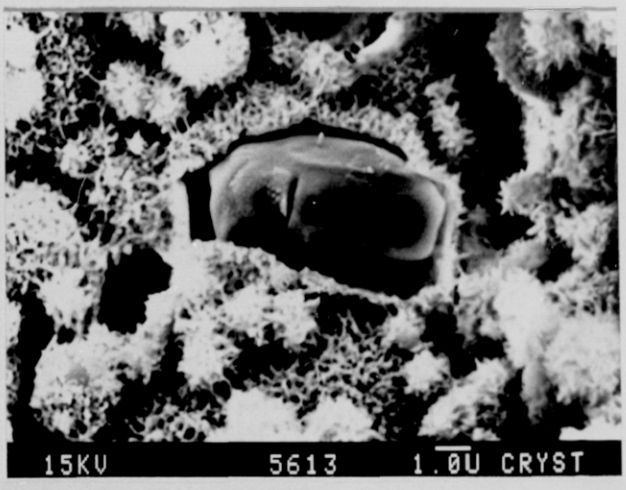
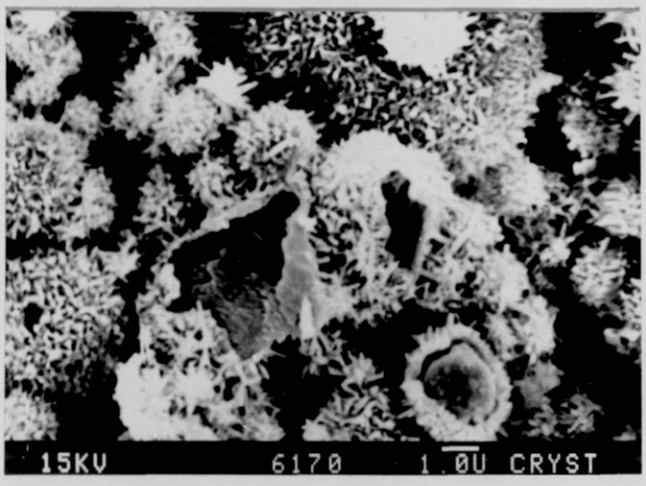


Figure 4.11 Micrographs of the $HgCl_2$ dosed Sealosafe sample showing hydration products on the PFA particles and normal products of cement hydration products - Hadley grains and C-S-H.



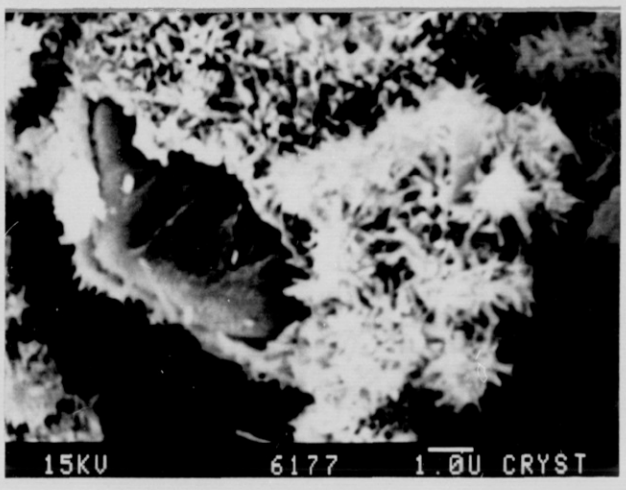


Figure 4.12 Micrographs of the $Hg(NO_3)_2$ dosed Sealosafe sample showing similar feature to the $HgCl_2$ sample but Hadley grains have a thicker shell.

Figure 4.2 shows the effect of adding sodium silicate to the cement matrix. Similar hydration products of C-S-H (typified by the Hadley grain), ettringite and C-H were observable, but were also areas of amorphous structure which did not show any resemblance to ordinary C-S-H of hydrated cement. These areas may have been formed from the reaction between Ca^{2+} from cement and SiO_3^{2-} from sodium silicate producing a calcium-silicate gel. Formation of such a gel accelerated the setting of cement and also increased the water demand of the system. Therefore no bleeding was observed when the paste was prepared, despite the high water/cement ratio (i.e. W/C = 1). Crystals of C-H were noticeably much smaller compared with those of pure cement.

The micrograph of the Zn-dosed sample (Figure 4.3) shows the effect of adding 2% Zn^{2+} to Chemfix. The hydration pattern of cement was significantly altered by the addition of Zn^{2+}. No ordinary fibrous C-S-H and massive C-H crystals were identifiable but the morphology was dominated by the large ettringite crystals occurring as hexagonal prisms and plates of monosulphates. Cement grains were covered by an amorphous layer of gel.

The effect of adding $HgCl_2$ to Chemfix is illustrated by Figure 4.4. Normal hydration products of cement typified by Hadley grains and fibrous C-S-H were observed. Also visible was the massive deposit of calcium-silicate gel resulting from the interaction between the calcium in the cement and the added sodium silicate. Comparision with Figure 4.1 shows that the hydration of cement was not significantly altered by the addition of $HgCl_2$.

Mercuric nitrate, on the other hand did have some effect on the hydration of cement as displayed in Figure 4.5. Although the hydration of cement proceeded to produce C-S-H as indicated by the Hadley grains the type of C-S-H formed was predominantly of

the reticular Type II. There was little fibrous Type I as normally encountered in the early stages of hydration.

Micrographs of the Cd-dosed Chemfix samples (Figure 4.6) show that the hydration of cement was retarded. Although the Hadley grain with its C-S-H formation was observed, the morphology was different to the normal hydration products. They showed a rather densely layered structure with few fibrous hydration products. Also observed were calcium aluminate sulphate hydrates typified by ettringite and monosulphates with the monosulphate dominating.

Electron micrographs of the as-received PFA particles are shown in Figure 4.7. It shows the particle sizes varying between 0.5 μm to 40 μm. The particles were mainly spherical in shape and generally have a relatively smooth surface although there were some very small structures extending from some of the particle surfaces. Also shown in the figure is the residual carbon forming a honeycomb around a few ash particles.

The effect of adding water and other metal solutions to PFA has been examined under the SEM. Generally all samples displayed similar features. A typical representation is shown in Figure 4.8. The most dominant feature was the long and sometimes thick rods of crystalline deposited. The surface of the PFA particles remained smooth although there were some signs of etching and reaction on the smaller particles.

Figure 4.9 shows micrographs of the PFA/OPC sample after 1 day's hydration in water. The PFA particles were covered by a thin film (Duplex film) of hydration products though it cannot be concluded whether these products were formed directly from a reaction between the alkaline pore solution and PFA particles or were merely deposited from the pore solution during cement hydration. Looking at the cement particles, hydration proceeded normally producing calcium silicate hydrates (C-S-H) typified by Hadley grains. Types of C-S-H produced were fibrous Type I and reticular Type II.

For the Zn-dosed PFA/OPC sample (Figure 4.10), the dominant feature was long rods of crystal which could be identified as ettringite by their hexagonal cross section. The PFA surface was smooth with few hydration products. On examining the cement particles, no identifiable C-S-H was observed but the grains were covered by an amorphous layer of precipitate.

Figure 4.11 shows the SEM micrograph of the $HgCl_2$-dosed Sealosafe sample. On the PFA surface, Duplex films similar to those observed in the distilled water mix were observed. Cement hydrated normally to produce fibrous Type I and reticulate Type II C-S-H. Hadley grains could also be seen.

The effect of the $Hg(NO_3)_2$ on the micro-structure (Figure 4.12) of the hydration products of PFA/OPC blended system was very similar to that of $HgCl_2$ with C-S-H formed on both PFA and cement surfaces.

The dominant feature under the SEM in the Cd-dosed sample was the hexagonal rods of ettringite crystals (Figure 4.13) which were associated with both the PFA and cement particles. A layer of amorphous precipitate was seen on some cement particles.

4.1.2.2 XRD

Two standard traces are produced in Figures 4.14 and 4.15 showing the x-ray diffraction patterns of anhydrous OPC and the PFA used in the study. Crystalline constituents identifiable in the anhydrous cement powder were Alite (C_3S), Belite (C_2S), tricalcium aluminate (C_3A) and the ferrite (C_4AF) phases. In the PFA powder, the major crystalline phases detected were mullite and quartizite.

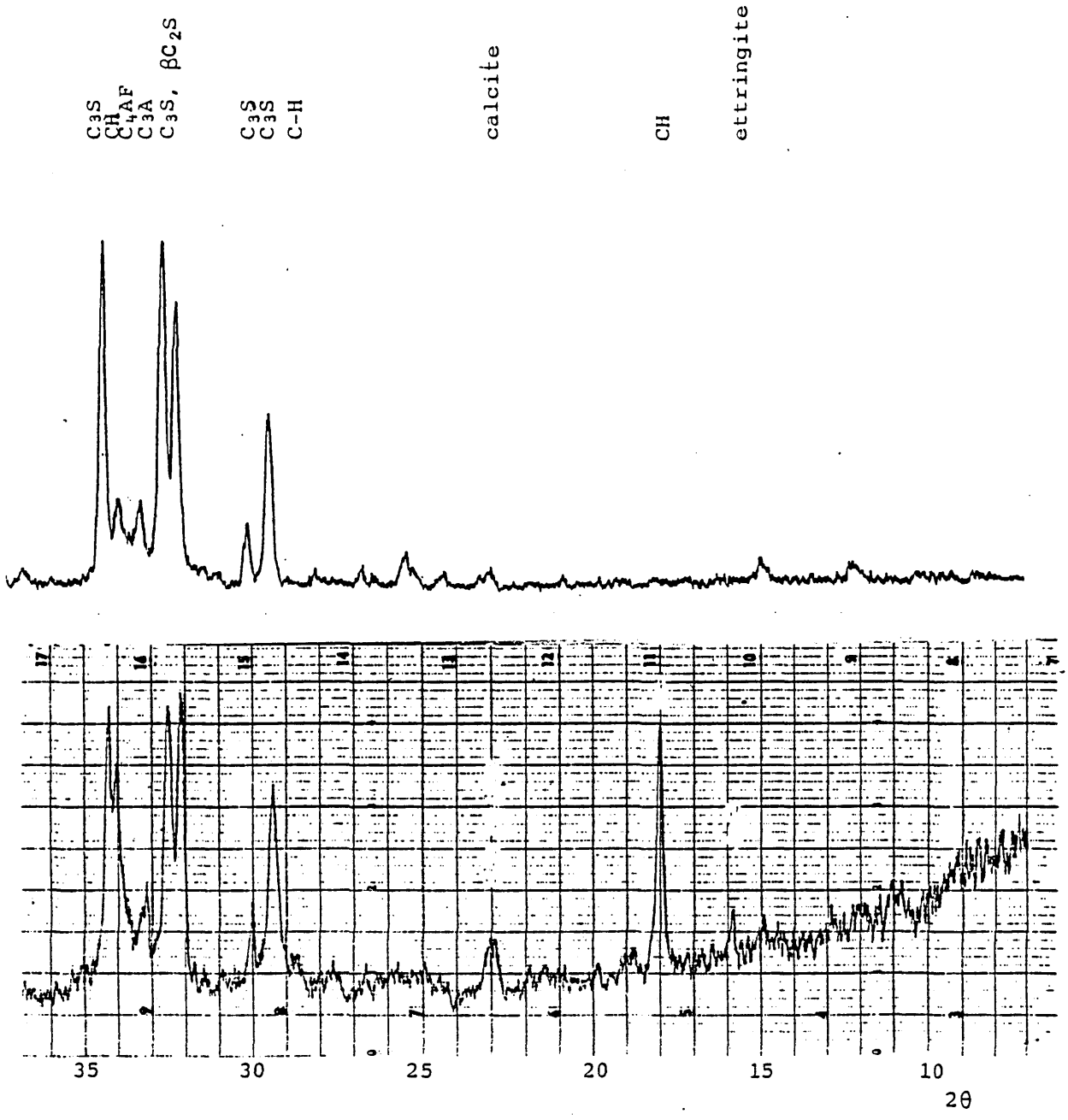


Figure 4.14 XRD pattern of anhydrous OPC and OPC hydrated in water for 1 day

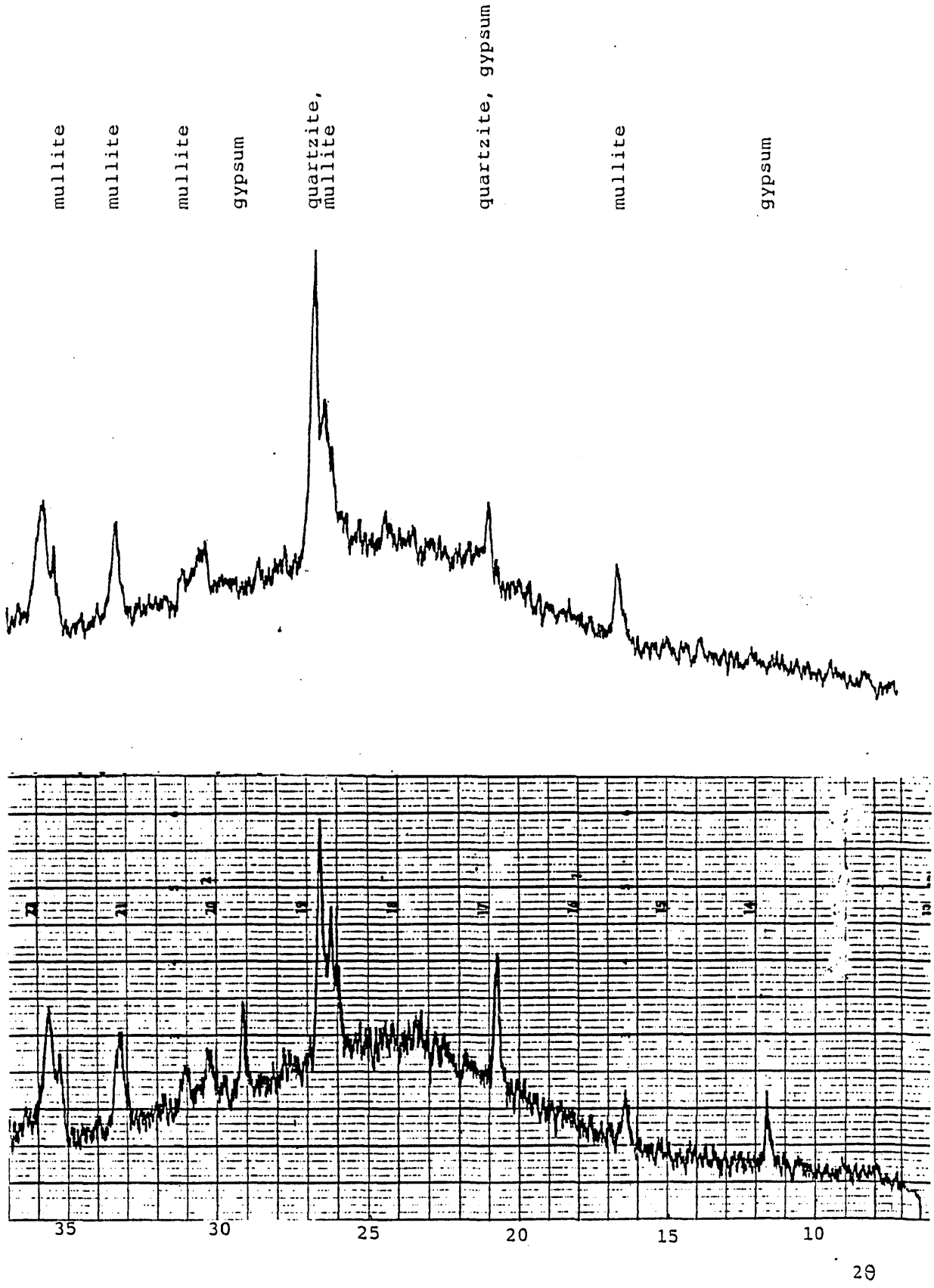


Figure 4.15 XRD pattern of anhydrous PFA and PFA hydrated in water for 1 day

Diffraction patterns in Figures 4.14 and 4.15 illustrate the effects of addition of water to cement and PFA after one day. The additional phase of interest in the cement sample was the C-H (calcium hydroxide) (peaks at 18.08°, 28.66° and 34.08°). In the PFA sample, peaks at (2θ = 11.70°, 20.80°, 23.47° and 29.19°) corresponding to the gypsum ($CaSO_4.2H_2O$) phase were detected.

The addition of different metal solutions to the PFA particles produced a similar crystalline composition to that of the water/PFA system. i.e. all the samples produced gypsum peaks with little other difference.

The addition of sodium silicate solution to cement in the Chemfix sample (Fig 4.16) resulted in a very similar crystalline constitutent to that of the pure water/OPC system. No new crystalline phase was detected.

This was also the case for the addition of other metal solutions to the Chemfix mix (Fig 4.16). The chemical effect of metals on the hydration of the cement, however, can be demonstrated by the semi-quantative analysis of the crystalline phases. The Zn-dosed sample displayed no C-H peaks but larger Alite and Belite intensities. The two Hg samples produced similar C-H and anhydrous cement peaks. While the C-H peaks in the Cd-dosed sample were smaller than the control Alite and Belite peaks were more intense than in the pure water/Chemfix mix. Comparing the 1 and 7 day diffraction patterns (Figs 4.16 and 4.17) it can be seen that the hydration of cement resulted in lower Alite and Belite intensities with larger C-H peaks.

The crystalline phases detected in the Sealosafe samples were the combination of the crystalline constituents of cement and PFA (Fig 4.18). The additional phase of interest was the C-H phase and its presence showed that the hydration of OPC had proceeded to form C-S-H and lime. Ettringite was also detected in the one day samples showing the reaction between the

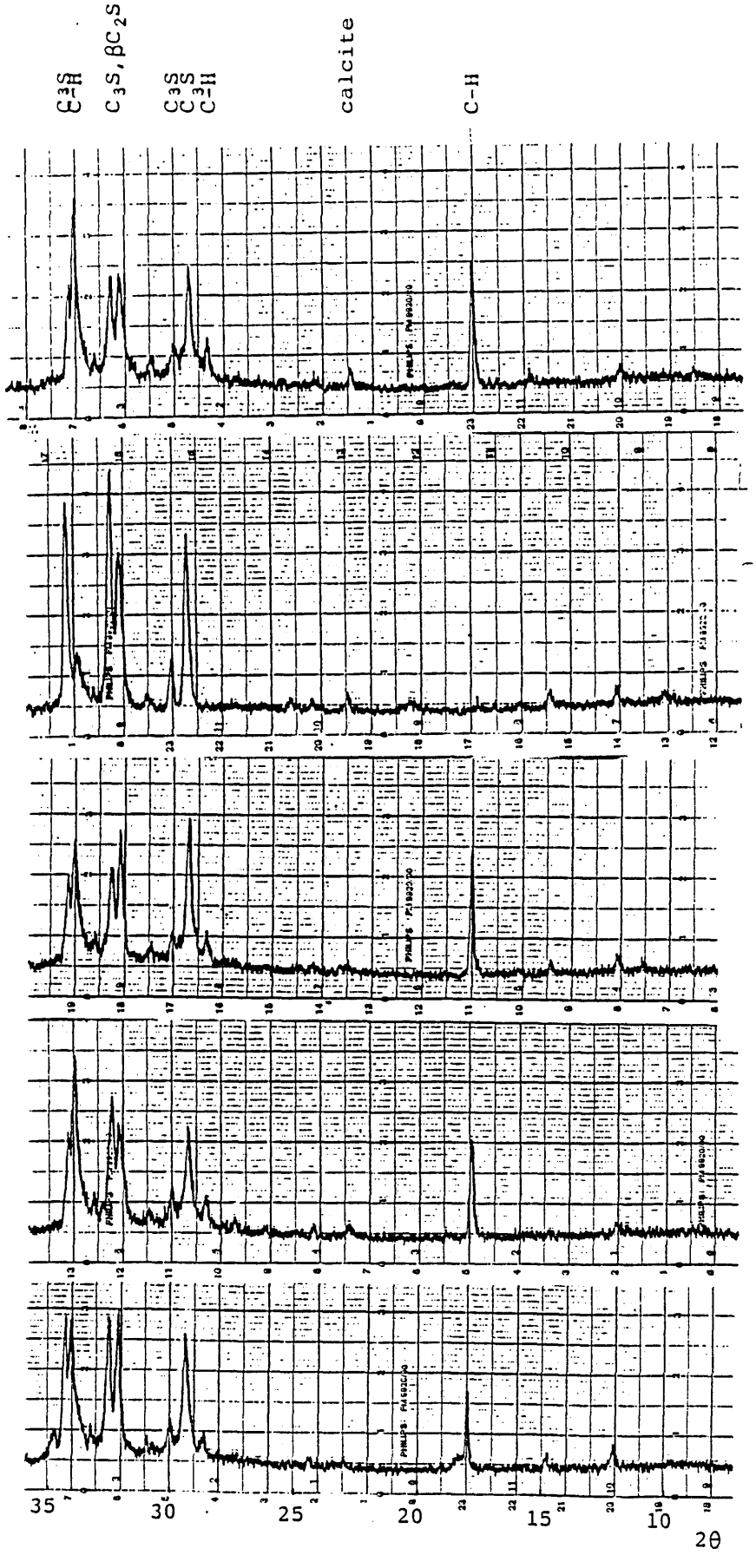


Figure 4.16 XRD pattern of OPC/silicate (Chemfix) hydrated for 1 day

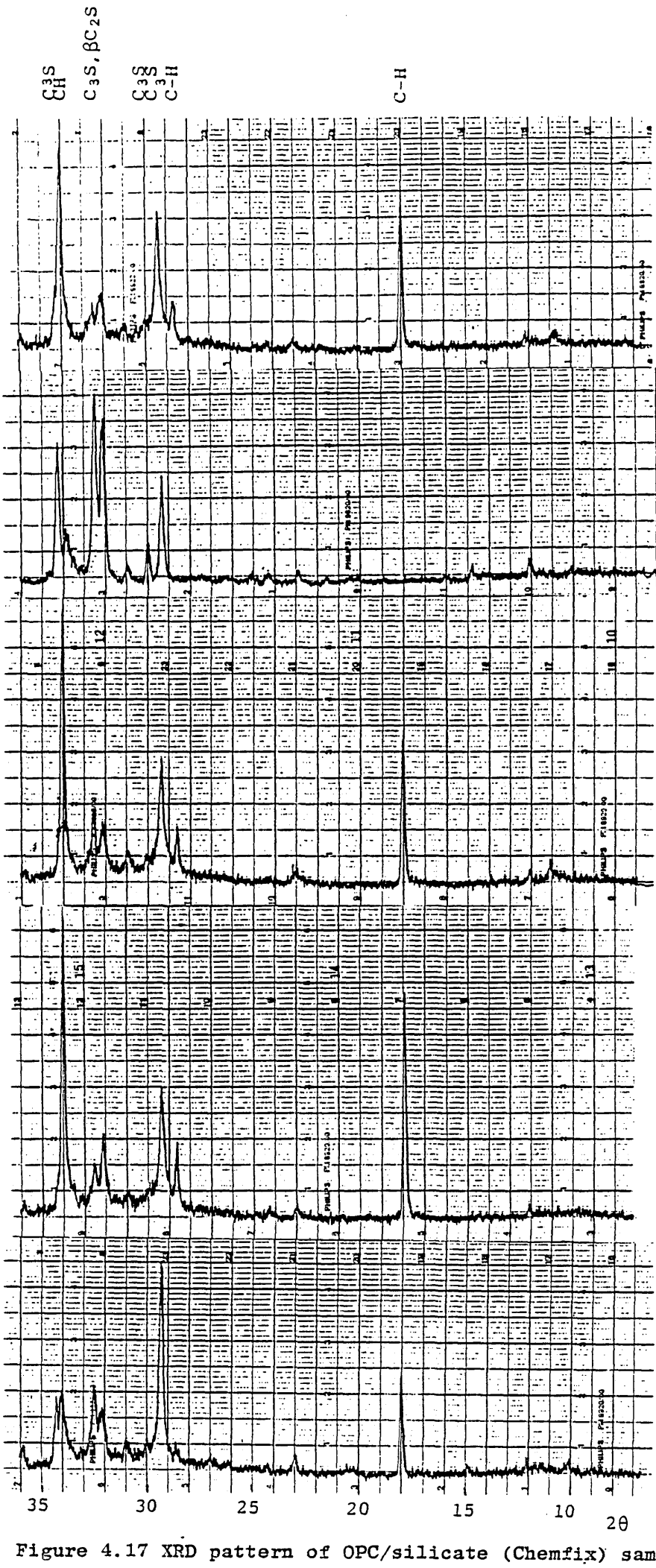


Figure 4.17 XRD pattern of OPC/silicate (Chemfix) samples hydrated for 7 days

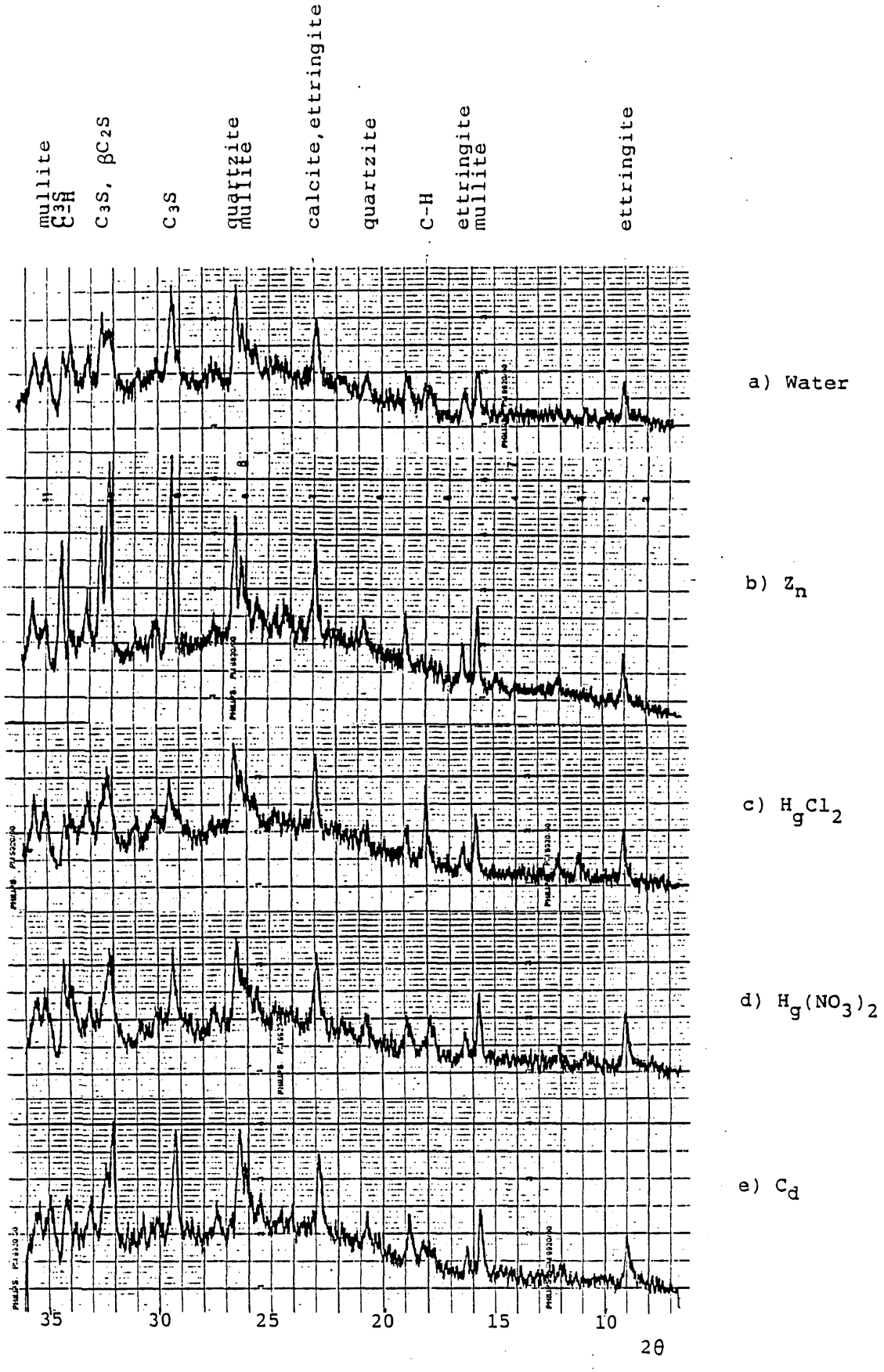
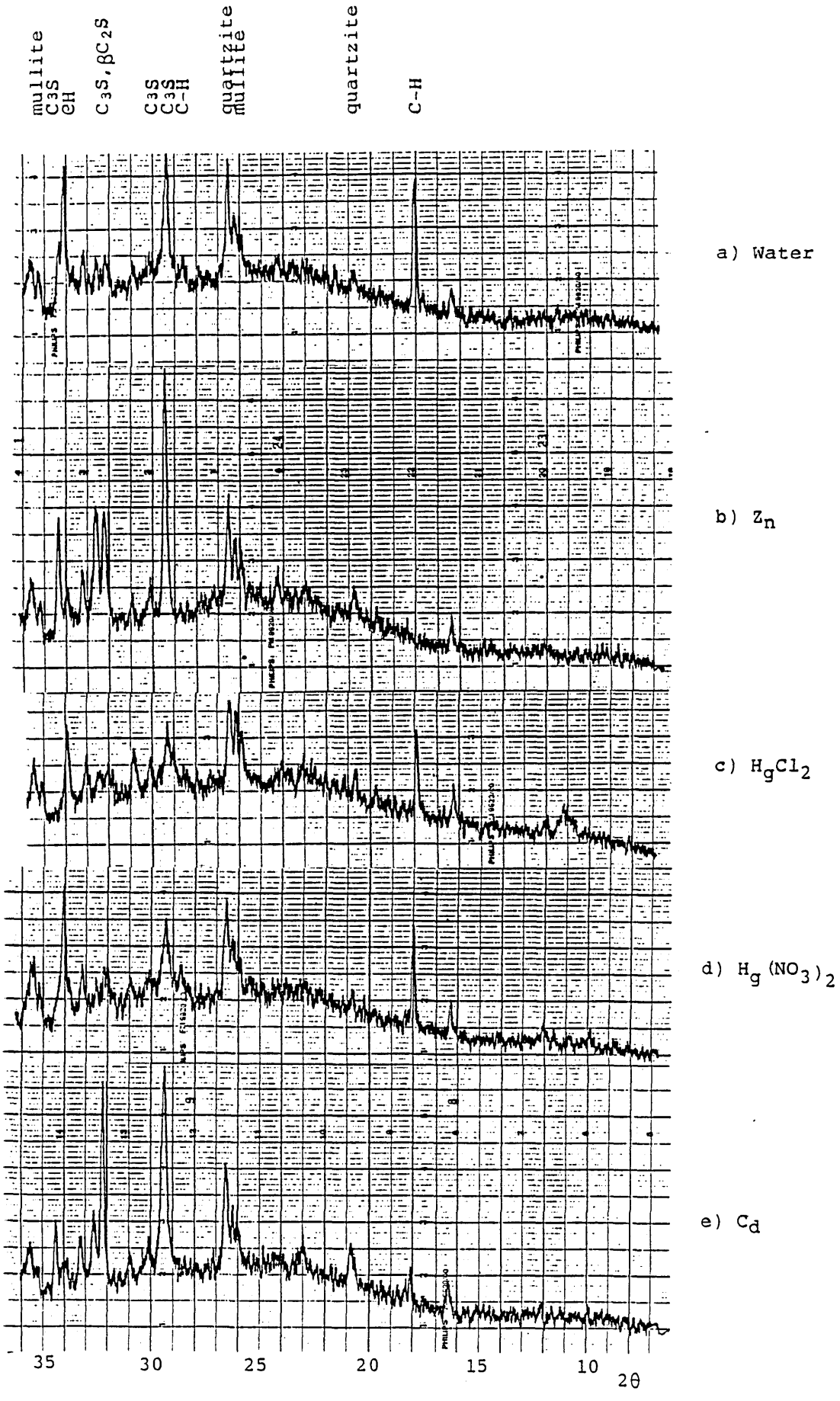


Figure 4.18 XRD pattern of OPC/PFA (Sealosafe) samples hydrated for 1 day

Figure 4.19 XRD pattern of OPC/PFA (Sealosafe) samples hydrated for 7 days



aluminate phase and gypsum. The addition of metal solutions to the Sealosafe matrices produced a similar effect to that in Chemfix, with the intensity of the C-H phase depressed in the Zn and Cd-dosed samples. The two Hg-dosed samples produced similar crystalline constituents to that of the control sample. It should be noted that the crystalline phases of the PFA (quartzite and mullite) were not modified by the hydration reaction as indicated in both the 1 and 7 day diffraction patterns (Figs 4.18 and 4.19).

4.1.2.3 MIP

The results of the porosity measurements are presented in Table 4.2 and the associated pore size distributions are presented in Figures 4.20 and 4.21.

The cement sample with a W/C = 0.6 had the smallest total intruded volume. The total intruded volume for the Chemfix samples were in the order of Zn > Cd > $Hg(NO_3)_2$ > water > $HgCl_2$. For the Sealosafe products this order was Zn > water > $Hg(NO_3)_2$ > Cd > $HgCl_2$.

Pore size distribution diagrams (Figures 4.20 and 4.21) show that both the Zn and Cd samples had a higher percentage of the pore volume in the larger pore radii. The two Hg samples, however, had a larger proportion of the pore volume in the smaller radii.

A simple ranking system was devised to assess the pore size distribution, and was based on the summation of the total percentage of intruded volume above 10,000A. Using this system, the calculated ranking is presented in Table 4.3. The Chemfix sample can be assessed as Cd > Zn > water > $Hg(NO_3)_2$ > $HgCl_2$ in descending order of pore size and the Sealosafe samples are in the order of Zn > Cd > water > $HgCl_2$ > $Hg(NO_3)_2$.

Table 4.2 Mercury Porosimetry Data

	Additive	Total intruded volume (mm^3g^{-1})
Cement	-	136.00
W/C = 0.6		
Chemfix	a water	527.97
W/C = 1	b 2% Zn	855.80
Si/C = 0.05	c 2% $HgCl_2$	473.94
Cured for 7 days	d 2% $Hg(NO_3)_2$	559.10
	e 2% Cd	625.95
Sealosafe	a water	435.69
	b 2% Zn	456.67
PFA/OPC = 3	c 2% $HgCl_2$	348.59
W/S = 0.5	d 2% $Hg(NO_3)_2$	400.11
Cured for 7 days	e 2% Cd	370.23

Table 4.3 Percentage of Pore Volume Greater Than 10,000 Å

Chemfix	a	Water	11
	b	Zn	28
	c	$HgCl_2$	2
	d	$Hg(NO_3)_2$	10
	e	Cd	33
Sealosafe	a	Water	15
	b	Zn	63
	c	$HgCl_2$	4
	d	$Hg(NO_3)_2$	1
	e	Cd	36

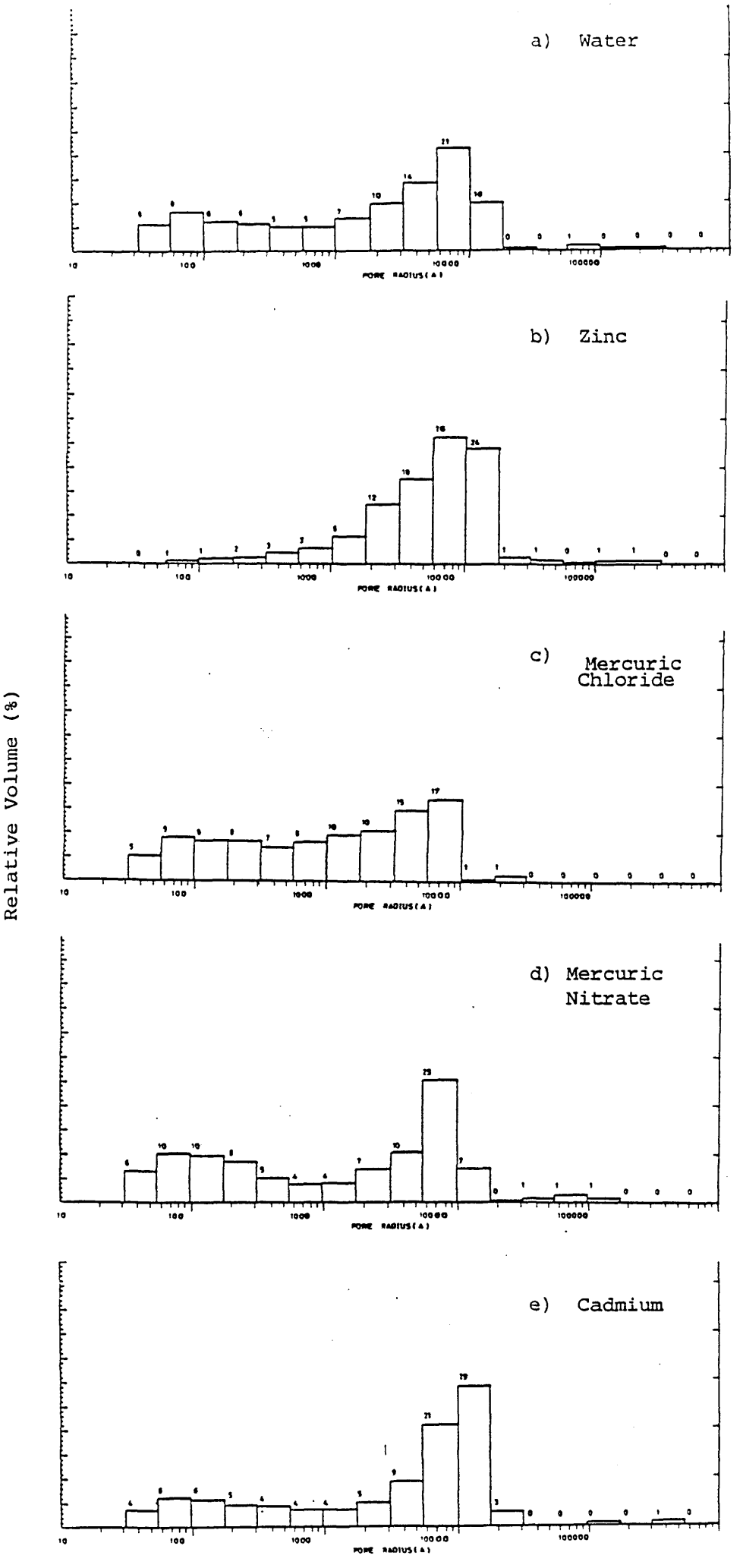


Figure 4.20 Pore size distribution of the Chemfix samples

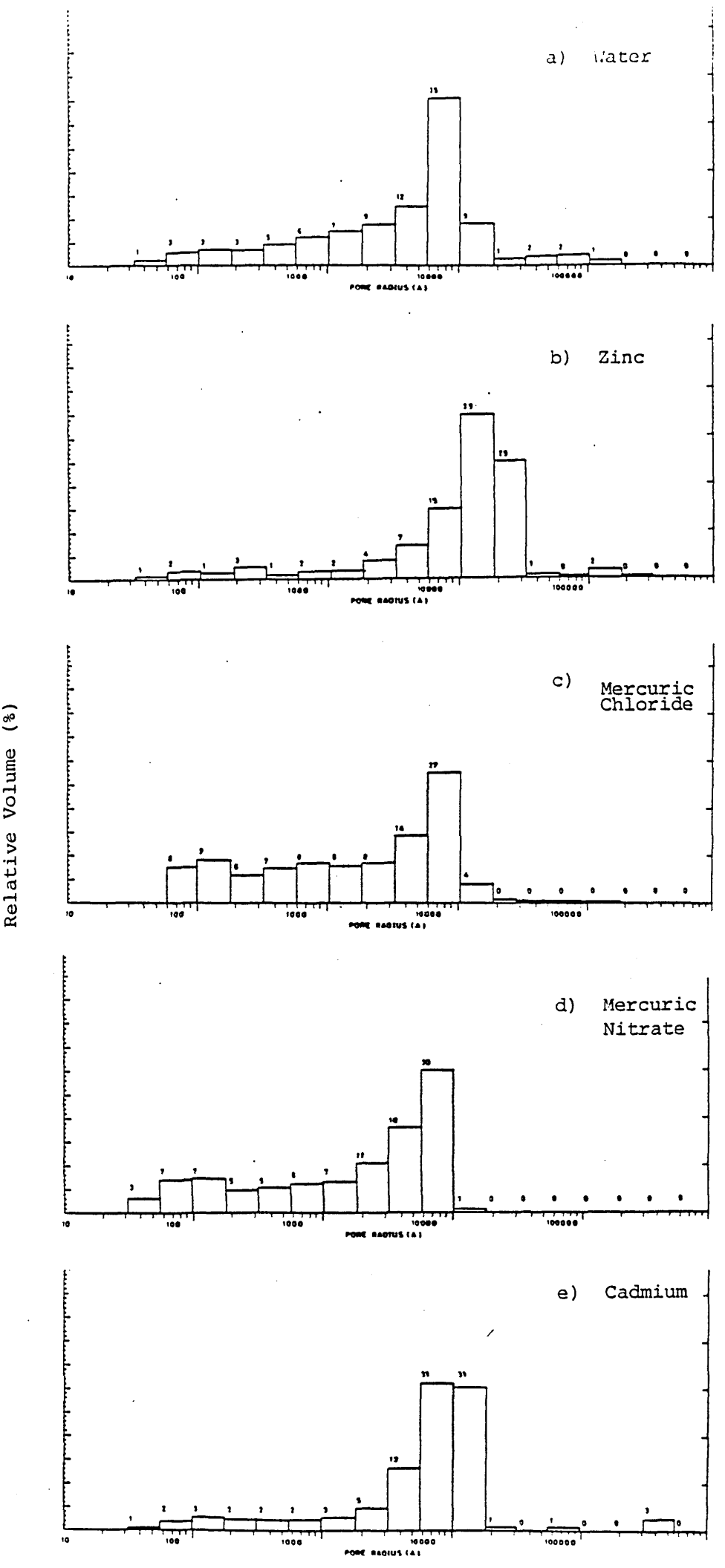


Figure 4.21 Pore size distribution of the Sealosafe samples

4.1.3 Discussion

Micro-structural analysis using SEM, XRD and porosimetry gave an understanding of the effect of different metal wastes on the hydration of the cementitious matrices.

The hydration of cement depends on many parameters. One parameter studied was the water/cement ratio. The results demonstrated that a high water/cement ratio facilitates the hydration process due to the larger amount of water available for reaction. Although a greater amount of hydration products with low densities were produced, the increased water content created more large pores in the matrices - indicated by the MIP data. These large pores were thought to be the point of weakness during fracture.

The hydration of cement was not significantly affected by the incorporation of sodium silicate solution. The main effect of adding the soluble silicate in the hydrating matrices was to produce a calcium-silicate gel as observed in the SEM. The XRD and SEM studies revealed that this gel was amorphous, without structure and was deposited randomly in the cementitious matrix. The removal of Ca from solution by this gel might increase the dissolution of cement at one time, as well as lower the amount of $Ca(OH)_2$ crystal precipitated, but the overall effect on the hydration of adding sodium silicate was small. This gel formation greatly increased the initial set rate and lowered the workability of the paste. Therefore a much higher water/cement ratio could be used in the Chemfix formulation to produce a solidified mass without significant loss of water from the matrix due to bleeding. The increase in water content resulted in high porosity as discussed above.

The incorporation of PFA in the cement matrix (the Sealosafe formulation) lowered the water demand (Sealosafe W/S = 0.5 ; Chemfix W/C = 1). This resulted in the lower porosity found in the Sealosafe formulation.The SEM study revealed that the

hydration of cement proceeded normally although it is controversial whether the PFA accelerates or retards the hydration of C_3S in cement. The exact nature of reaction is still unclear (53).

It has been suggested that the sulphate released from PFA contributes to the retardation of hydration of cement (43). The SEM and XRD studies detected the precipitation of secondary gypsum when PFA was hydrolysed in water. This gypsum was replaced in the OPC/PFA matrices probably due to the formation of sulphate bearing calcium aluminate sulphate hydrates (ettringite and monosulphate). Duplex film-like hydration products were observed on the PFA particles in the OPC/PFA blended system. It has been suggested that these products resulted only from the deposition of precipitates in solution and are not due to the hydration of PFA particles (52). The pozzolanic reaction between PFA and lime is thought to take place only after a long period of hydration. Ettringite was the only phase frequently found on the flyash surface which had directly originated from the particle.

The addition of metal solutions affected the hydration and the microsctructure of the cementitious matrices. Zinc greatly retarded the hydration of cement and PFA by forming a layer of amorphous gel on the particles. The formation of ettringite, however, was enhanced by Zn with long and large rods of crystalline observed under the SEM in both solidification systems. This ettringite was randomly distributed in the pore spaces of the cementitious matrices and is believed to be formed from a through solution mechanism (i.e. crystals formed as a precipitate from the aqueous phase of the system). These crystals expanded the pore structure and resulted in increased pore volume and large proportion of pore space with large radii. The X-ray diffraction revealed that no C-H was present in the Zn-dosed samples, indicating that this phase played an important role in the fixation of Zn in the solidification systems.

The addition of Hg in the form of $HgCl_2$ and $Hg(NO_3)_2$ did not result in significant changes in the cementitious matrices. Porosity measurements, however illustrated the $HgCl_2$-dosed samples to have a lower total pore volume than the control. This is probably due to the chloride molecules promoting the hydration of C_3S and resulting in more hydration products to fill the pore space. Mercuric nitrate, however, gave a similar pore structure to the control. Although $Hg(NO_3)_2$ did slightly retard the reaction, the hydration of cement and PFA/OPC blended systems proceeded relatively normally to produce C-S-H and C-H as revealed in the SEM and XRD studies.

Cadmium induced moderate changes in the microstructure of both the solidification systems. The hydration of cement was retarded. This can be shown by the partially hydrated cement grains producing the Hadley grain like structure. The presence of the C-H (though depressed) peaks in the XRD pattern indicated that the hydration reactions of the main clinker phases (C_3S and C_2S) were not totally inhibited. The production of calcium aluminate sulphate hydrate phases typified by monosulphate and ettringite increased the total pore volume of the Chemfix sample and shifted the pore size distribution of both Chemfix and Sealosafe to larger pore sizes.

The micro-structural evidence based on SEM, XRD and mercury porosimetry indicated that the effects of metals addition on the hydration of Chemfix and Sealosafe systems were very similar. Generally, both Zn and Cd retarded the hydration of the main clinker phases of the cement by forming an amorphous gel around the cement particles, probably by reaction with lime forming a complex hydroxide. The retardation was greater in the case of Zn. Both of these metals promoted the formation of calcium aluminate sulphate hydrates (ettringite and monosulphate) which induced expansion at the pore structure. This resulted in large intruded volumes and a higher proportion of pore volume with larger pore radii. The two Hg solutions did not induce significant changes to the micro-structure in terms of the

morphology and the crystalline constituents of the hydration products. The porosity measurement also indicated that they had similar pore structures to the control.

The use of PFA in the Sealosafe formulation did not significantly modify the mode in which cement reacted with the metal solution. It did, however, add to the calcium aluminate sulphate crystal content of the hydrated structure which may further retard the hydration of cement. The replacement of cement by PFA also reduced the water demand of the mix resulting in lower porosity. The pozzolanic reaction between the lime liberated from cement and the PFA particle was not observed in the short period of hydration. The Duplex film structures seen in some of the mixes were thought to result from the precipitation of the constituents from the pore solution. It was evident that further reaction of the PFA particles with lime must take place via the thin film. The overall reaction of PFA particles with different metal solutions, therefore, did not modify the morphology of the surface or the crystalline components of the particles. This indicates that any reaction between metal ions and PFA particles probably took place through sorption or cation exchange without modifying the surface structure.

4.2 Extended X-ray absorption fine structure (EXAFS)

This technique measures the variation of absorption of x-ray photon energy at energies above the absorption edge of an atom. When an atom is bombarded by monochromated x-ray radiation, an abrupt increase in the absorption energy occurs corresponding to the energy level of a particular atom. For isolated atoms, this absorption decreases monotonically but for atoms either in a molecule or embedded in a condensed phase, a sinusoidal variation of the x-ray absorption as a function of photon energy is observed (54). The resulting spectrum is known as EXAFS (Figure 4.22)

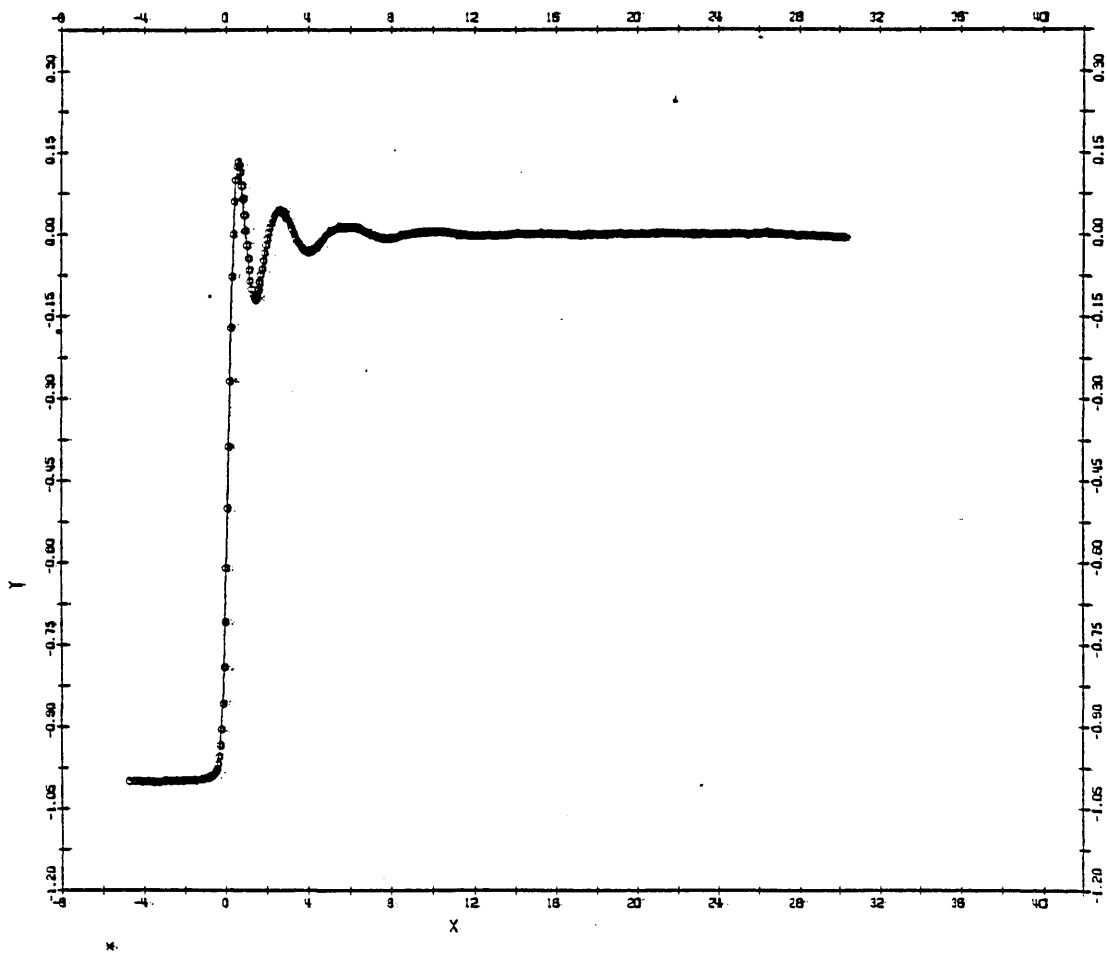


Figure 4.22 An example of EXAFS spectrum.

EXAFS differs from x-ray diffraction being of short range order and thus able to analyse materials which are amorphous in nature.

Theory has been developed to describe this phenomenon in terms of backscattering of outgoing photelectrons by neighbouring atoms (54). Valuable structural information can be obtained by analysis of the EXAFS which describes a function of the local environment of the central atom. Structural information such as the nature of neighbouring atoms, bond distance, bond angles and the co-ordination number can be extracted from the EXAFS by proper manipulation of the spectrum - usually involving complex computational analysis.

EXAFS is usually measured utilising a high energy x-ray radiation such as a synchrotron radiation. Measurement is generally made in the transmission mode for concentrated samples and in the fluorescence mode for dilute samples.

Analysis of the EXAFS spectrum utilises the computing programme at Daresbury Laboratory (55). Generally the procedure comprises four steps.

1 Isolate and normalise the oscillatory part of the absorption spectra.

2 Transform the resulting EXAFS from E-space (energy) to K* space (wave vector) and produce a radial distribution of atoms round the central atom.

3 Curve fitting by the least square refinement of the normalised EXAFS or the Fourier transformed radial distribution function to give structural information.

4 Sometimes selected energy range of the EXAFS can be obtained by Fourier filter technique, and the filtered

spectrum, can be curve fitted to obtain structural information.

$$*K = \sqrt{\frac{2m}{\hbar^2}(E-E_o)}$$

m = mass of electron
$\hbar$ = Plank's constant
E_o = threshold energy level
E = incident energy level

The analysis can be made simpler by first obtaining the EXAFS and hence the structural information of model compounds with known structure which are similar to the structure of the substance being investigated. By comparing the resulting EXAFS of the known and unknown compounds and feeding into the computation analysis, the local environment of the unknown can be obtained.

4.2.1 Method

EXAFS studies were made at the Synchrotron Radiation Source at the Daresbury Laboratory. Only two metals were studied because of the limited availability of beam time. The model compounds were run in the transmission mode while EXAFS of the samples were obtained in the fluorescence mode.

The samples and model compounds prepared for EXAFS study are listed in Table 4.4

Table 4.4 Mixes prepared for EXAFS study

Zinc (K edge)
Model compound: a) ZnO
b) $ZnSiO_3$*
c) $Zn(OH)_2$*
d) Zn Orthosilicate

Table 4.4 Cont'd

Sample:		
a) cement	$^{+}$solution/OPC =	0.6 cured 1 day & 3 day
b) Chemfix	solution/OPC =	1.0 cured 1 day & 3 day
	silicate/OPC =	0.1
c) Sealosafe	PFA/OPC =	3 cured 1 day
	solution/solid =	1.0

$^{+}$ The solution used was 2% $Zn(NO_3)_2$

* Prepared by precipitation of 2% $Zn(NO_3)_2$ in saturated $Ca(OH)_2$ solution and Na_2SiO_3 solution.

Mercury (L(III) edge)

Model compound:	a)	HgO
	b)	$HgCl_2$
	c)	$Hg(NO_3)_2$

Sample :

a) cement	$^{+}$solution/OPC =	0.6 cured 1 day
b) Chemfix	solution/OPC =	1.0 cured 1 day
	silicate/OPC =	0.1 cured 1 day
c) Sealosafe	PFA/OPC =	3.0 cured 1 day
	solution/solid =	1.0

$^{+}$Two Hg solutions were used: 2% $HgCl_2$ and 2% $Hg(NO_3)_2$.

Additional spectra were obtained for the samples from the aqueous chemical experiment (Section 5.1) on Hg.

The samples were first pretreated by acetone washing to arrest cement hydration. The powdered samples were then prepared for examination by grinding with a pestle and mortar and mounted on the specimen container held in position by Sellotape.

4.2.2 Results

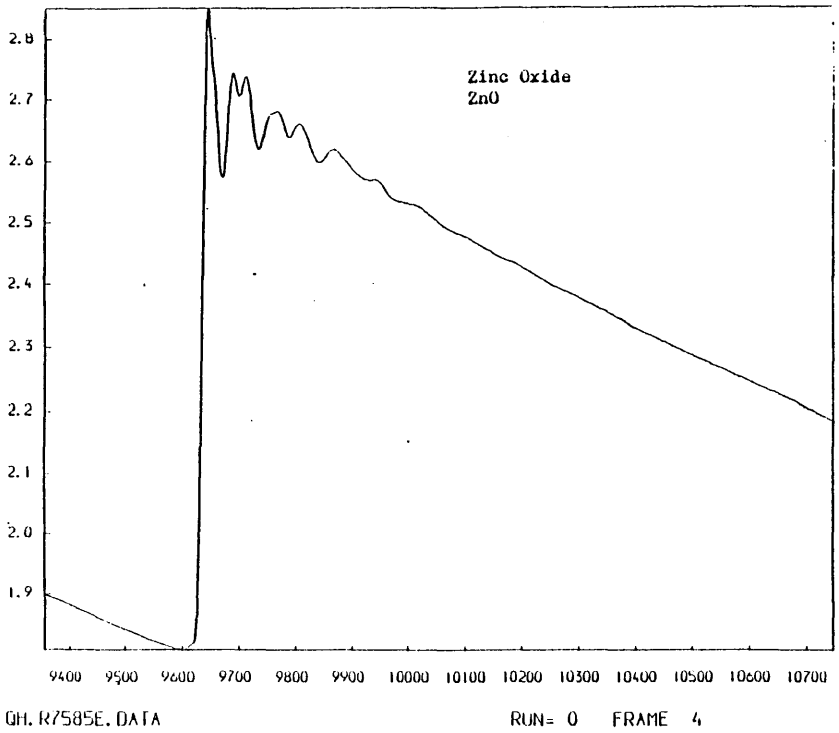
The normalised spectra of the Zn and Hg samples are presented in Figures 4.23. to 4.30.

The background subtracted spectra were analysed using the EXAFS computer program at Daresbury Laboratory. The analytical procedures used were least square refinement and Fourier Transformation curve fitting techniques. An example of the analysis is presented in Appendix F.

4.2.3 Discussion

Comparing the normalised spectra of the four Zn model compounds (ZnO, $Zn(OH)_2$, $ZnSiO_3$ and Zn_2SiO_4) the difference in their local environments can be observed. Detailed analysis of the EXAFS of the ZnO showed that it contained a single shell of 4 oxygen at a distance of 1.93 Å from the central atom. For the $Zn(OH)_2$ two distinct shells were detected at distances of 1.94 Å and 3.54 Å; although the exact co-ordination and composition of these two shells were not determined. The zinc silicates displayed two shells closely packed together at distances of 1.95 Å and 3.17 Å respectively, from the central atom.

There was little difference in the EXAFS of the five Zn-dosed cementitious samples studied. The spectra obtained did not resemble any of the model compounds. This indicated that Zn had formed a compound in the cementitious system which was not simply a $Zn(OH)_2$, ZnO or $ZnSiO_3$. Detailed analysis of the



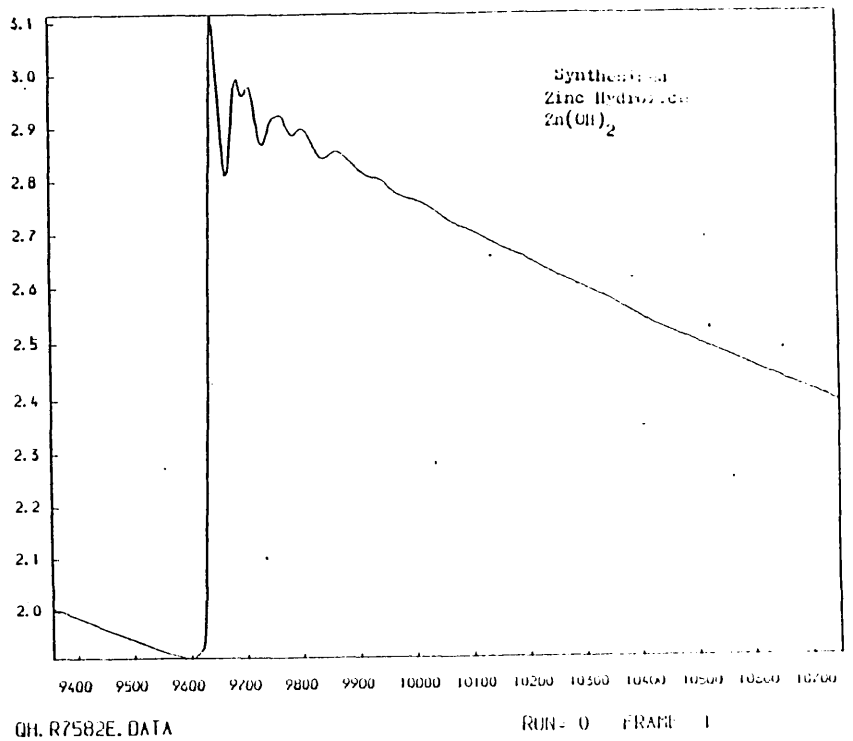
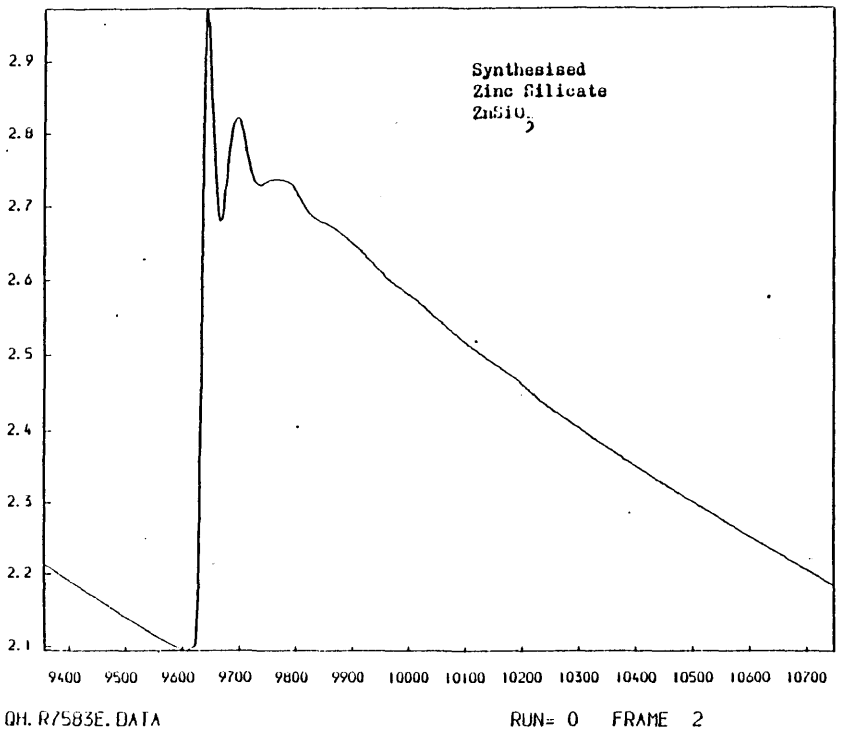


Figure 4.23 Normalised spectra of zinc model compounds



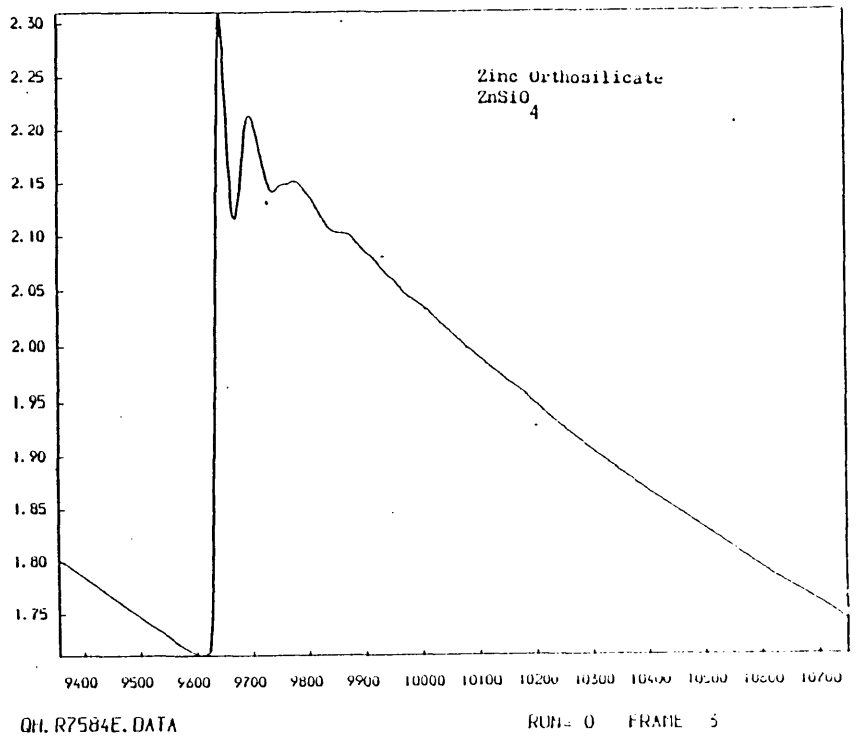
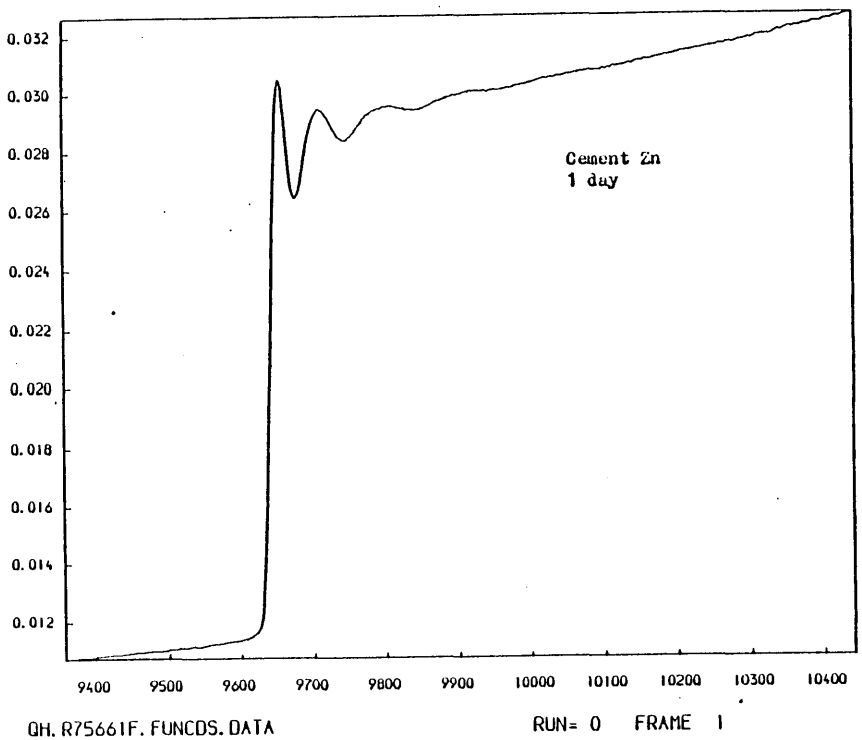


Figure 4.24 Normalised spectra of zinc model compounds



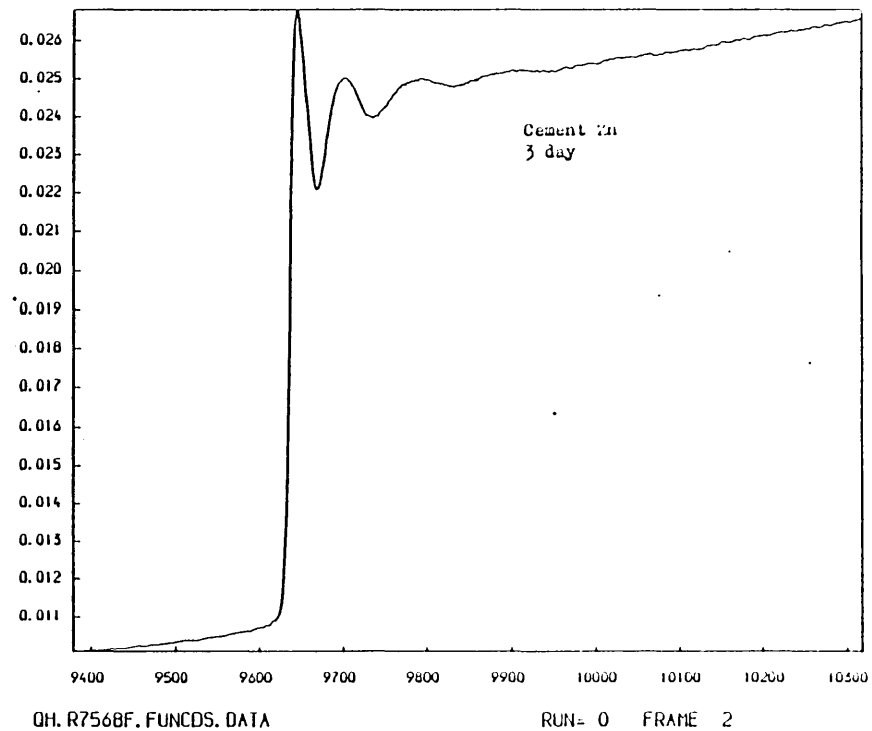
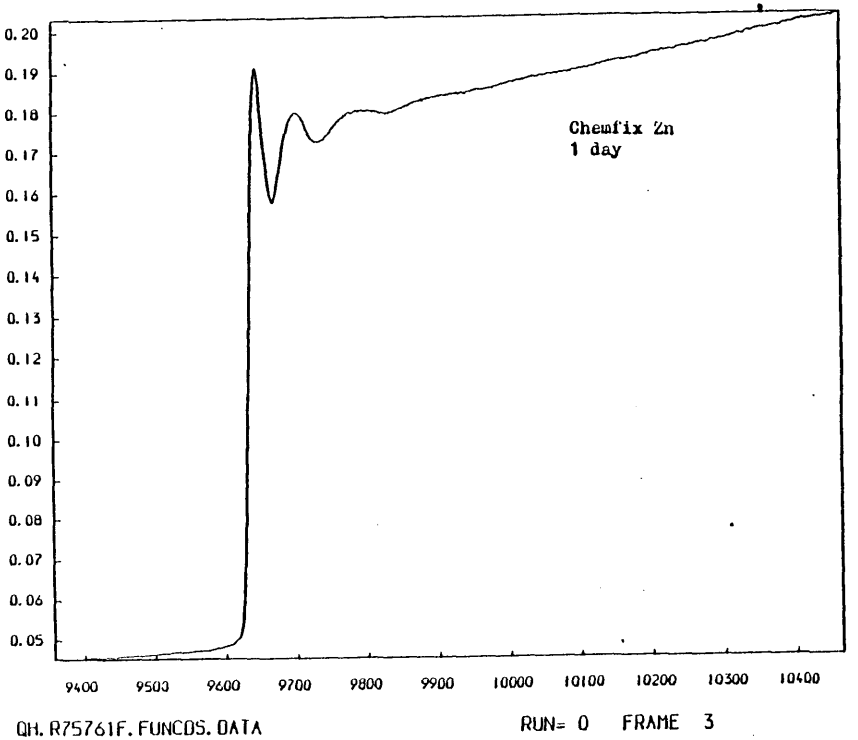


Figure 4.25 Normalised spectra of Zn dosed cement samples.



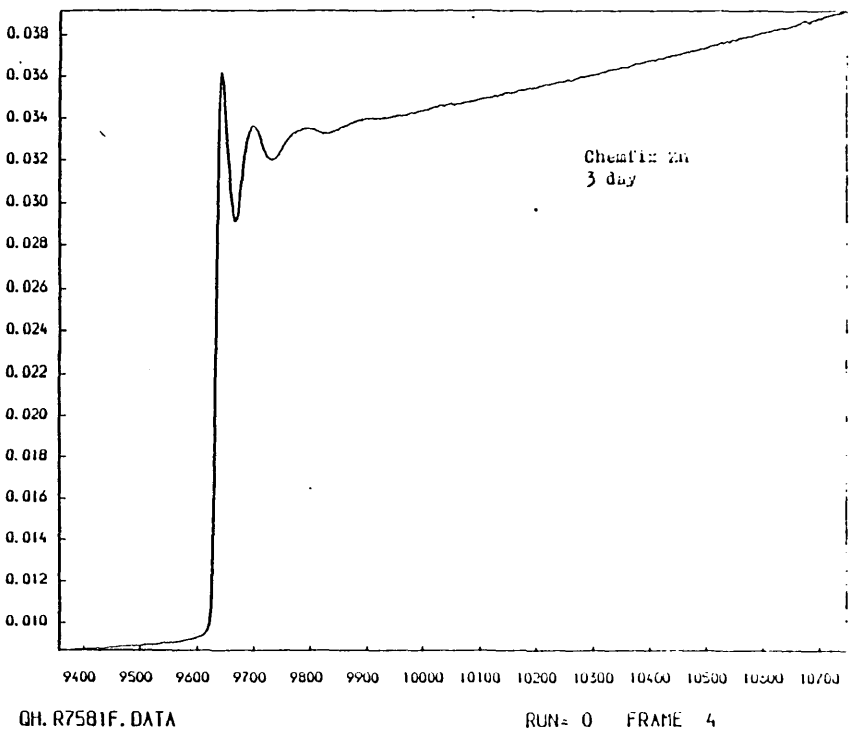


Figure 4.26 Normalised spectra of Zn dosed Chemfix samples

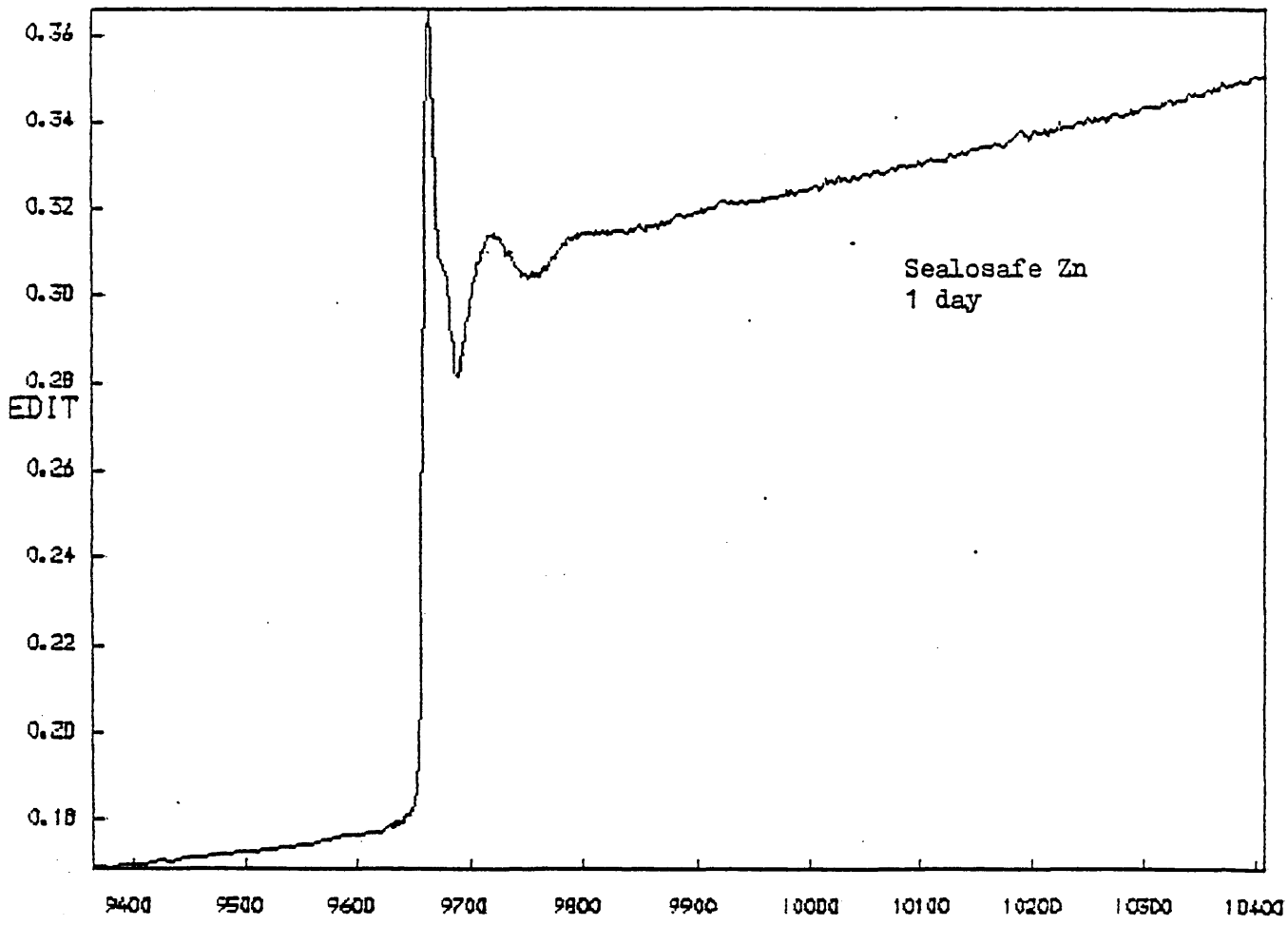
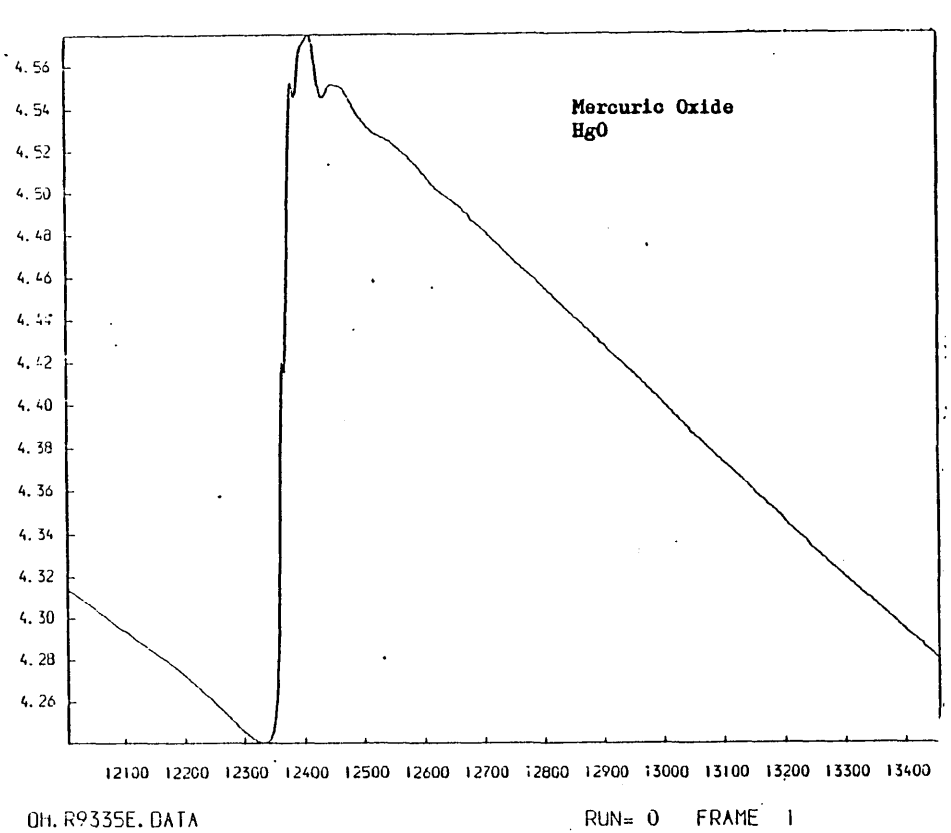


Figure 4.27 Normalised spectrum of Zn dosed Sealosafe sample



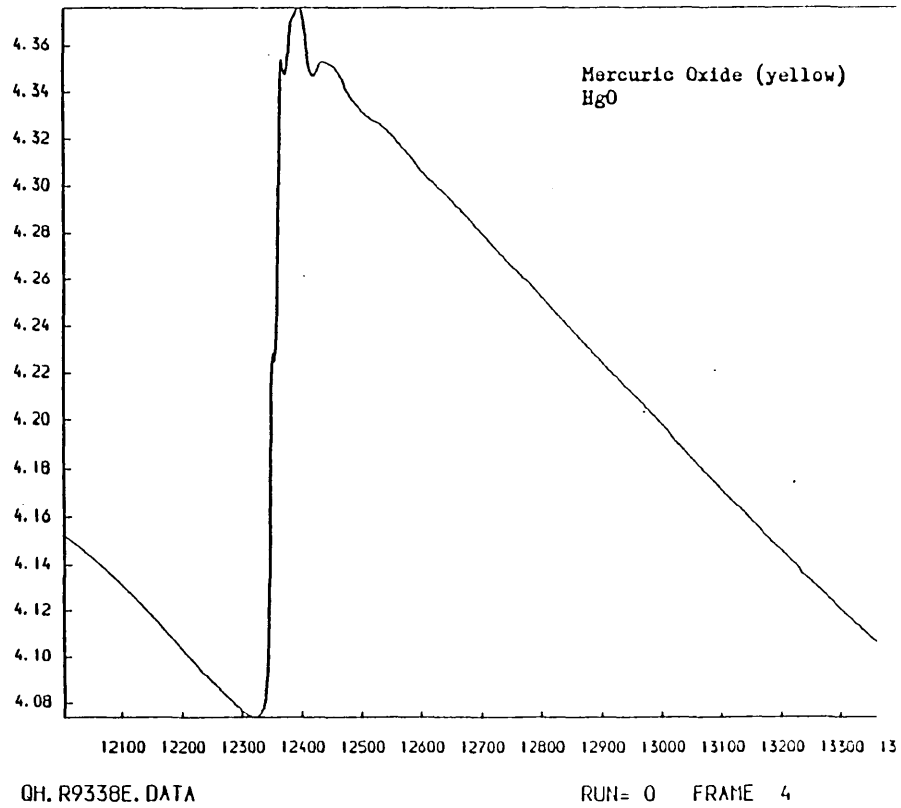
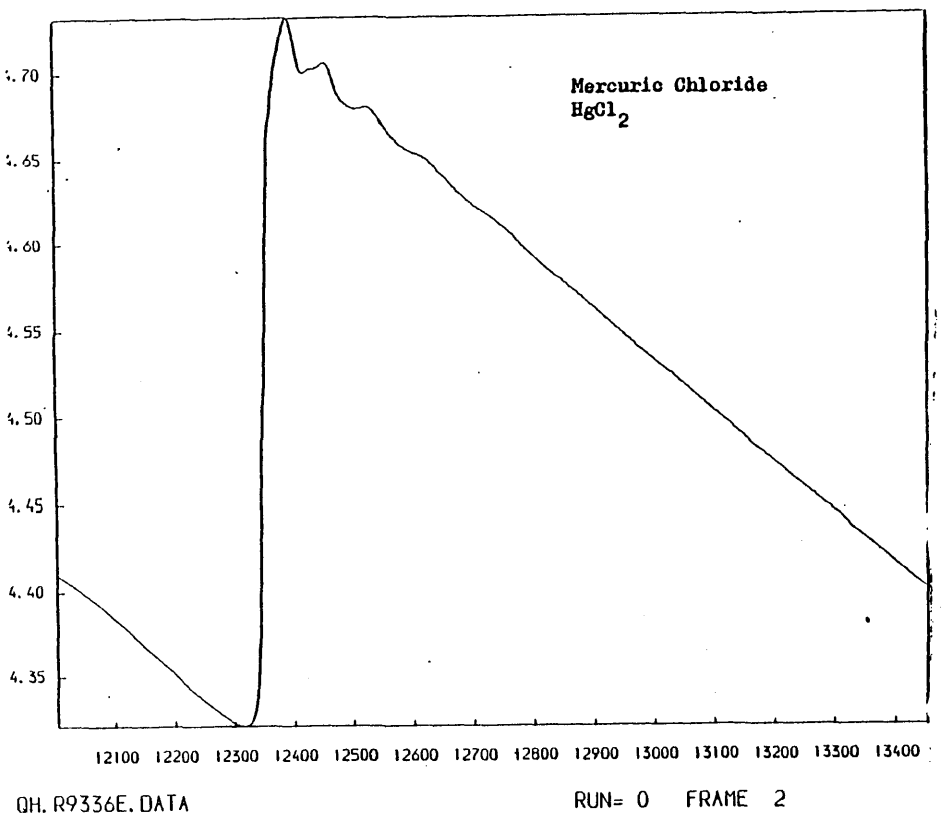


Figure 4.28 Normalised spectra of mercury model compounds.



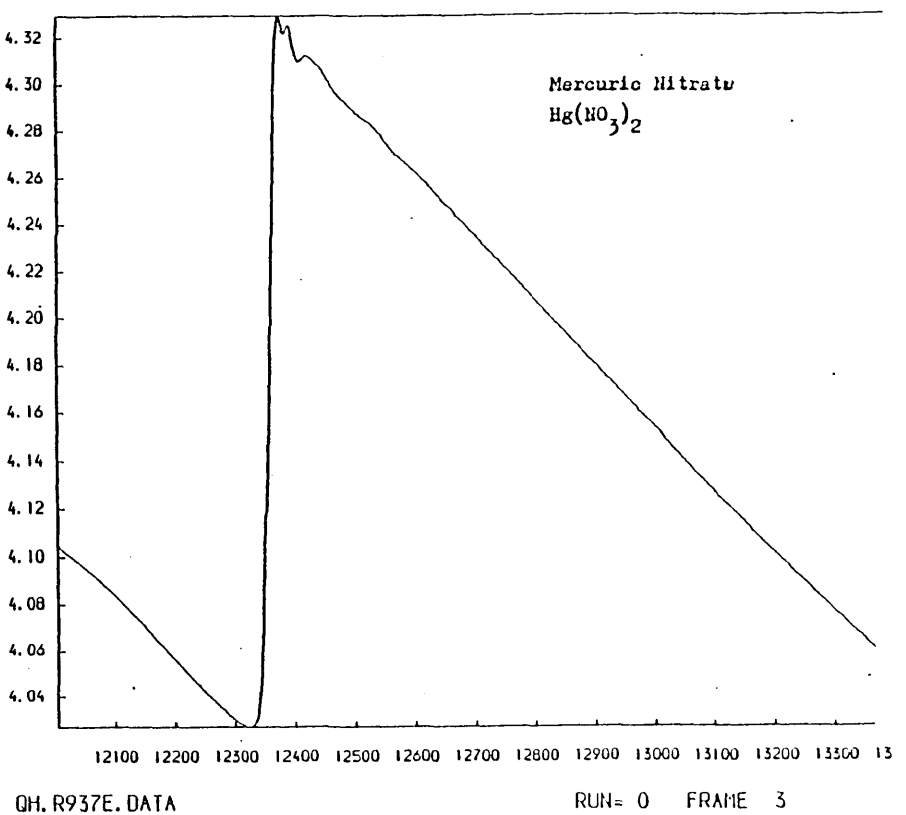
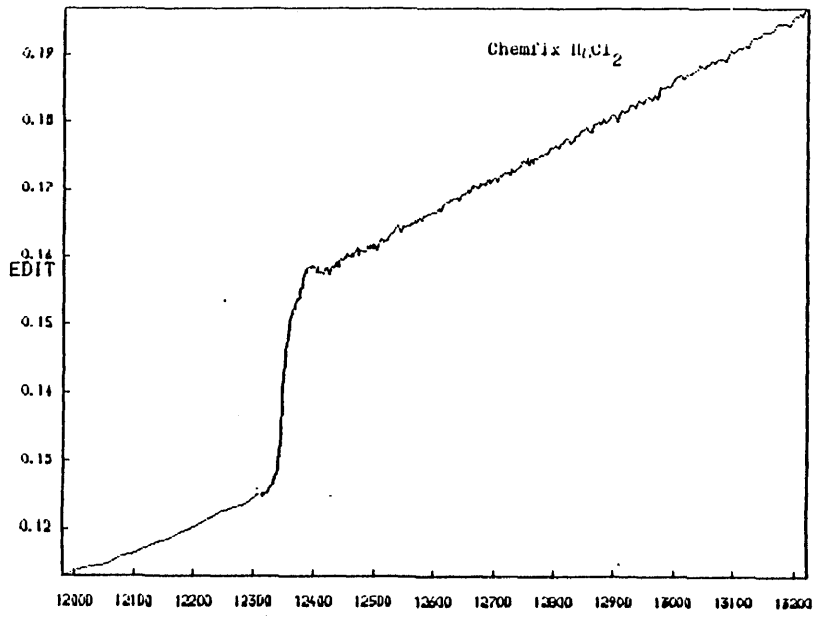
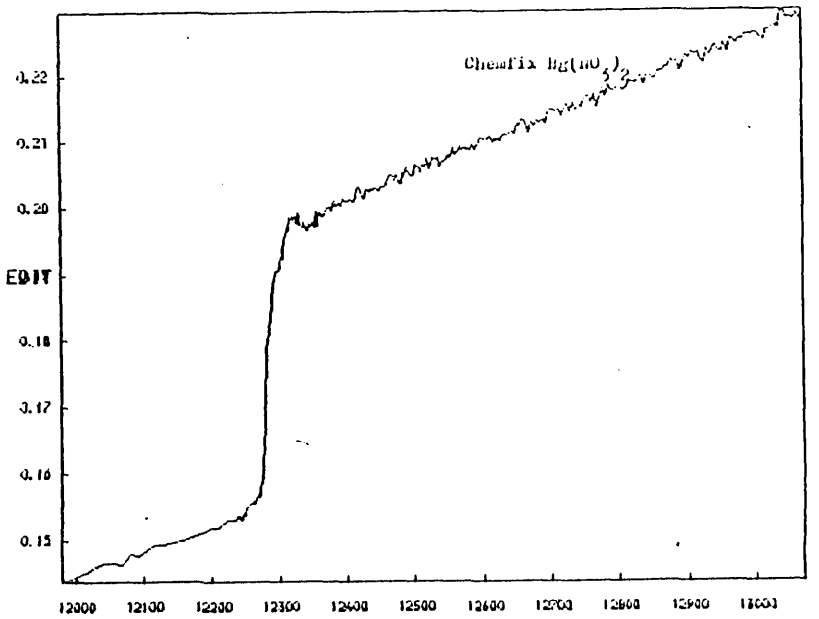
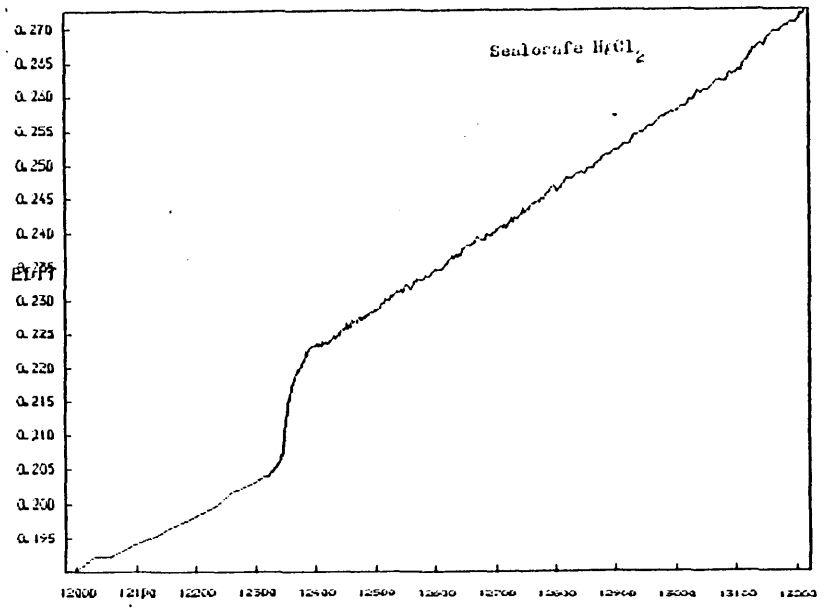


Figure 4.29 Normalised spectra of mercury model compounds







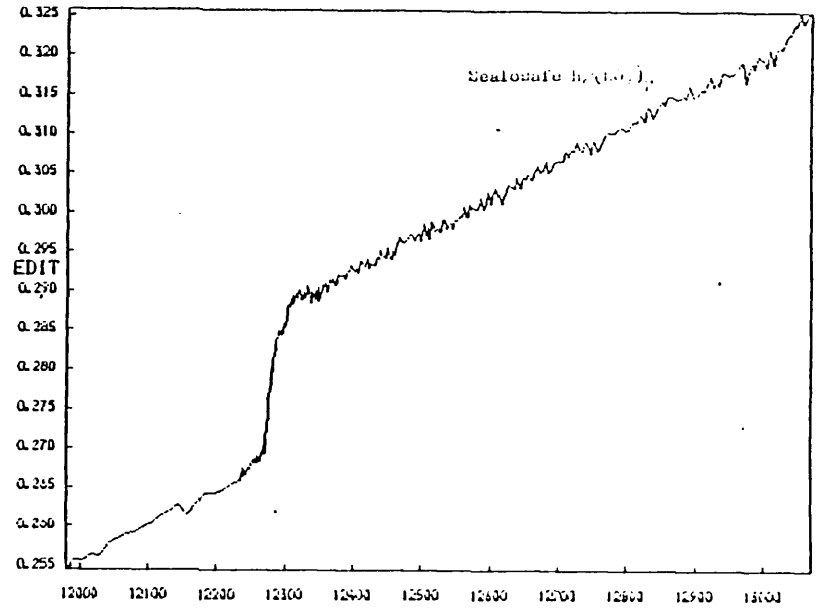
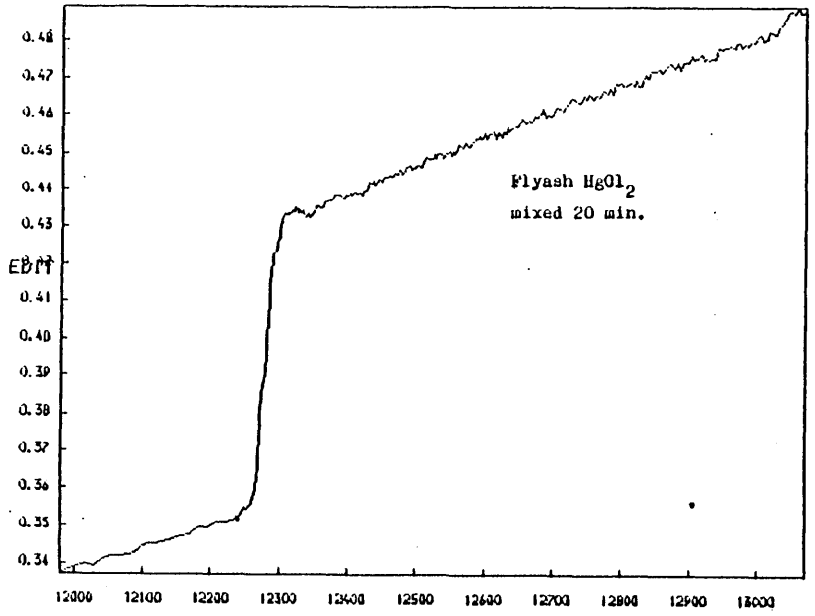
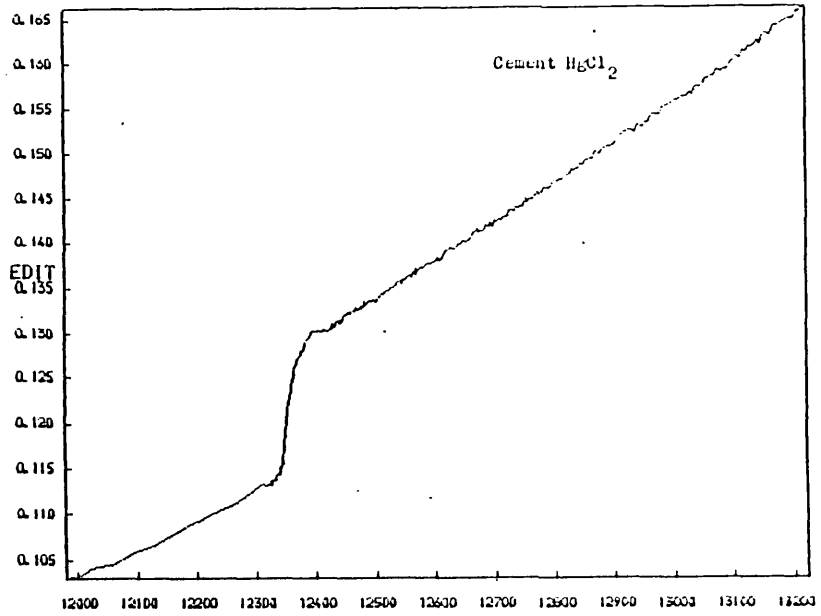
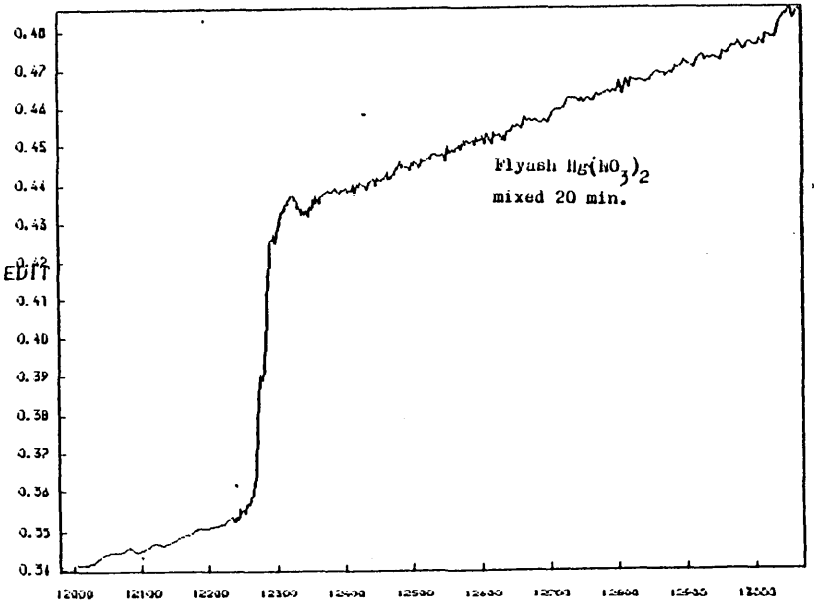


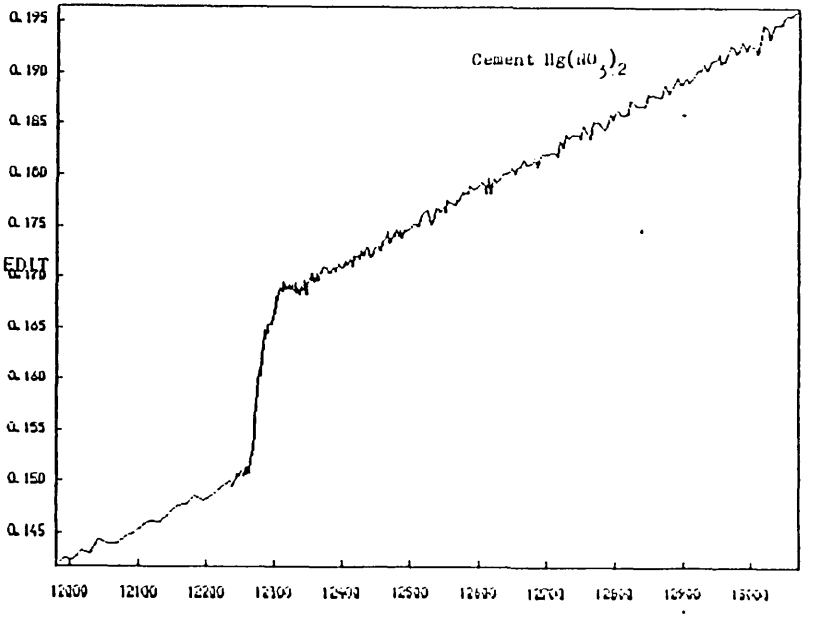
Figure 4.30 Normalised spectra of mercury dosed samples,

Figure 4.31 Normalised spectra of mercury dosed samples









EXAFS using least square refinement and Fourier Transformation techniques revealed that the Zn atom in all the cementitious samples were 4 oxygen co-ordinated at the 1st shell at a distance of 1.92 Å - 1.93 Å. The structure became disordered beyond this distance and made detailed analysis of the 2nd shell impossible. This was probably due to the Zn atom being located in a mixture of sites beyond the first 4 oxygens. The fact that the cement, the Chemfix and the Sealosafe samples all produced similar EXAFS and structures demonstrated that the local environment of the Zn was not significantly altered by the incorporation of either sodium silicate solution or PFA. The results of the 1 and 3 day old samples closely resembled each other and this indicated that the site in which the Zn atoms was situated had not changed during ageing.

The three Hg model compounds (HgO, $HgCl_2$ and $Hg(NO_3)_2$) displayed distinct local environments, giving strong EXAFS. The normalised spectra of all Hg-dosed cementitious samples (both $HgCl_2$ and $Hg(NO_3)_2$) possessed little EXAFS. This indicates that Hg atoms in the cementitious matrices were situated in a highly disordered local environment - probably a mixture of sites. The signal-to-noise ratio of the samples was low making detailed analysis of the spectra impossible. The fact that the $HgCl_2$ and the $Hg(NO_3)_2$ solutions in the cement, Chemfix and Sealosafe matrices produced similar spectra indicated that different ligands did not significantly modify the site in which the Hg atom was located.

A slight difference, especially at the post edge region, was detected in the two Hg samples (Fig 4.31) obtained from the aqueous chemistry experiments on PFA. Although a detailed analysis of this difference was not possible, this distinction of EXAFS may account for the difference in uptake of $HgCl_2$ and $Hg(NO_3)_2$ by PFA in the aqueous phase (Section 5.1). The fact that this contrast was not noticed in the two Sealosafe samples was probably due to the incorporation of cement, making the Hg site more dispersed.

It has been shown from the EXAFS study that Zn was capable of producing a definite and local chemical environment similar in cement, Chemfix and Sealosafe matrices. Mercury, on the other hand, produced a disordered local structure. These results related to the difference in chemical interactions and fixation mechanisms of these two metals in the solidification processes.

5 MACRO ANALYSIS

5.1 Aqueous chemical environment

An important factor governing the physical and chemical stabilisation of waste is the initial chemical environment pertaining when the processing agents and hazardous material are mixed in water.

The aqueous chemical environment has been investigated by mixing Ordinary Portland Cement (OPC) and flyash (PFA) in water-and-metal solutions in the ratio of liquid/solid = 5 (l:s = 5). The experiment was performed under an inert (nitrogen) atmosphere to prevent reaction with air, in particular with carbon dioxide.

5.1.1 Method

Systems that have been studied are listed in Table 5.1

Table 5.1 Mixes prepared for the aqueous chemical environment test

I	OPC	
	a)	Distilled water
	b)	0.2% $Zn(NO_3)_2$
	c)	0.2% $HgCl_2$
	d)	0.2% $Hg(NO_3)_2$
	e)	0.2% $Cd(NO_3)_2$

Table 5.1 (Cont'd)

II	PFA	
	a)	Distilled water
	b)	0.2% $Zn(NO_3)_2$
	c)	0.2% $HgCl_2$
	d)	0.2% $Hg(NO_3)_2$
	e)	0.2% $Cd(NO_3)_2$
III	Chemfix	
	(OPC + 40% sodium silicate solution) (1:sodium silicate = 80) sodium silicate solution was added after 3.5 minutes of mixing.	
	a)	Distilled water
	b)	0.2% $Zn(NO_3)_2$
	c)	0.2% $HgCl_2$
	d)	0.2% $Hg(NO_3)_2$
	e)	0.2% $Cd(NO_3)_2$
IV	Sealosafe	
	(OPC and PFA) (PFA/OPC ratio = 3.0)	
	a)	Distilled water
	b)	0.2% $Zn(NO_3)_2$
	c)	0.2% $HgCl_2$
	d)	0.2% $Hg(NO_3)_2$
	e)	0.2% $Cd(NO_3)_2$

Table 5.1 (Cont'd)

V	Sealosafe and Chemfix	
	(OPC, PFA and sodium silicate solution)	
	a)	Distilled water
	b)	0.2% $Zn(NO_3)_2$
	c)	0.2% $HgCl_2$
	d)	0.2% $Hg(NO_3)_2$
	e)	0.2% $Cd(NO_3)_2$

The mixes were agitated by a magnetic stirrer; samples were periodically extracted from the slurry and filtered through a 0.45 μm membrane for analysis.

5.1.2 Results

The results of the study are presented in graphical form in Figures 5.1 to 5.5. The data itself is presented separately in Appendix B (Tables B1 to B5).

System I (Figure 5.1 , Table B1)

The OPC/distilled water system (Ia) produced a highly alkaline environment (pH 12.5 - 12.9). Calcium was continually released from the OPC matrix and increased steadily from 1005 ppm to 1400 ppm over a period of 50 minutes.

All four metal solutions produced pH values lower than that of the control. Zinc gave the lowest value followed by Cd and the two Hg solutions. The Ca concentrations released from the metal dosed systems were higher than the control and were in the order of Zn > $HgCl_2$ > $Hg(NO_3)_2$ > Cd. The concentrations of Zn and Cd

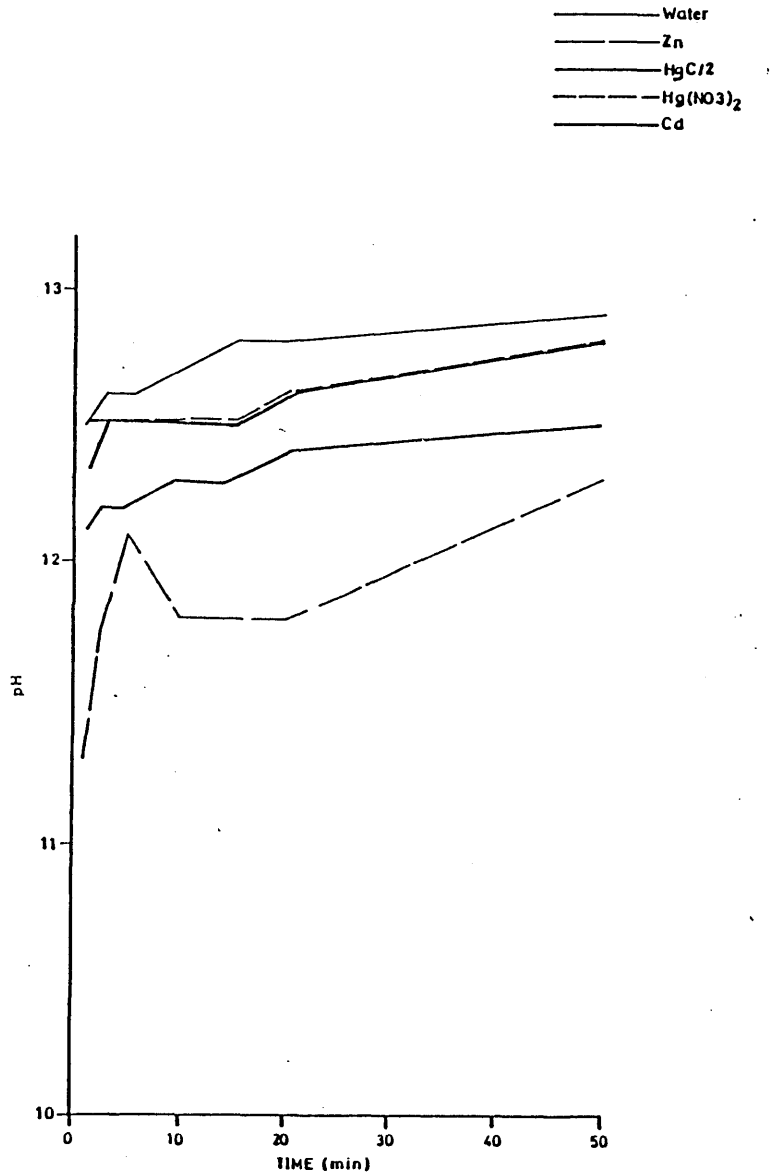


Figure 5.1a pH of System I (OPC)

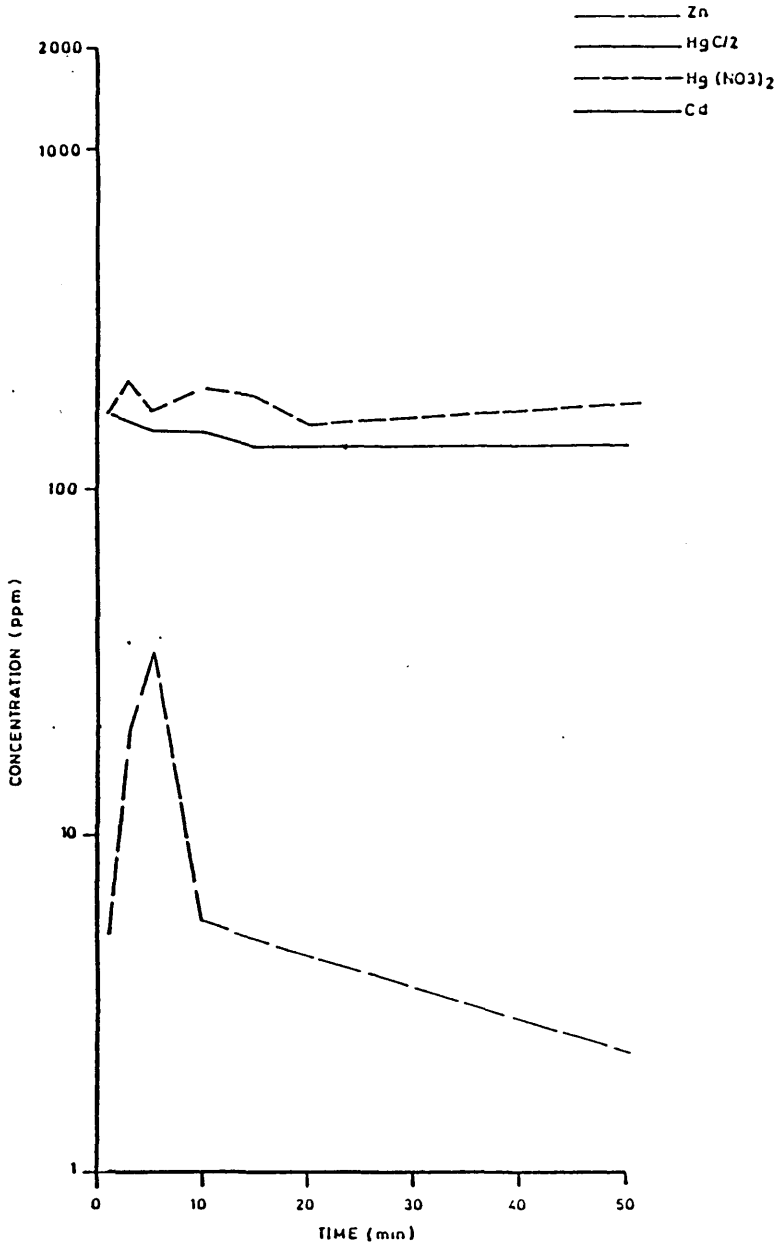


Figure 5.1b Metal concentrations in System I (OPC)

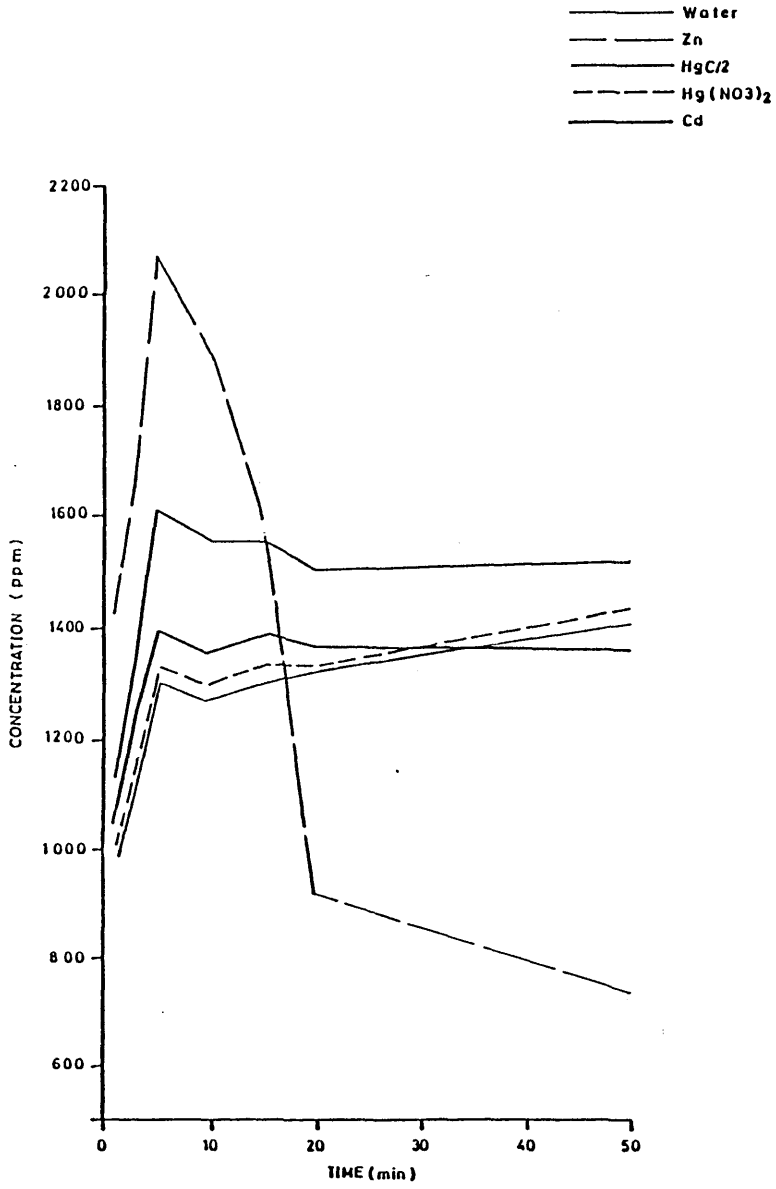


Figure 5.1c Ca concentration in System I (OPC)

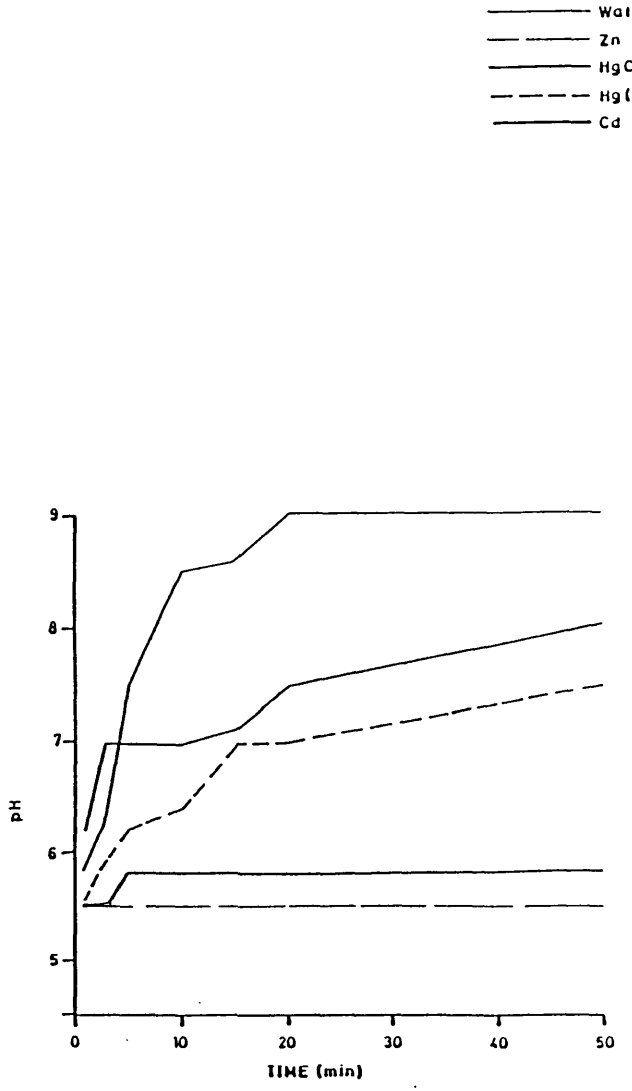


Figure 5.2a pH of system II (PFA)

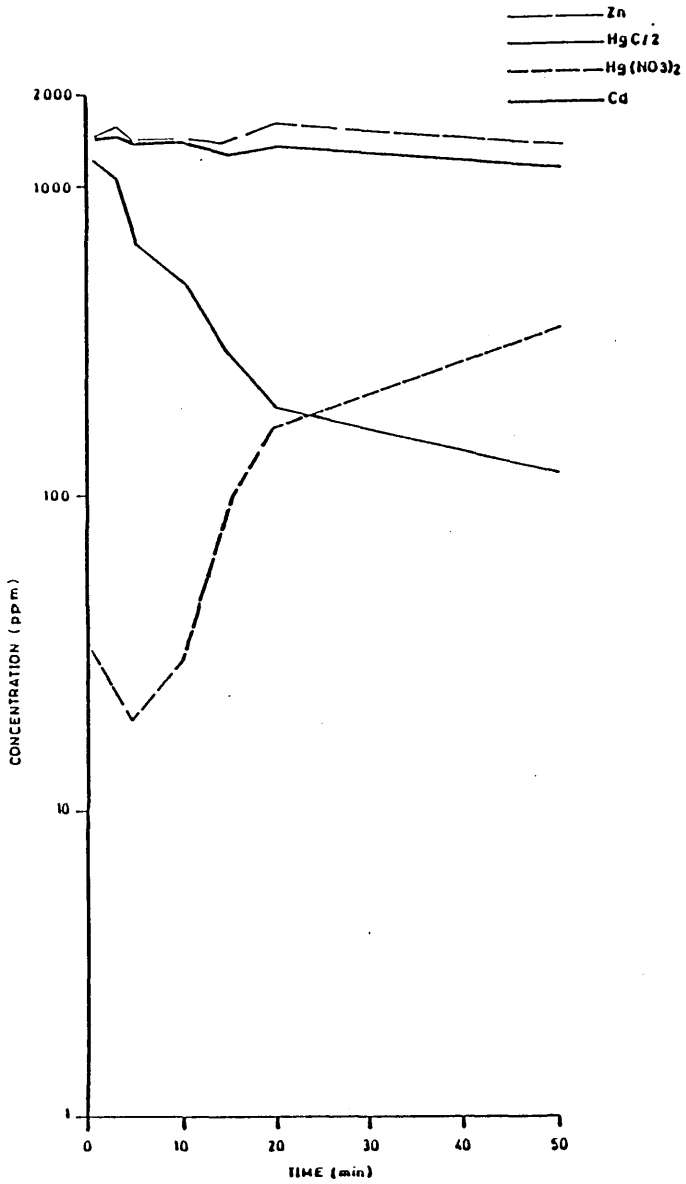


Figure 5.2b Metal concentrations in system II (PFA)

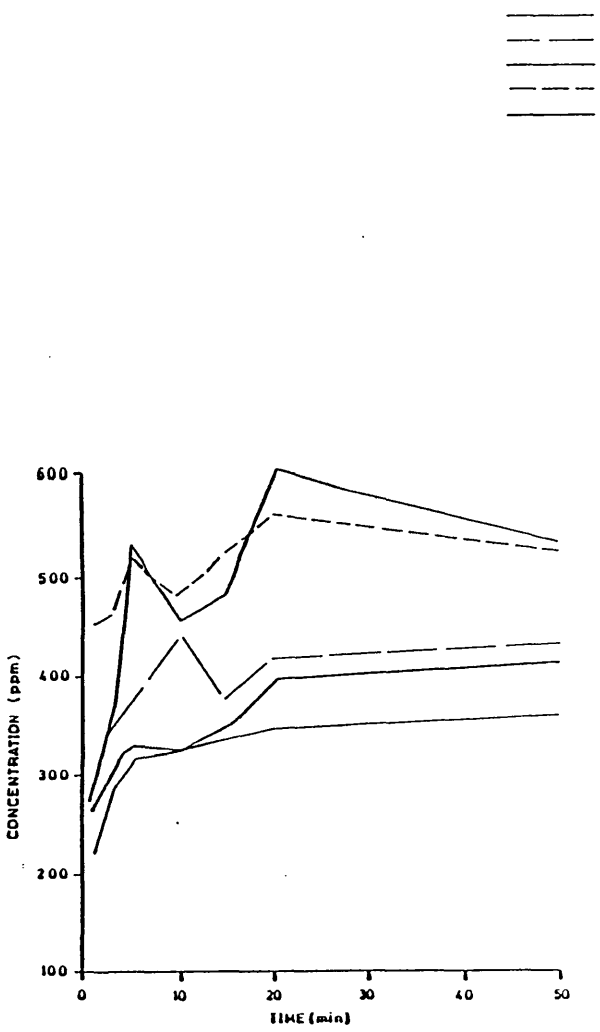


Figure 5.2c Ca concentration in system II (PFA)

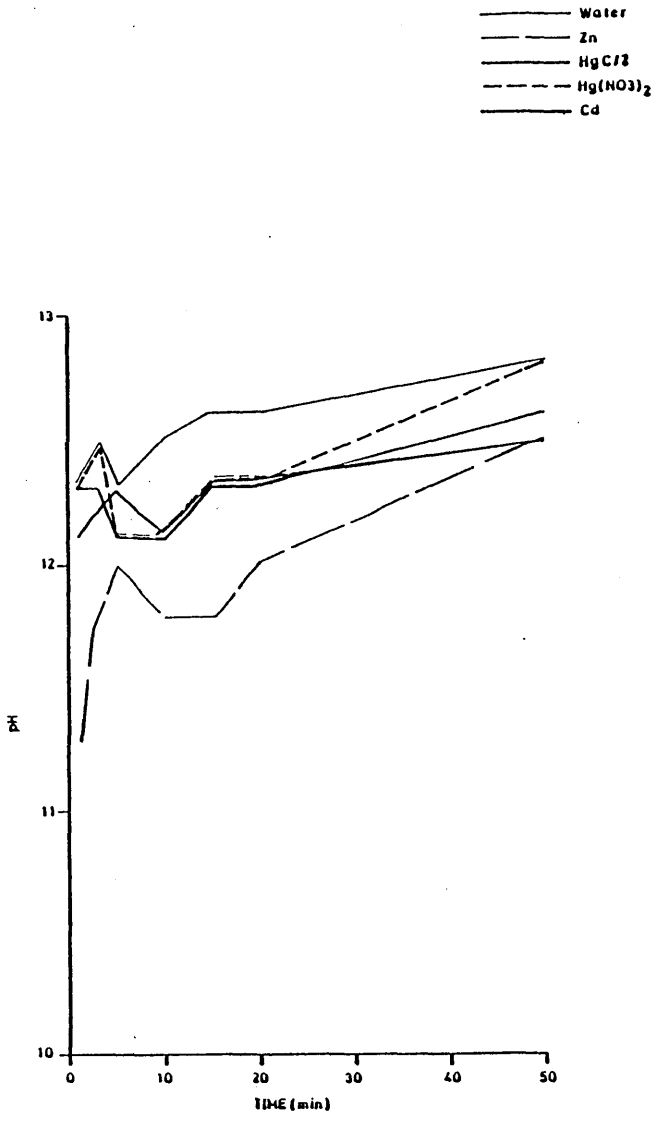


Figure 5.3a pH of system III (Chemfix)

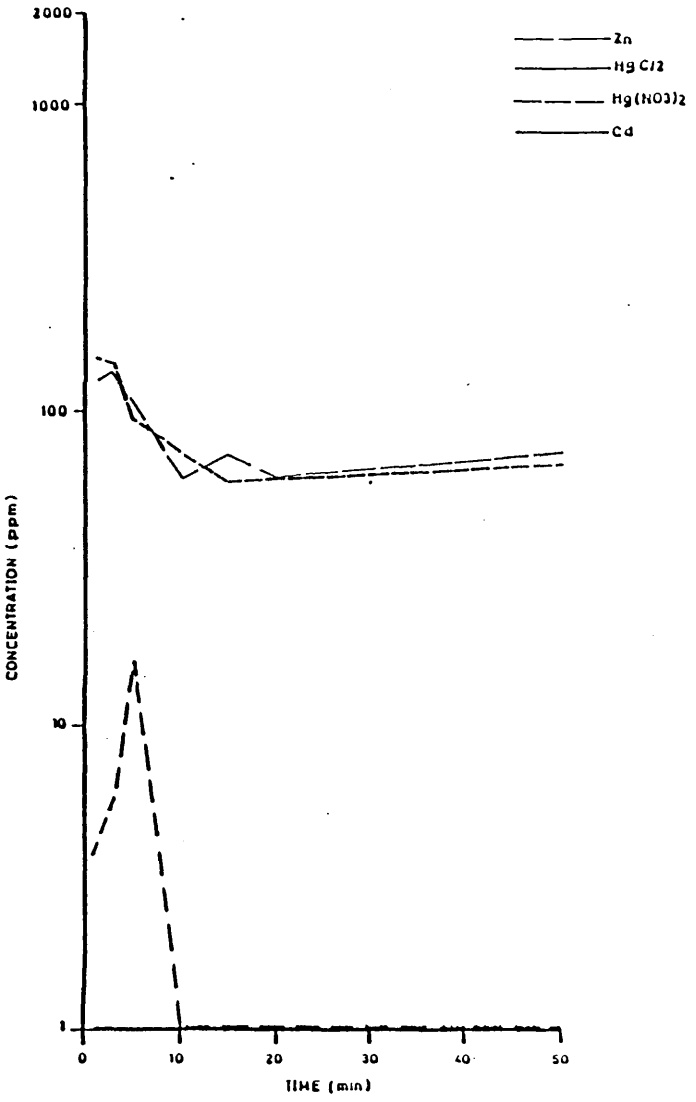


Figure 5.3b Metal concentrations in system III (Chemfix)

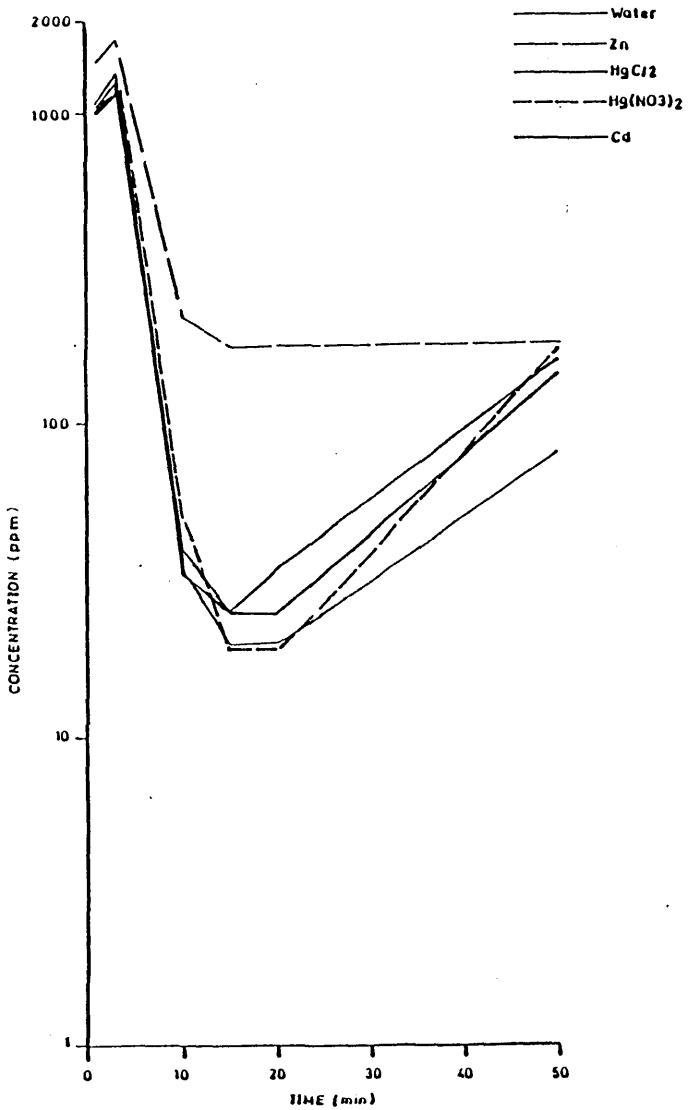


Figure 5.3c Ca concentration in system III (Chemfix)

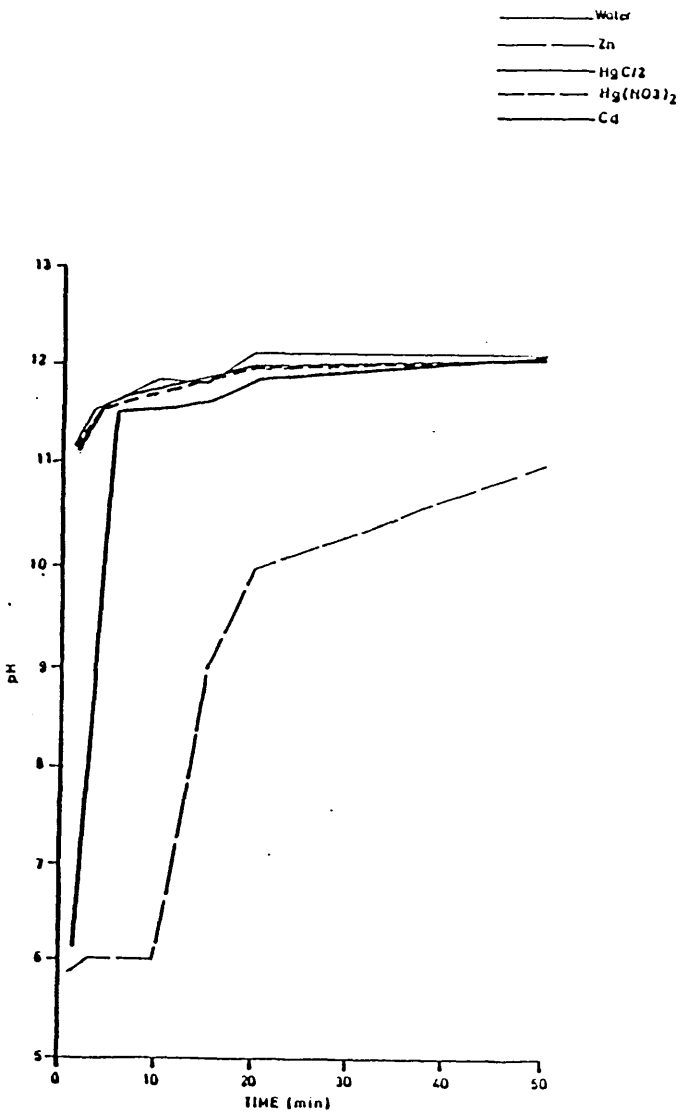


Figure 5.4a pH of system IV (Sealosafe)

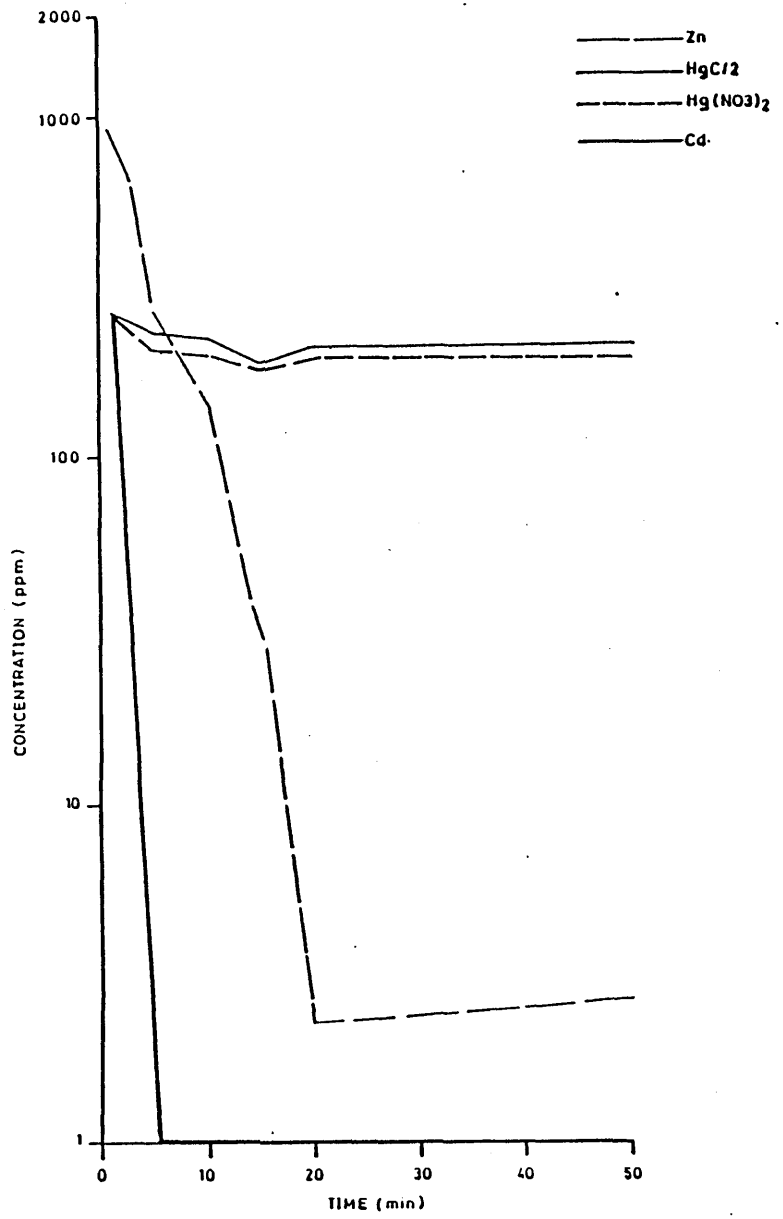


Figure 5.4b Metal concentrations in system IV (Sealosafe)

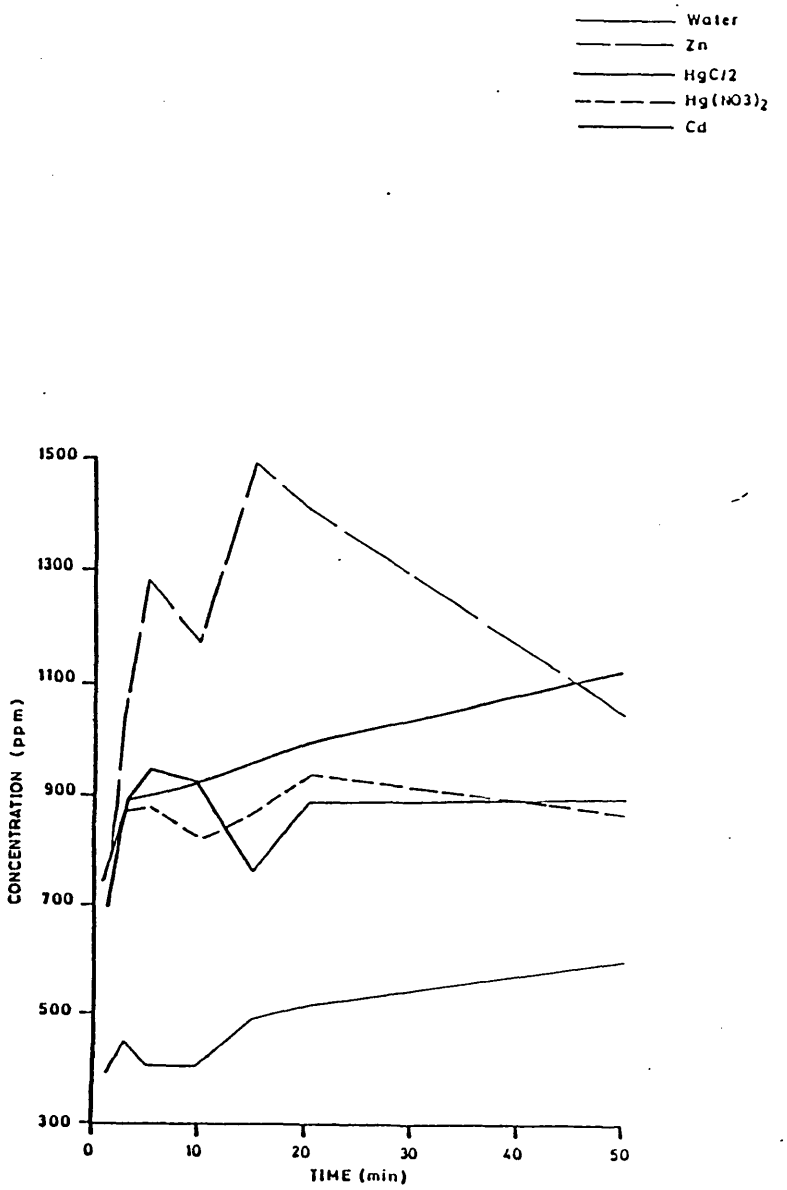


Figure 5.4c Ca concentrations in system IV (Sealosafe)

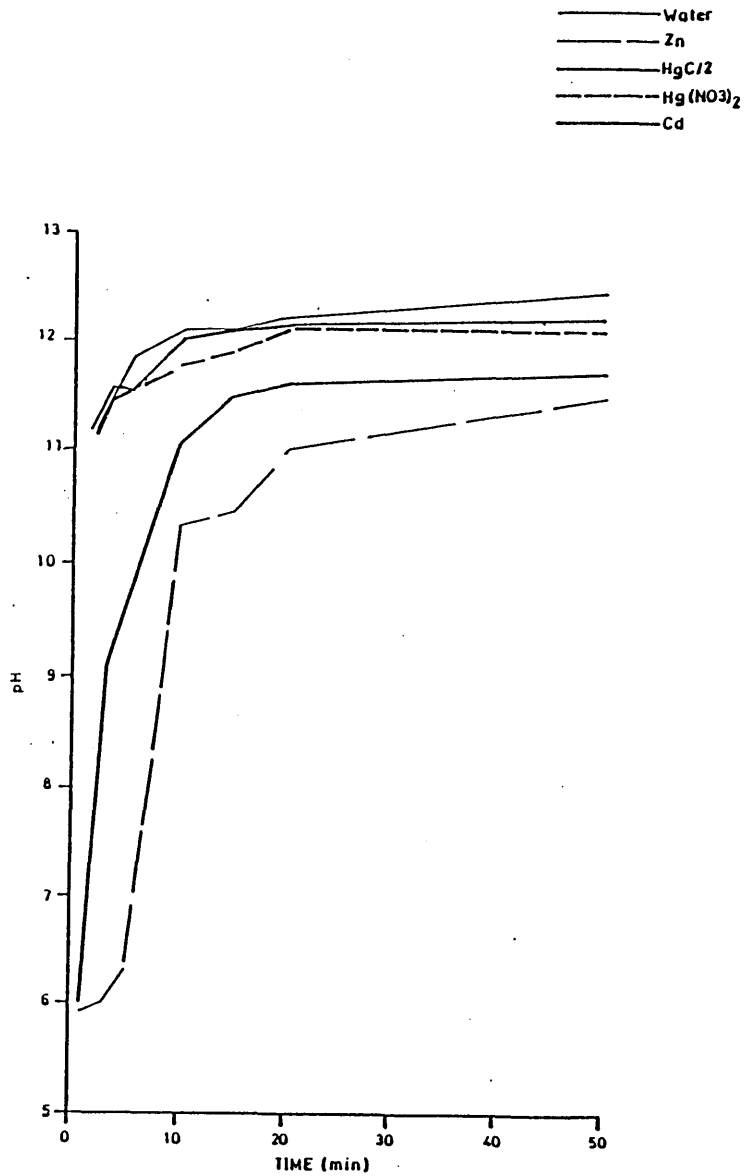


Figure 5.5a pH of system V (OPC/PFA/silicate)

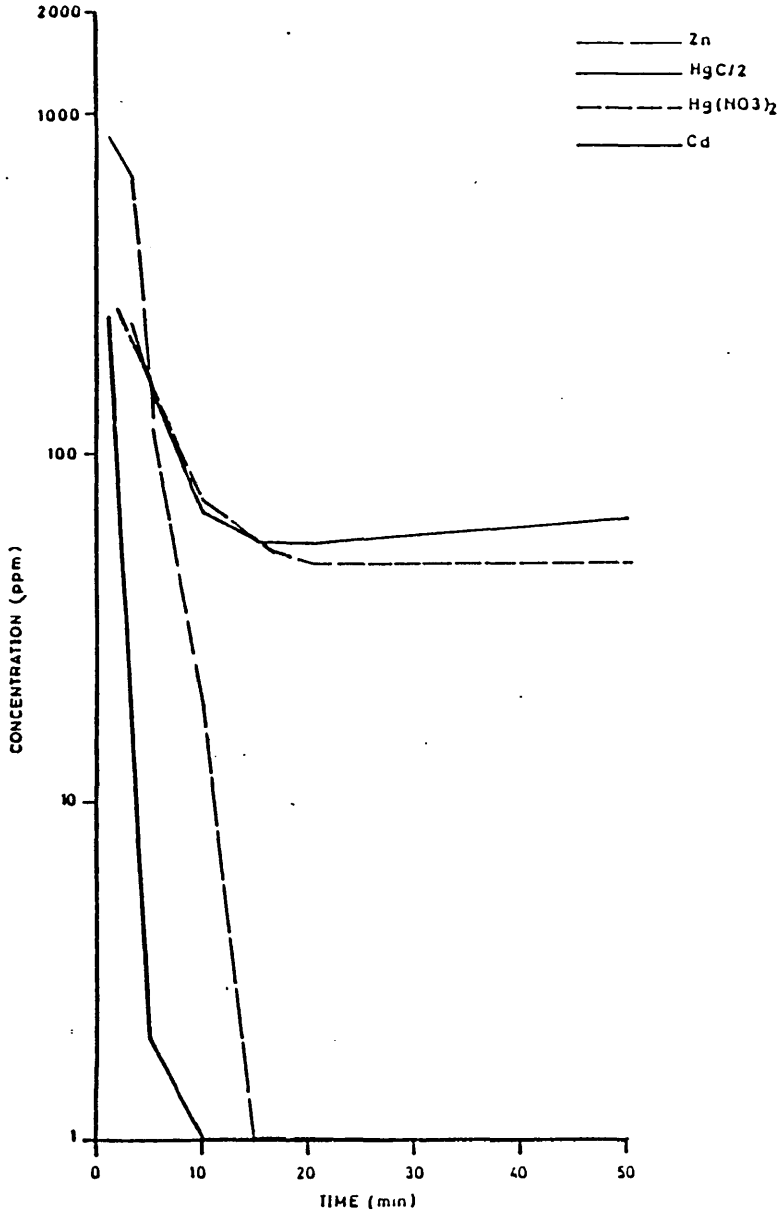


Figure 5.5b Metal concentrations in system V (OPC/PFA/silicate)

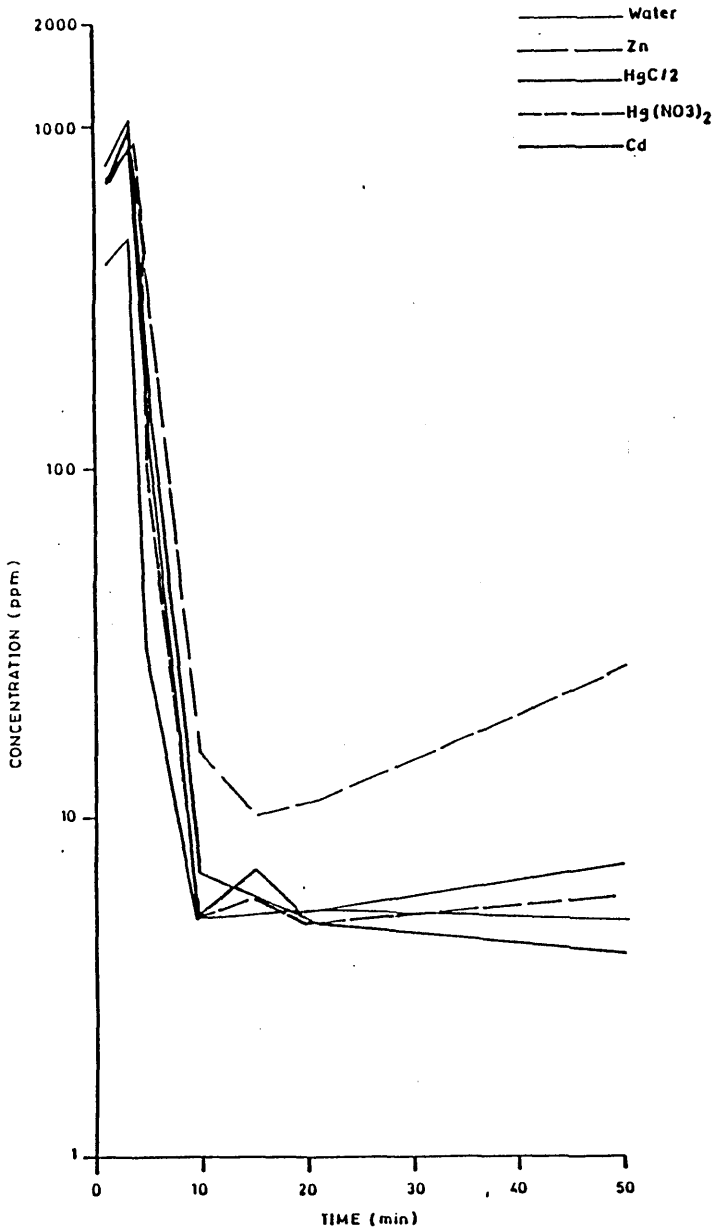


Figure 5.5c Ca concentration in system V (OPF/PFA/silicate)

decreased immediately after mixing (Zn from 2000 ppm to 4 ppm and Cd from 2000 ppm to a undetectable level). After an initial drop in value, the Zn concentration increased to 23 ppm after 5 minutes but subsequently decreased gradually to 2 ppm after 50 minutes of mixing. The Cd concentration, however, remained at the undetectable level for the rest of the mixing period.

System II (Figure 5.2, Table B2)

The PFA/distilled water mixture gave a low initial pH (5.8) which then increased gradually to pH 9 over a period of 50 minutes. At the same time the Ca concentration increased steadily from 220 ppm to 347 ppm.

The effect of the heavy metals on PFA was similar to that found in System I. All lowered the pH of the solutions in the order: $HgCl_2$ > $Hg(NO_3)_2$ > Cd > Zn. Both Zn and Cd solutions remained acidic during the course of the experiment. The Hg solutions, however, were initially acidic but increased gradually to a slightly alkaline pH after 50 minutes.

All the metal solutions gave a higher Ca concentration than the control. Generally the concentration was in the order of $Hg(NO_3)_2$ > $HgCl_2$ > Zn > Cd.

Zinc and Cd concentrations remained generally high throughout the experiment although a slight decrease was observed after 50 minutes. Mercury from the $HgCl_2$ solution decreased gradually from 1183 to 115 ppm over the same period. However, the Hg concentration in the $Hg(NO_3)_2$ solution stayed around 30 ppm for the first 20 minutes but increased to 335 ppm by the end of the mixing period.

System III (Figure 5.3, Table B3)

In the Chemfix/water system, the pH values increased from pH = 12.3 to 12.8 over 50 minutes. The Ca concentration rose from

1005 to 1125 ppm during the first three minutes of mixing. After the addition of sodium silicate solution it decreased to 20 ppm at 20 minutes and then increased to 80 ppm at 50 minutes.

The pH values for the metal-dosed Chemfix solution were similar to those found in the OPC (System I). The Zn and the two Hg solutions increased the initial Ca concentrations whereas Cd gave similar values to the control. In all cases, however, the concentration decreased after the addition of sodium silicate.

The concentration of Zn and Hg decreased gradually over 50 minutes with Zn decreasing at a faster rate. Both concentrations were further decreased after the addition of sodium silicate. No Cd was detected in the solution throughout the experiment.

System IV (Figure 5.4, Table B4)

The alkaline content of OPC was reflected in the relatively high pH which was lowered by the addition of the metal ions. All the metal solutions promoted the release of Ca from the system.

The initial Zn concentration in the solution was high (866 ppm) but decreased steadily to 2.69 ppm after 50 minutes. Concentrations of both Hg solutions were moderate decreasing from 260 to 200 ppm in 50 minutes. The initial Cd concentration was high (225 ppm) but rapidly decreased to an undetectable level after 15 minutes.

System V (Figure 5.5, Table B5)

A very similar trend to systems II and IV was noticed in the pH values and Ca concentrations. The initial concentrations of heavy metals were high and the addition of sodium silicate reduced all metal concentrations.

Zinc produced the highest Ca concentration in the solution but this decreased gradually after 5 minutes mixing and finally fell below that of the control. For the other three solutions ($HgCl_2$, $Hg(NO_3)_2$ and Cd) Ca concentrations increasd in the solution with respect to that of the control in the order: $HgCl_2$ > $Hg(NO_3)_2$ > Cd.

The concentration of Zn decreased from 2000 ppm to 5 ppm after 1 minute, slightly increasing to 24 ppm after 5 minutes. This was followed by a gradual decrease to about 2 ppm after 50 minutes.

Both Hg solutions gave a relatively high Hg concentration by 1 minute (164 and 159 ppm) remaining relatively constant at this level during the rest of the mixing period. The Cd concentration, however, decreased immediately after mixing, to a non-detectable level.

5.1.3 Discussion

When cement was mixed with water, (System Ia), a hydrolysis reaction was initiated. The high pH values which resulted, accompanied by the increased Ca concentrations, were due to the dissolution of the constituents of OPC, particularly the lime.

The low pH values encountered in the PFA/water (IIa) aqueous environment showed that the PFA had a very low lime content which was in turn reflected in the low Ca concentration in the solution.

Replacing part of the PFA by cement (IIIa) increased the initial pH considerably from 5.8 to 11.1. Such an increase in pH was accompanied by the correspondent small increase of Ca concentration in the solution. The reason for such a small increase must be due to the precipitation of Ca-containing products when the PFA reacted with cement in the aqueous environment.

The addition of sodium silicate solution in OPC and PFA/OPC mixes did not result in any significant increase of pH value. The Ca concentration in the solution, however, was reduced. It is proposed that this is due to the reaction of Ca^{2+} ions in the solution and the SiO_3^{2-} ions from sodium silicate to produce calcium-silicate gel. It should be noted that this gel was different from the calcium silicate hydrate produced from the normal hydration of cement. The latter is formed under specific conditions and by a different mechanism.

Another factor contributing to the low Ca concentration was the possibility of the inhibiting action of this gel. The inhibition probably took the form of a coating layer being formed and thus reducing the possible sites for reaction. The coating was presumably then displaced enabling further hydrolysis to take place as the concentration of Ca started to rise again after 50 minutes.

The addition of heavy metals lowered the pH of all systems investigated. This is due to the utilisation of lime to neutralise the acidic nature of the solutions involved. Zinc and Cd produced the lowest pH, while $HgCl_2$ and $Hg(NO_3)_2$ had only a slight effect. Consequently, the Ca concentration in all systems (except II) increased with metal addition. This increase was greatest for Zn which produced the lowest pH values. This can be accounted for by considering the solubility of $Ca(OH)_2$ which suggests that more Ca would remain in the solution with the lower pH environment. However, in systems Ib and IIb the Ca concentration decreased after 5 minutes indicating the formation of Ca-containing precipitates in the mixes.

The Ca concentrations in the two Hg solutions in all (except II) systems closely resembled each other. This demonstrated that the reaction mechanisms of these two forms of Hg with OPC and OPC/PFA with or without sodium silicate were very similar. The data indicated that the Ca concentrations of these two Hg solutions did not significantly differ from the control in these systems. It

also showed that the initial hydration mechanism of OPC was not significantly affected by Hg addition.

In system II, the Ca concentration displayed a different behaviour from that in the other systems. Although all metals increased the Ca concentration in the solution, the Hg solution had a significantly higher Ca concentration than that of Zn and Cd. Since PFA itself possesses little lime, the Ca was mainly derived from the PFA particles. The mechanism for such release might be due to cation exchange and experimental results indicate that the Hg solutions promoted such an exchange more than the Zn and Cd solutions.

The concentration of Zn, Hg and Cd in all systems (except II) decreased with respect to time. The rate of decrease was in the order: Cd > Zn > Hg. The two Hg solutions behaved similarly despite containing different anion species. This difference in the rate of decrease could be partly accounted for by the difference in initial precipitation of Zn, Cd and Hg in the alkaline environment. Zinc and Cd could be precipitated as complex hydroxide while Hg could only be precipitated as a partially soluble oxide. Cadmium demonstrated a much lower concentration than Zn due to the lower solubility product of $Cd(OH)_2$ ($K = 10^{-14}$) in comparison with $Zn(OH)_2$ ($K = 10^{-11}$) (35). Furthermore, $Zn(OH)_2$ is more soluble than would be expected from the constant owing to the equilibrium:

$$Zn(OH)_2\ (s) = Zn(OH)_2\ (aq)\quad K = 10^{-6} \qquad (5)$$

Comparing the rate of decrease in metal concentration in systems I (OPC) and IV (PFA/OPC) the former gave a much faster rate of decrease which can be explained by the difference in lime content.

In system II (PFA) the concentration of Zn and Cd remained high and it is therefore probable that PFA alone did not stabilise both metals. This was due to the low lime content of the PFA. For the two Hg solutions, however, different mechanisms were demonstrated to be in operation. The Hg concentration of $HgCl_2$ solution

decreased gradually from 1183 ppm to 115 ppm. The Hg concentration in the $Hg(NO_3)_2$ solution stayed low ($\triangleq$ 30 ppm) after 20 minutes and then increased. Two mechanisms are thought to be operative for the retention of Hg, namely: (i) a simple precipitation of HgO with lime and (ii) a sorption uptake of Hg by the PFA particles. In the case of $HgCl_2$, the progressive decrease in concentration was mainly due to the precipitation of oxide. It was less probable for the neutral convalent mercuric chloride molecules that sorption occured in the PFA particle. In the case of $Hg(NO_3)_2$, however, the main species in solution were $Hg(NO_3)_2$, $HgNO_3^+$ and Hg^{2+} which were capable of reacting with the hydroxyl ion as well as being chemisorbed onto the -ve charged PFA surface. The fact that more Ca was released from the mixes containing these two Hg solutions than those containing other metals indicated that the PFA surface must have been more negatively charged in the Hg solutions.

The sorption of the positively charged Hg on the PFA surface is thought to be the predominant mechanism in reducing the Hg concentration in the solution. This is because the pH of the solution was too low for significant precipitation of HgO to occur. Also, in comparison with system I, the Hg concentration was lower in system II where the pH value was also low.

Desorption occured in the $Hg(NO_3)_2$ solution when the pH increased beyond 7. This was probably due to the reduction in sorption sites on the PFA surface. As the pH increased beyond 7, the Ca concentration in the solution was decreased, hence the proportion of -ve charges on the PFA surface was also decreased. The pH itself was still too low for most of the desorbed Hg ion to be precipitated as oxide.

The addition of sodium silicate to the OPC and PFA/OPC blended mixes lowered the Ca concentration in all systems. Sodium silicate itself contributed marginally to the decrease in concentration of Zn and Cd as these two metals would have already precipitated in the alkaline environment. It did, however, contribute to the reduction of Hg in both Hg solutions. The mechanism for this is

probably not due to the promotion of the precipitation of HgO (as seen from the pH values) but to sorption of Hg on the calcium-silicate gel formed.

The main effect of adding sodium silicate into a cementitious matrix was to promote the rapid precipitation of calcium-silicate gel. This gel had a high specific surface and greatly increased the water retention potential of the system.

5.2 Leaching Tests

The successful use of stabilisation/solidification processes for the disposal of hazardous waste depends on the ability of the stabilising material to reduce the leachability of the solidified waste. Leaching can be defined as the process by which a component of waste is removed mechanically or chemically into solution from the solidifed matrix by the passage of a solvent such as water.

Factors which affect the leaching potential of a waste include ions present, pH, stoichiometry, temperature, electrostatic charge (surface effect), presence of ligand or chelating compounds, oxidation - reduction (redox) potential and many other parameters (56). The leaching process is also affected by the occurrence of many complex reactions and thus the pollutant leach rate cannot usually be expressed by a conventional mathematical model - although this has been attempted in a few simplified and carefully controlled conditions (57).

Leaching tests, therefore, have been devised either to classify the solidified waste as hazardous according to present regulations or to produce a time based prediction of the quality of leachate that would be produced by a waste when placed in a landfill environment. The US Environmental Protection Agency Extraction Method (58) is the procedure most commonly used for the classification of waste but a realistic estimation of the leachate characteristics should be founded upon the mechanisms that allows leachate to be produced.

It has been pointed out that leach tests should be meaningful, reproducible, quick and inexpensive methods of simulating the effect of rain or groundwater on a fixed waste. A leaching test should ideally determine four characteristics about the release of constituent X from a waste (59):

(i) The highest concentration of X in the leachate;
(ii) The factors controlling the concentration;
(iii) The total amount of X releasable from a given amount of waste, and
(iv) the release pattern of X with time.

Such a test ranges from a simple elutrate procedure which involves simply mixing water or the selected leaching fluid with the solidified material and then analysing the leachate after filtering, to a cyclic extraction process using specially controlled physical and chemical conditions. There is no agreed standard leaching test procedure available to assess the leachability of solidified material amongst the companies who market, and the government bodies who regulate the use of solidification processes.

However, two types of leaching procedure are commonly used for determining leaching potential. These are column and batch tests. A column test involves the continuous flow of liquid through a fixed bed of solidified waste. The batch method, on the other hand, involves the mechanical mixing of the leaching fluid with the waste materials - either conducted singlely or sequentially.

Many variations of these two types of test exist and are exhibited in Tables 5.2 and 5.3. These demonstrate the lack of concensus on a standardised testing procedure and the difficulties in correlating results from different laboratories.

Table 5.2 Variations in column test procedure (1977 ASTM D-19.12 survey) (60)

Liquid used	
Natural water	3 laboratories
Synthetic water	3 laboratories
Distilled water	3 laboratories
Deionized water	4 laboratories
Liquid/waste ratio (v/w)	
Maximum	13:1
Minimum	1.6:1
Column diameter, in	
Maximum	8
Minimum	1
Bed height, in	
Maximum	73
Minimum	2
Contact time, min	
Maximum	28,800 (20 days)
Minimum	400

Table 5.3 Variations in batch test procedures (1977 ASTM D 19.12 survey) (60)

Liquid used	
Natural water	7 laboratories
Synthetic water	3 laboratories
Distilled water	6 laboratories
deionized water	9 laboratories
Agitation method	
Diffused air	2 laboratories
Gang stirrer	1 laboratory
Electric stirrer	2 laboratories
Magnetic stirrer	1 laboratory
Reciprocating shaker	1 laboratory
Mechanical	2 laboratories
Tumbler	2 laboratories
Water circulation	1 laboratory
Vibrating table	1 laboratory
Hand	1 laboratory
Liquid/waste ratio (v/w)	
Maximum	100:1
Minimum	1:1
Contact time, hr	
Maximum	100
Minimum	0.5

It should be noted that major variables encountered in comparing leaching procedures from this survey are:

(i) Nature of the leaching solution.
(ii) Liquid to solid (waste) ratio.
(iii) Surface to volume ratio of waste.
(iv) Contact time between leaching liquid and waste.
(v) Mechanical extraction effort used.

These two forms of leaching tests provide separate information of the leaching characteristics of waste. A recent study by Jackson et al. (61) on the comparision of column and batch procedures for assessing hazardous waste approved both test methods for their relative accuracy in predicting the levels of leachates from the waste materials. The advantages and disadvantages of column and batch tests are summarised in Table 5.4.

Table 5.4 Advantages and disadvantages of column and batch tests

Batch test	
Advantages	Disadvantages
Edge effect in column test is avoided	Do not simulate the leaching environment in a landfill site.
Time required for test is less than column test	Do not measure true leachate but equilibrium concentration.
Results are more reproducible.	A standard filtering procedure is required.

Table 5.4 (Cont'd)

Column test (59)	
It simulates the waste-leachate content (except around the column) and the slow leachate migration found in landfill.	Channelling and non-uniform packing.
	Clogging.
Provides prediction of the release pattern with time.	Biological growth.
	Edge effects.
	Time requirements.
	Reproducibility.

A simple method based on thin layer chromotography for assessment of leachability has been developed during this present research and is included in Appendix E. The method measures the mobility of waste within the solidified matrix. There was a fair degree of correlation between the results obtained from this method and the traditional leaching tests. The method is rapid, requiring no tedious chemical analysis, only colour development on the plate is needed and provides a good visual indication of the retention of different hazardous waste by the solidified matrix. However, the method is currently limited to qualitative or semi-quantitative application. Some refinement is necessary before applying the method for quantitative measurement of leaching potential.

Since there is no standardised laboratory scale leaching procedure which closely simulates the field environment, two accelerated test procedures were formulated for this study. These test procedures were designed to give an indication of the leaching characteristics of each solidification process for comparative purposes and to study the long term stability of the solidified waste. A fundamental study on the leaching mechanism was also conducted by extending the leaching test coupled with SEM analysis to determine the relationship between leaching and the micro-structure of the solidified matrices.

A batch test approach was chosen because of the easy availability of equipment in the laboratory and because the parameters are more easily controlled than in the column test.

(i) Dynamic batch test

The dynamic batch test involved the crushing of the solid waste into small particles passing through a 2 mm sieve. The crushed solid was then mixed with the leaching fluid for a set period of time. The leachate produced was filtered and analysed for the pollutants of concern.

(ii) Static batch test

This test involves the placing of a specially prepared solidified product in monolith form in the leaching liquid. The solidified mass was allowed to equilibrate with the leaching fluid without mechanical disturbance at room temperature. After a specific period of time the resulting leachate was replaced by a fresh quantity of leaching fluid, filtered and analysed.

5.2.1 Method

5.2.1.1 Dynamic leaching test

Mix proportion:

Chemfix	solution/OPC	= 5
	sodium silicate/OPC	= 0.24
Sealosafe:	PFA/OPC	= 3
	solution/*solid	= 0.5

*solid = PFA + OPC

Waste solutions:

(i) 2000 ppm Zn (nitrate), Hg (chloride)
(ii) 2000 ppm Cd (nitrate)
(iii) 2000 ppm Hg (chloride)
(iv) 2000 ppm Hg (nitrate)
(v) 2000 ppm phenol

In addition to these, separate dynamic leaching studies were conducted on divalent and heptavalent manganese (MnO_4^- and Mn^{2+}) solidified using the Chemfix formulation.

The solutions were solidifed according to the above formulae and the solidified product was cured at room temperature for 28 days. A 0.15 M buffered acetic acid (pH = 4.6) was used as the leaching liquid. A liquid to solid (wet w/w) ratio of 2.5 was used. The mixture of crushed solid and liquid was transferred to a sealed container and agitated using a rotational shaker (29 r.p.m.). After 24 hours, the slurry was filtered through a 0.45 μm membrane. A fresh portion of acetic acid was added and the process repeated over several days. After pH measurement, filtrates were preserved in a nitric acid solution and analysed for metals by a Pye Unicam SP 192 Atomic Absorption

Spectrometer (Cambridge, UK). Phenol was analysed by a colourmetric method using 4-amino-phenozone as reagant (94).

5.2.1.2 Static batch test

Mix proportion:

Chemfix:	solution/OPC	1
	sodium silicate/OPC	0.05
Sealosafe:	PFA/OPC	3
	solution/solid	0.5

The simulated waste used in these experiments was a 2000 ppm solution of Zn (nitrate), Hg (chloride) and Cd (nitrate).

Solidified samples were prepared first by mixing the solution with the required amount of solid for 3 minutes. Sodium silicate solution was then added as required and the mixture agitated to produce a homogenous slurry.

The resulting slurries were cast into specially prepared 40 mm cube moulds, compacted using a vibrating table and cured at 20°C and 58% RH. After 24 hours, the solidified products were removed from the moulds and further cured for 27 days under the same conditions carefully avoiding any mechanical disturbance.

The resulting monolithic cubes were immersed in leaching fluid (0.15 M buffered acetic acid) with a liquid/solid ratio of 2.5 (v/v) within a sealed, covered container. No agitation was induced after the immersion. The leaching fluid was renewed after 2, 7 and 12 days and at weekly intervals thereafter.

The resulting leachates were filtered to remove any dissoluted solid using a 0.45 μm membrane and, after pH measurement, were preserved in a dilute nitric acid solution and analysed for

metals by atomic absorption spectroscopy as described previously.

5.2.1.3 Extended leaching test

Selected mixes were subjected to extended leaching using different leaching fluids to investigate the leaching mechanisms.

Three leaching fluids of constant pH ($\triangleq$4.6) but with different buffering capacities (Table 5.5) were used.

Table 5.5 Buffering index (β) of leachate

Leaching fluid	Buffering Index (β)
0.15 M HAC/0.15 M NaAc	0.160
0.3 M HAC/0.3 M NaAC	0.315
0.5 M HAC/0.5 M NaAC	0.528

The buffering capacities were calculated from the buffering index (β) which indicates the number of moles of acid or base required to produce a given change in pH. This can be calculated from the following equation: (62).

$$= 2.303 \left(\frac{K_w}{(H^+)} + (H^+) + \frac{CK_A(H^+)}{(K_A+(H^+))^2} \right) \quad (6)$$

$$K_w = (H^+)\,(OH^-) = 10^{-14} \quad (7)$$

The dissociation constant of an acid,

$$K_a = \frac{(H^+)\,(A^-)}{(HA)} \quad (8)$$

(HA) = concentration of acid

(A^-) = concentration of conjugate base

$$C = (HA) + (A^-) \quad (9)$$

The dynamic batch test procedure was used for this investigation. Leached solidifed waste samples of every leaching period from the 0.5 M buffered acetic acid experiment and the preleached solidified waste were oven dried at 105°C. The powdered samples obtained were examined without pregrinding in the form of a thin particulate layer dispersed on specimen stubs held in place by double-sided adhesive tape. The samples were then coated with gold or carbon film prior to SEM examination using a JEOL 35 CF + EDAX system.

5.2.2 Results

5.2.2.1 Dynamic leaching test

The results of the dynamic leaching tests are presented in Tables 5.6 to 5.16.

Acetic acid buffered to pH 4.6 was used as leachate in the test in order to simulate those extreme conditions encountered in landfill sites. The shaking action produced an accelerated leaching environment. Under these conditions, the results demonstrated that leachates had a very high initial alkalinity, probably due to the dissolution of lime and hydrated cement in the cementitious matrix. Chemfix samples gave a higher initial pH than Sealosafe samples. The results demonstrate that the leaching potential for the three metals studied decreased in the order of Hg > Zn > Cd for both Chemfix and Sealosafe processes. Generally, the leachate concentrations in the Sealosafe matrices were less than the Chemfix formulations, especially in the $HgCl_2$-dosed samples.

Table 5.6 Dynamic leaching test results of Chemfix with Zn and Hg

Elution	1	2	3	4	5
pH	11.8	11.6	11.2	11.0	10.0
Zn (ppm)	1.3	0.1	0.1	0.1	0.2
Hg (ppm)	42	32	27	16	14

Table 5.7 Dynamic leaching test results of Sealosafe with Zn and Hg

Elution	1	2	3	4	5
pH	11.8	11.4	10.9	10.4	9.9
Zn (ppm)	0.13	0.05	0.05	0.05	0.04
Hg (ppm)	3.7	1.5	1.0	1.5	1.5

Table 5.8 Dynamic leaching test results of Chemfix with Cd

Elution	1	2	3	4	5
pH	12.4	12.3	12.0	11.5	11.2
Cd (ppm)	<0.01	<0.01	<0.01	<0.01	<0.01

Table 5.9 Dynamic leaching test results of Sealosafe with Cd

Elution	1	2	3	4	5
pH	12.2	11.9	11.4	10.8	9.3
Cd (ppm)	0.01	0.01	0.01	0.01	<0.01

Table 5.10 Dynamic leaching test results of Chemfix with $HgCl_2$

Elution	1	2	3	4	5
pH	12.5	12.1	11.7	11.4	11.2
Hg (ppm)	23.5	20.0	11.5	7.5	5.4

Table 5.11 Dynamic leaching test results of Chemfix with $Hg(NO_3)_2$

Elution	1	2	3	4	5
pH	12.5	12.3	11.9	11.6	11.4
Hg (ppm)	3.3	3.3	2.9	0.8	1.2

Table 5.12 Dynamic leaching test results of Sealosafe with $HgCl_2$

Elution	1	2	3	4	5
pH	12.2	12.0	11.4	11.0	10.1
Hg (ppm)	3.9	1.4	1.7	0.7	0.7

Table 5.13 Dynamic leaching test results of Sealosafe with $Hg(NO_3)_2$

Elution	1	2	3	4	5
pH	12.2	12.0	11.5	11.1	10.3
Hg (ppm)	3.2	1.6	0.7	1.4	nd.

Table 5.14 Dynamic leaching test results of Chemfix with Phenol

Elution	1	2	3	4	5
pH	12.2	11.8	11.5	11.2	11.0
Phenol (ppm)	596	102	9.9	11.8	2.6

Table 5.15 Dynamic leaching test results of Sealosafe with Phenol

Elution	1	2	3	4	5
pH	11.8	11.6	11.0	10.8	10.4
Phenol (ppm)	160	22.1	2.3	6.1	0.8

Table 5.16 Dynamic leaching test results of Chemfix with Mn

Elution	1	2	3	4	5
Mn^{2+} (ppm)	0.06	0.07	0.09	0.10	0.11
MnO_4^- (ppm)	349	211	28	1.22	0.08

Zinc and particularly Cd, remained at a constant low concentration during the initial stages of leaching. However, the Hg concentrations of the $HgCl_2$-dosed samples were initially high and decreased through successive elutions.

The use of two Hg salts in this study was due to the insolubility of $Hg(NO_3)_2$ which was unstable in an aqueous environment. This Hg salt tends to hydrolyse to form a red precipitate of HgO. Although $HgCl_2$ is largely covalent in nature it readily dissolved in water to give a true concentration of Hg (2000 ppm) solution. Comparing the leachate concentration of these two Hg-dosed samples for Chemfix (Tables 5.10 and 5.11) and Sealosafe (Tables 5.12 and 5.13), mercuric nitrate was retained better than $HgCl_2$ in the Chemfix matrix, but had a similar retention in the Sealosafe mix.

Comparing Tables 5.6 and 5.10 the Hg concentration in the leachate was higher when Zn was added simultaneously. This shows that different types of waste pollutants interacted with each other in the solidified material and affected their fixation and leaching mechanisms.

The addition of manganese in the form of Mn^{2+} and MnO_4^- produced significantly different results in leaching characteristics. The results show that Mn^{2+} was well retained by the cementitious matrix and MnO_4^- was easily released. In fact, almost 40% of the dosed manganese in the form of MnO_4^- leached out from the matrix in 1 day. These results demonstrate the different stabilising mechanisms in operation for the retention of metals carrying a positive charge and anion metal species.

Tables 5.14 and 5.15 show that neither Chemfix and Sealosafe were capable of retaining phenol. Phenol concentrations in the leachate were initially high, decreasing exponentially with time or elution.

5.2.2.2 Static leaching test

The results of the static leaching test are presented in Tables 5.17 to 5.18 for the Chemfix and Sealosafe samples respectively.

Immersing the Chemfix sample in the 0.15 M buffered acetic acid solution increased the solutions pH from 4.6 to 6.5 after 2 days. The pH gradually increased to 7.2 after 12 days but then decreased slowly to 6.4 after 54 days.

The Sealosafe sample gave a lower pH than the Chemfix sample. However, it displayed a similar trend to the Chemfix sample as the solution pH increased initially from 4.6 to 6.6 after 2 days and 6.7 after 12 days. The pH values subsequently decreased to an acidic value of 5.4 after 54 days.

Considering the heavy metal concentrations in the Chemfix sample, Zn and Cd gave moderate concentrations in the leachate during the first 12 days (1 - 2 ppm) and then increased in value. Mercury concentrations, however, remained at a relatively constant level throughout the 54 day period.

There is no consistent trend in the Zn and Cd concentrations leached from the Sealosafe sample in solution before the 12th day but both metal concentrations increased gradually in the course of the experiment. The concentration of the Hg was high initially (11 ppm) and decreased gradually to a constant level of 5 ppm until the 33rd day when the concentration again increased slightly to 8 ppm.

Table 5.17 Static leaching test results of Chemfix with Zn, Hg and Cd

Day	2	5	12	19	26	33	40	47	54
pH	6.5	7.2	7.2	7.0	6.9	6.4	6.9	6.8	6.4
Zn (ppm)	1.91	1.02	1.31	3.55	2.40	6.75	2.42	3.75	7.56
Cd (ppm)	1.89	1.61	1.56	1.88	1.34	4.49	2.82	3.16	6.67
Hg (ppm)	2	2	3	3	3	2	2	2	4
Ca (ppm)	2487	2225	2712	2875	2920	2977	2985	3075	3150

Table 5.18 Static leaching test results of Sealosafe with Zn, Hg and Cd

Day	2	5	12	19	26	33	40	47	54
pH	6.6	6.6	6.7	6.6	6.3	6.2	6.0	5.9	5.4
Zn (ppm)	5.98	7.95	7.88	6.70	7.38	5.0	9.50	12.0	12.3
Cd (ppm)	6.20	9.79	8.54	9.33	9.15	11.54	13.7	14.8	12.75
Hg (ppm)	11	10	5	5	5	4	6	8	6
Ca (ppm)	3100	2825	2712	2787	2925	3090	2967	2652	2657

Calcium was released relatively consistently from both samples despite their difference in total Ca content. This indicates that Ca was released at a faster rate from the Sealosafe sample than from the Chemfix sample.

Comparing the release of heavy metals from the Chemfix and Sealosafe samples, larger amounts of all three metals were released from the latter. It should be noted that the Chemfix sample contained higher doseages of metal than the Sealosafe sample because of the higher liquid/solid ratio used. An indication of total metal content in the two samples is given in Table 5.19.

Physical examination of these two samples revealed that the surfaces of both samples had been etched and attacked by the leaching fluid. The extent of this attack was greater with the Sealosafe sample as small lumps of particulate were seen loosened from the mass.

5.2.2.3 Extended leaching test

Extended leaching tests, with different leaching fluids were conducted on one Chemfix and one Sealosafe sample. The results are presented in Figures 5.6 to 5.10 and Tables D1 to D5.

The results illustrate that there was a drastic increase in the concentrations of both Zn and Hg in the Chemfix and Sealosafe samples. This breakthrough point was reached at different numbers of elutions for the 0.15, 0.3 and 0.5 M buffered acetic acid leaching fluids for each sample.

Concentrations of Ca released from the cementitious matrices during leaching are also presented in Figures 5.6 to 5.10 and Tables D1 to D5. Further information on the release of Ca from the matrices is presented in Table 5.20 where it can be

seen that for both the Chemfix and Sealosafe samples in different leachates, with different buffering capacities, similar percentages of Ca were released before the breakthrough occured.

The microstructure of the Chemfix sample underwent a number of changes through successive leaching periods. This is demonstrated by micrographs presented in Figures 5.11 to 5.15. Figure 5.11 shows the microstructure of the preleached Chemfix sample. Identifiable structures included clusters of calcium silicate hydrates (C-S-H), calcium aluminate sulphate hydrates typified by the ettringite (AFt) and monosulphate (AFm) phases, unhydrated cement grains, calcium hydroxide (C-H) and calcium-silicate gel formed from the reaction between Ca^{2+} from cement and SiO_3^{2-} from sodium silicate. Also presented in Figure 5.11 is the corresponding elemental analysis of the sample by energy dispersive analysis of x-rays (EDAX) in association with the SEM. The two major peaks are Si and Ca (1.74 and 3.69 ev respectively). The relative intensity of the peaks shows the relative amount of Ca to Si and indicates that the sample contained more Ca than Si though it should be emphasised that the EDAX spectrum might have different proportion in relation to their element concentration. X-ray signals obtained for different elements depend not only on the concentration but also on the binding energy of the K-shell electron of the concerned element. However in the present study, the analysis enabled the relative amount of Si to Ca in the sample to be estimated.

Micrographs of the sample after 1 day's leaching with 0.5 M acetic acid are presented in Figure 5.12. The AFt and AFm phases were still identifiable but the structure of C-S-H was deformed. The EDAX analysis indicated that the sample still contained more Ca than Si.

The microstructure of the sample after 3 day's leaching is shown in Figure 5.13. This illustrates that the sample has

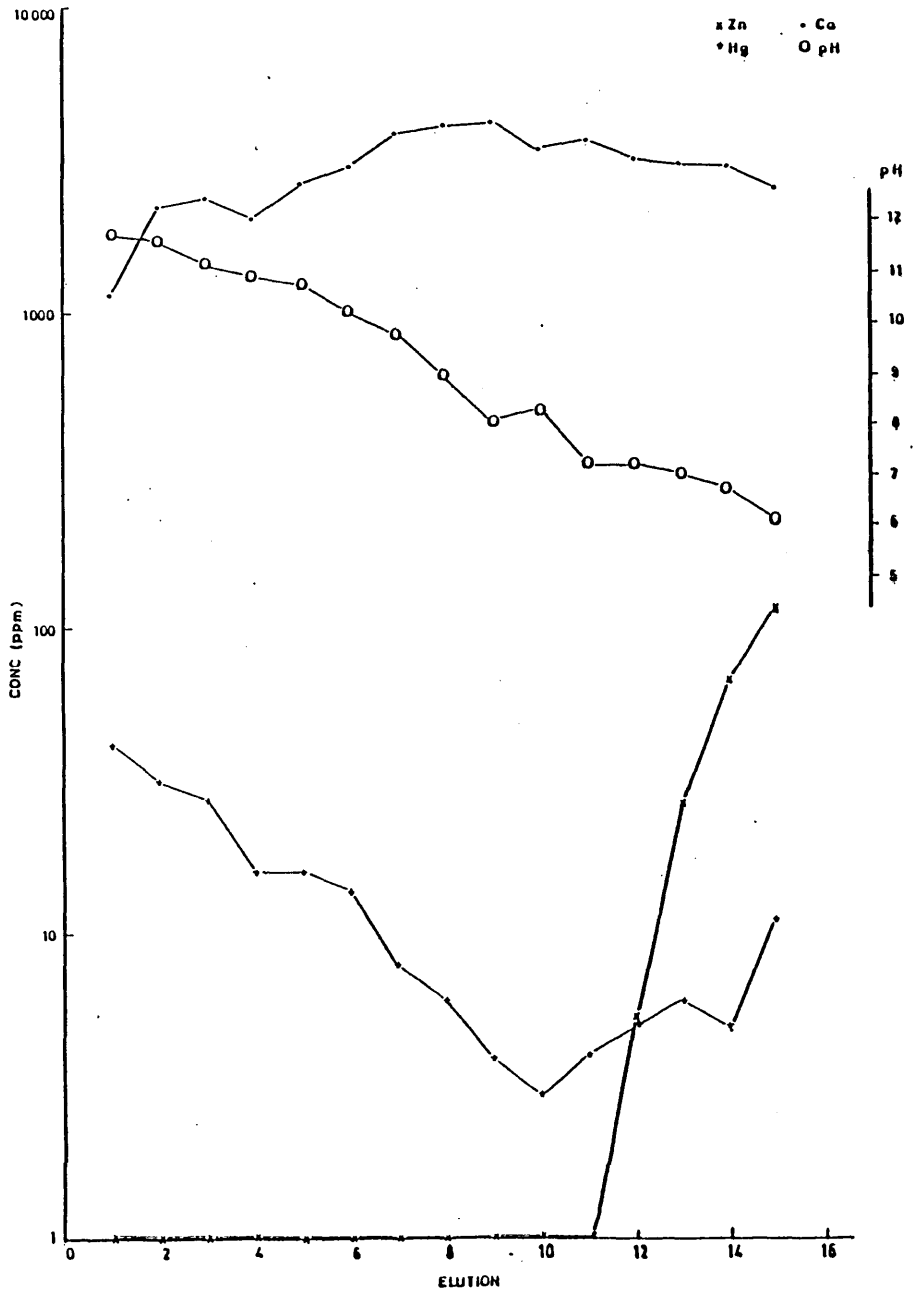


Figure 5.6 Leaching results of 0.15 M buffered HAC leachate (Chemfix)

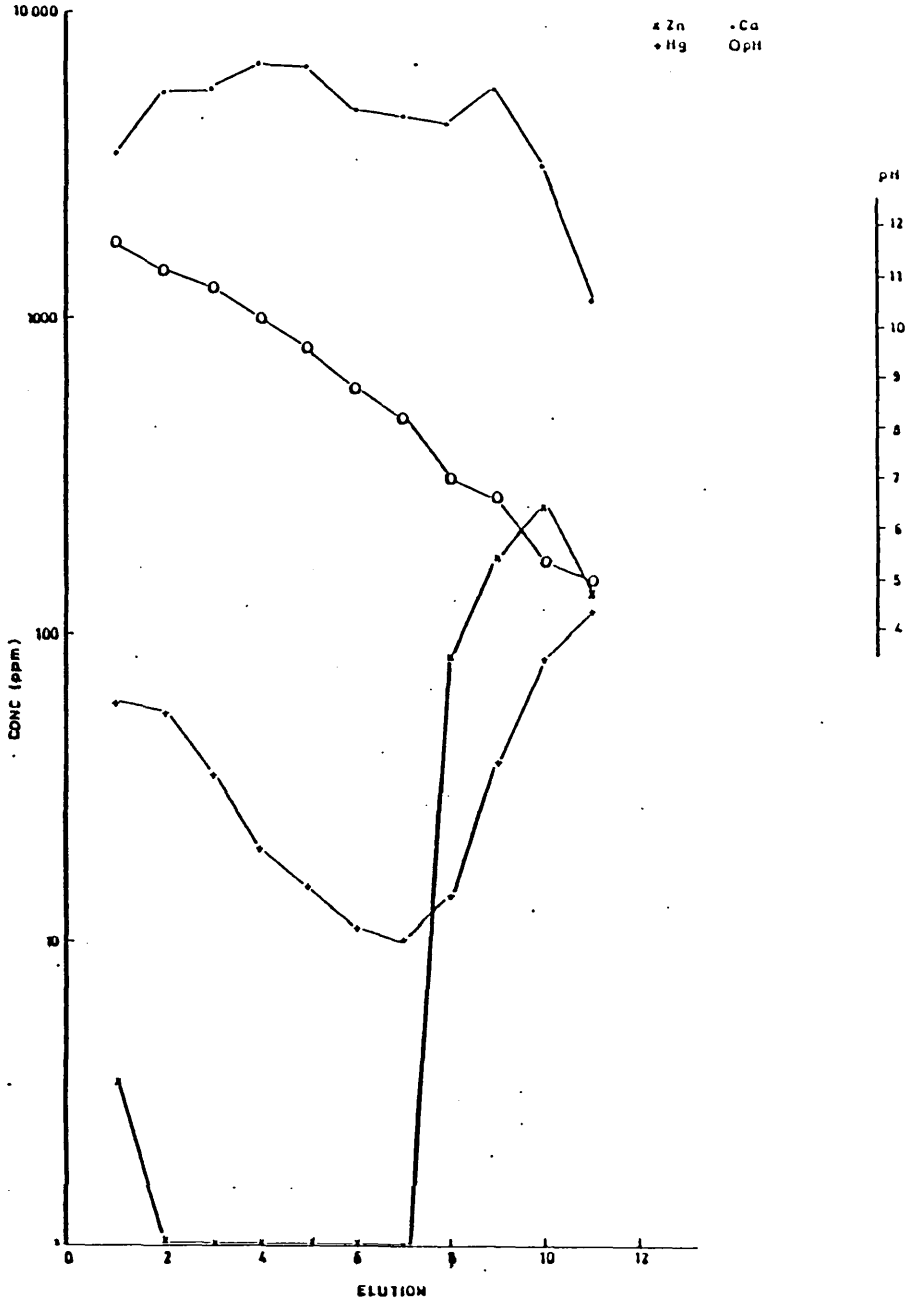


Figure 5.7 Leaching test results of 0.30 M buffered HAC leachate (Chemfix)

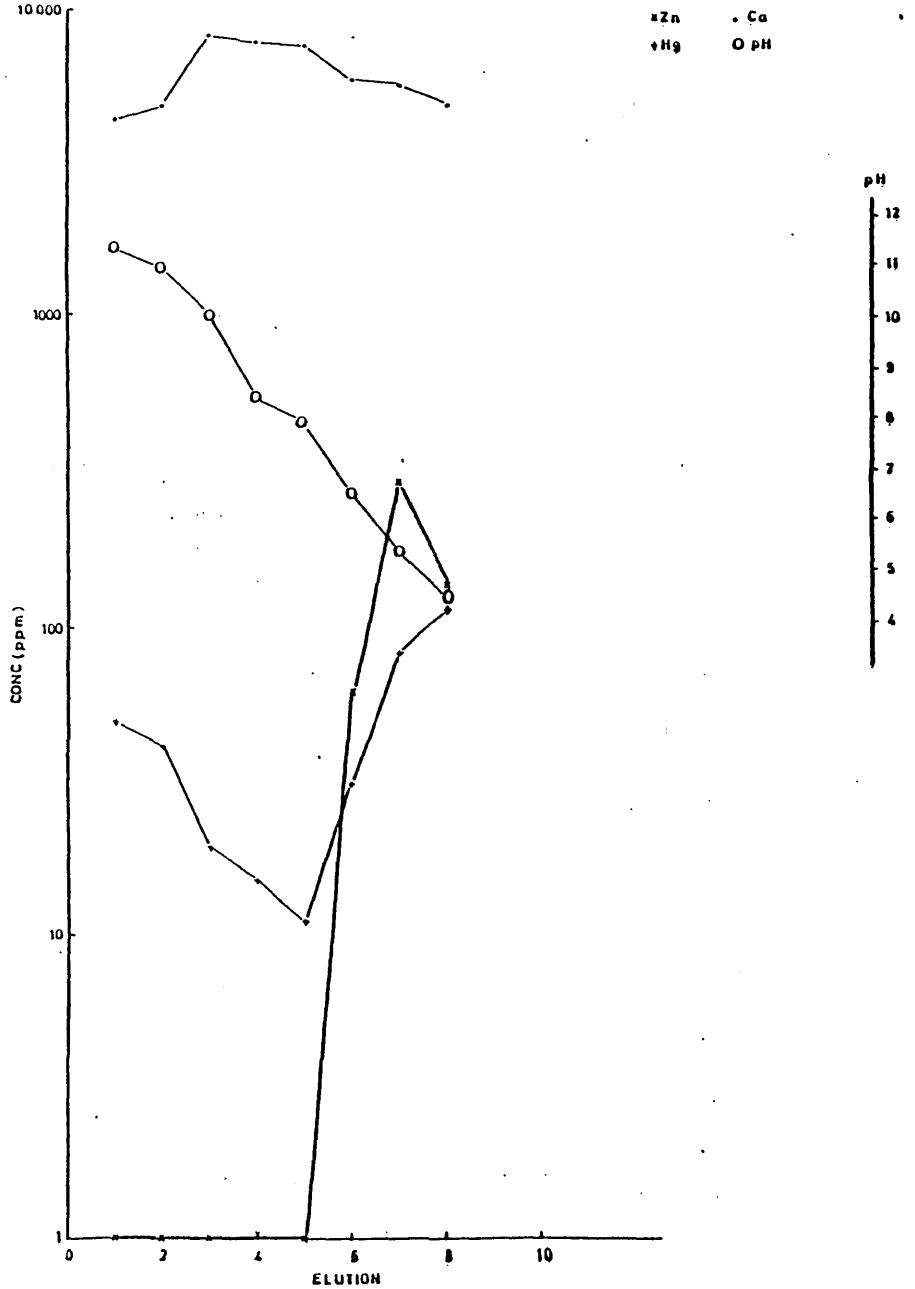


Figure 5.8 Leaching test results of 0.50 M buffered HAC leachate (Chemfix)

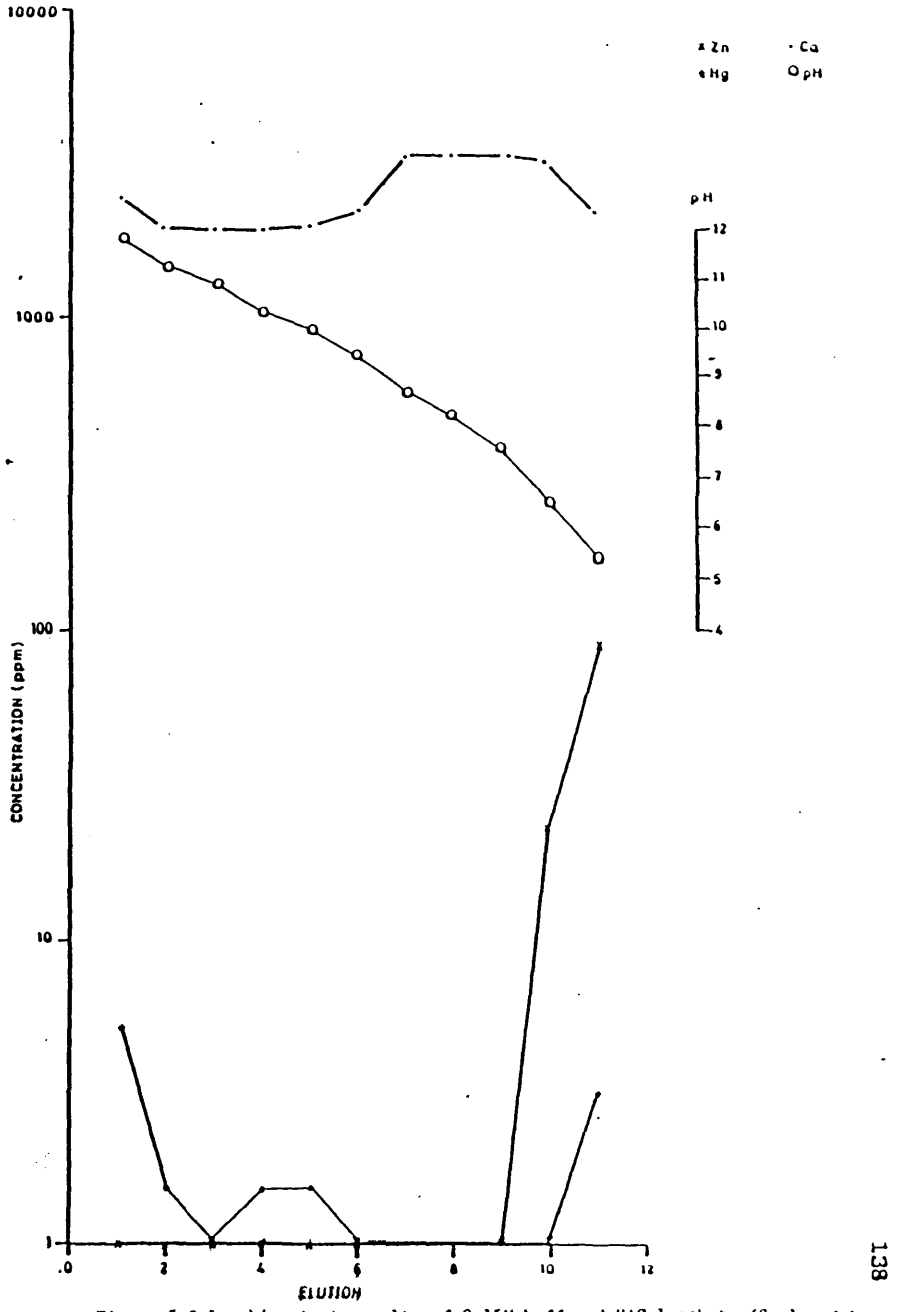


Figure 5.9 Leaching test results of 0.15M buffered HAC leachate (Scalosafe)

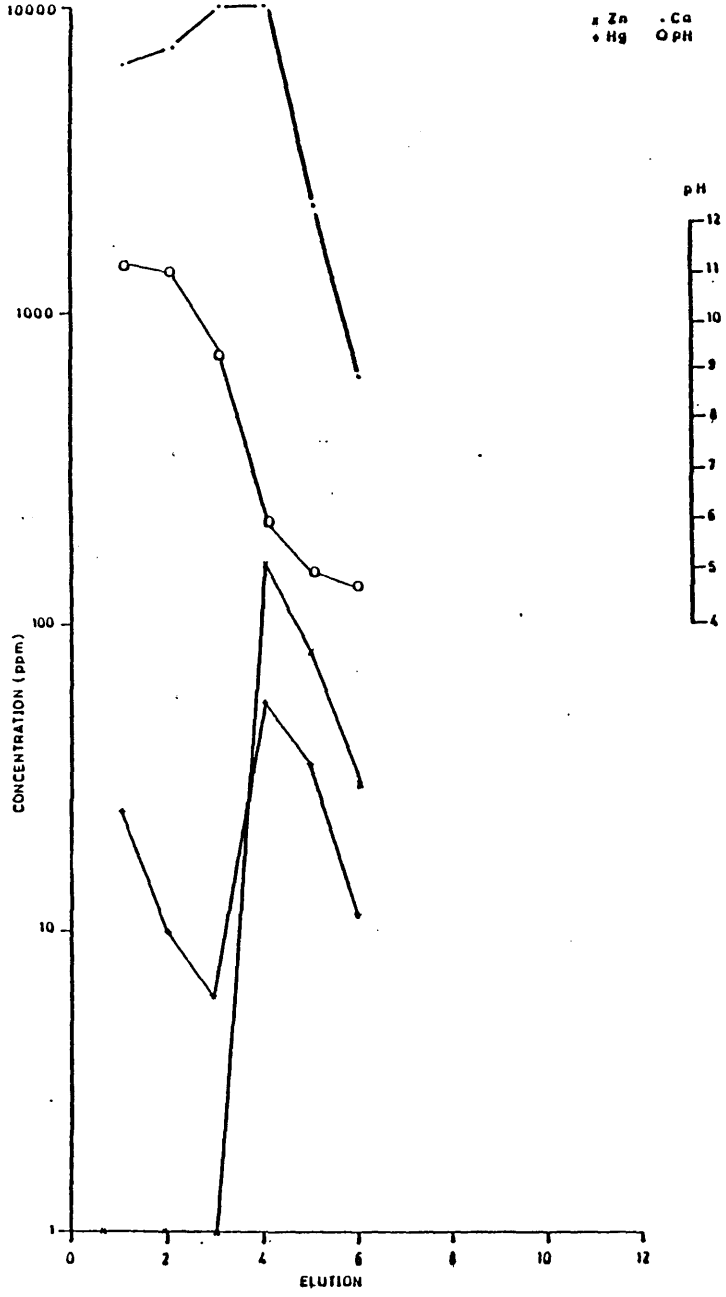


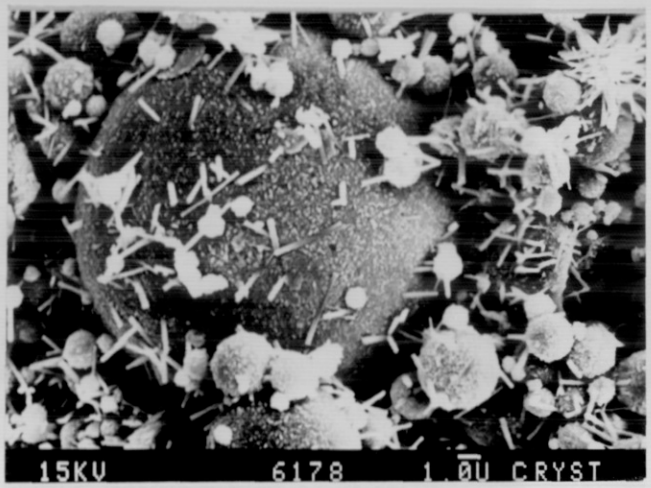
Figure 5.10 Leaching test results of 0.5M buffered HAC leachate (Sealosafe)

Table 5.19 Total metal content in solidified product

Chemfix	94.6 mg 21.6 g	Zn, Hg, Cd Ca
Sealosafe	72 mg 9.74 g	Zn, Cd, Hg Ca

Table 5.20 Calcium release data

Sample	Leachate	Percentage (%)
Chemfix	0.15 M	57
	0.3 M	58
	0.5 M	49
Sealosafe	0.15 M	53
	0.5 M	60



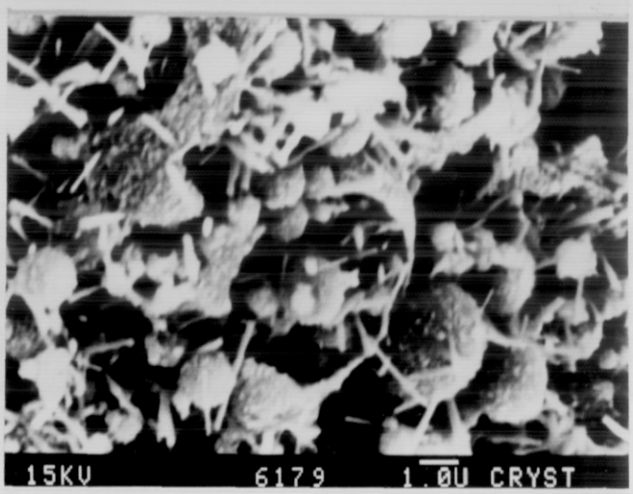
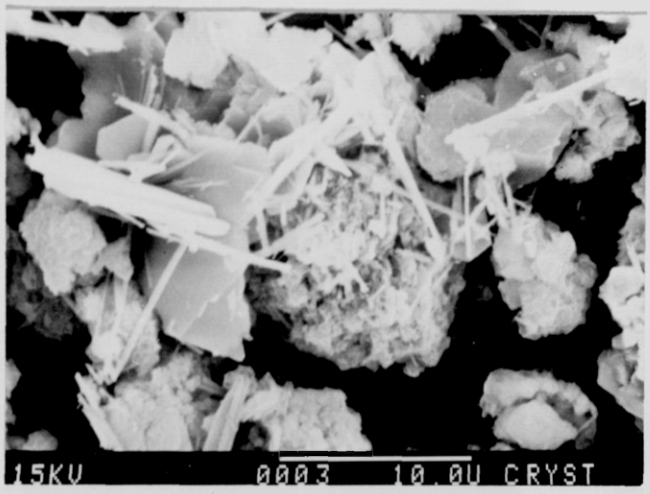


Figure 4.13 Micrographs of the Cd dosed Sealosafe sample showing rods of ettringite and deposition of hydration products on PFA particles. Cement gave a very thick Hadley grain shell like structure.



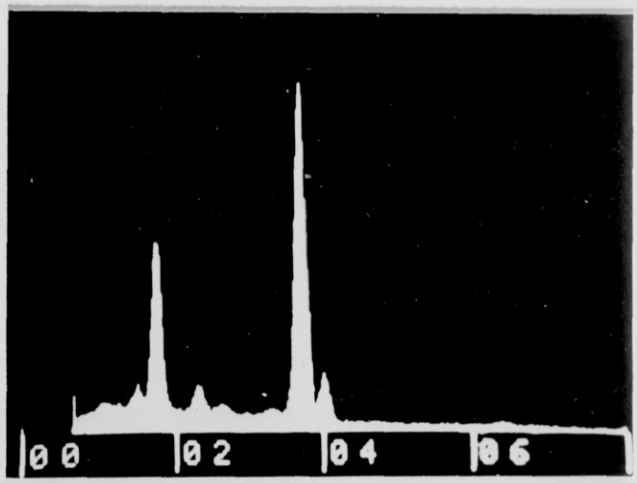


Figure 5.11 Micrographs of the pre-leached Chemfix sample and associated EDAX analysis.

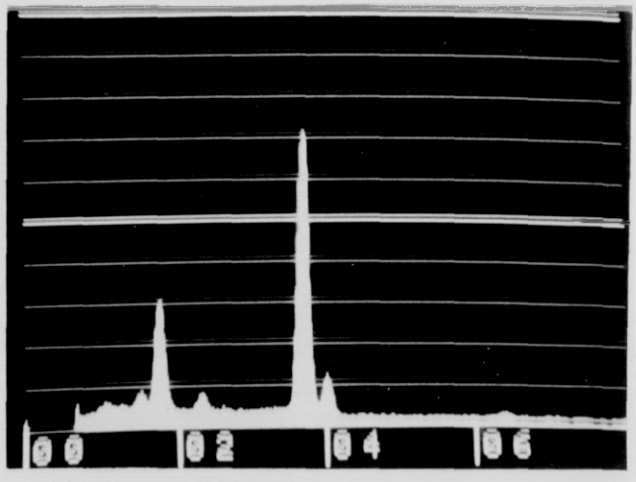


Figure 5.12 Micrographs of the 1 day leached Chemfix sample and EDAX analysis.

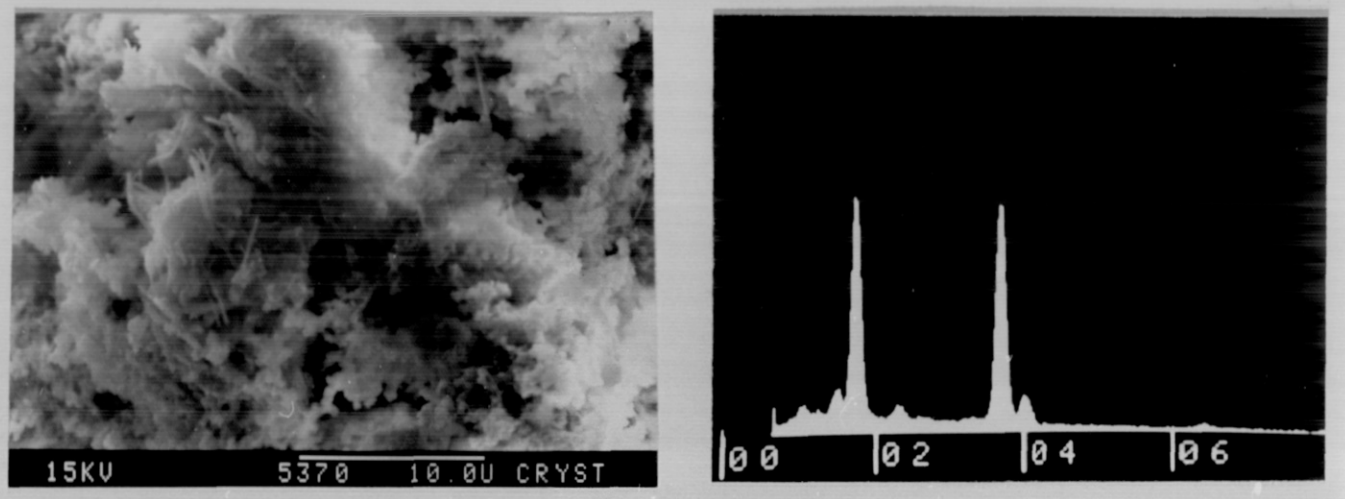


Figure 5.13 Micrographs of the 3 day leached Chemfix sample and EDAX analysis.

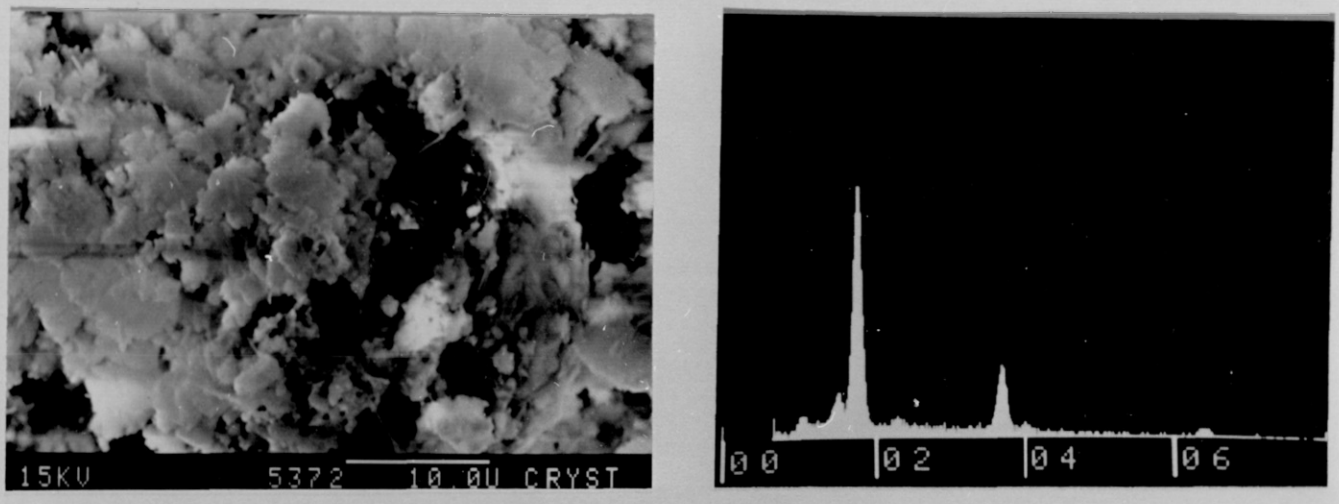


Figure 5.14 Micrographs of the 4 day leached Chemfix sample and EDAX analysis.

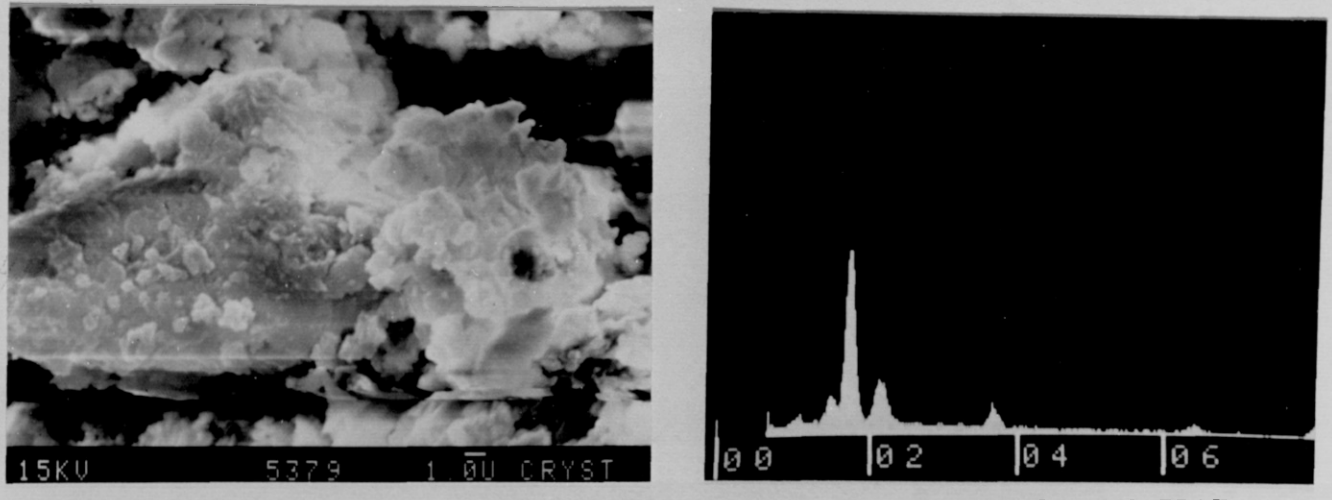
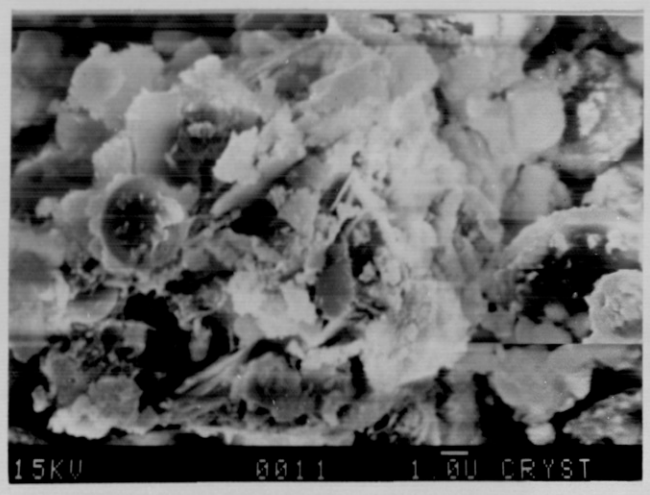


Figure 5.15 Micrographs of the 5 day leached Chemfix sample and EDAX analysis.



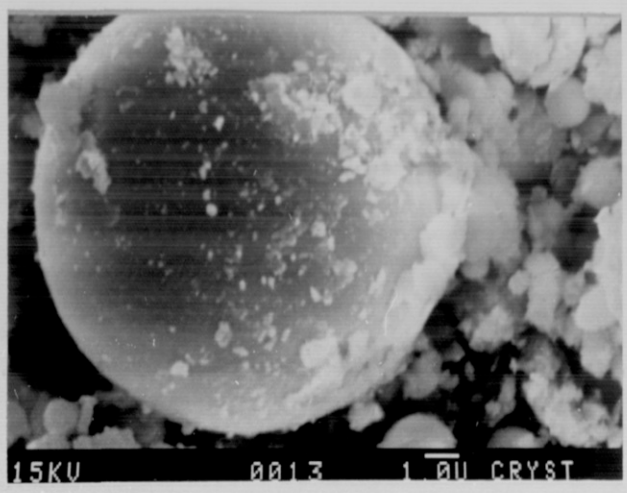


Figure 5.16 Micrographs of the pre-leached Sealosafe sample.

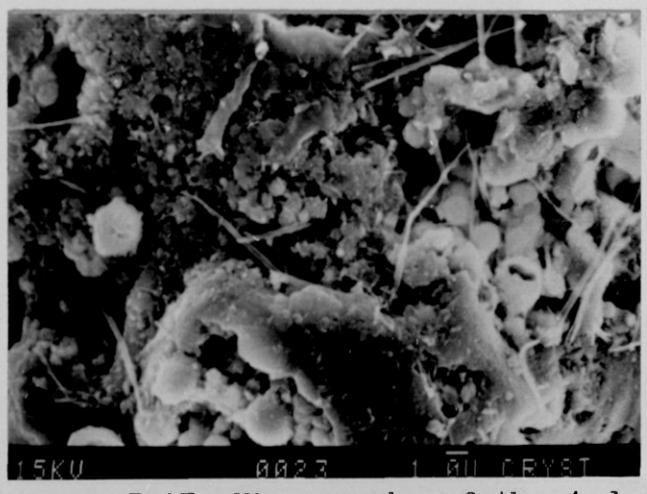
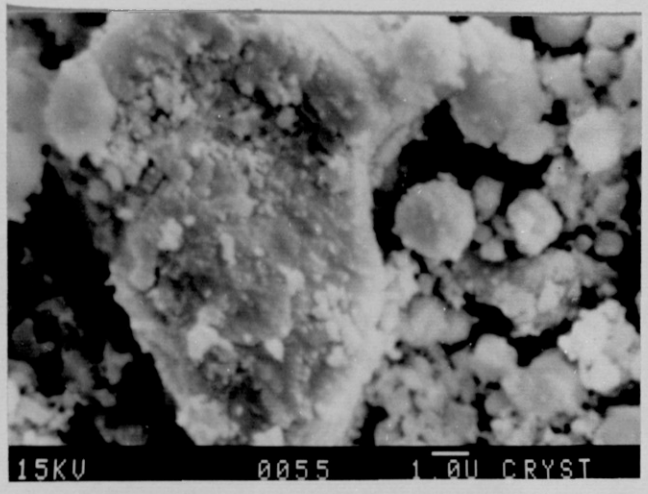


Figure 5.17 Micrographs of the 1 day leached Sealosafe sample.



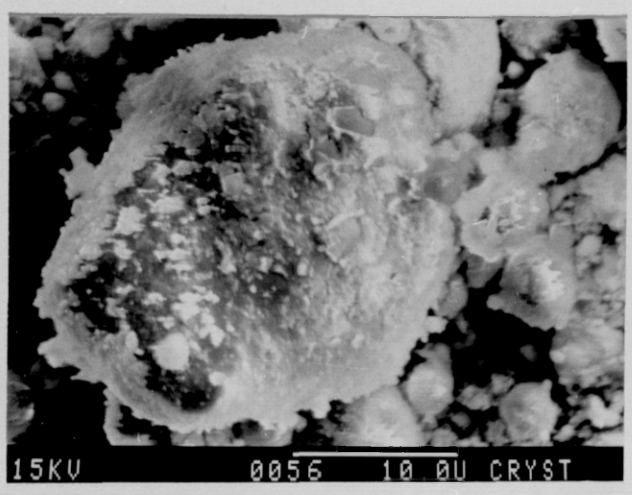


Figure 5.18 Micrographs of the 2 day leached Sealosafe sample.

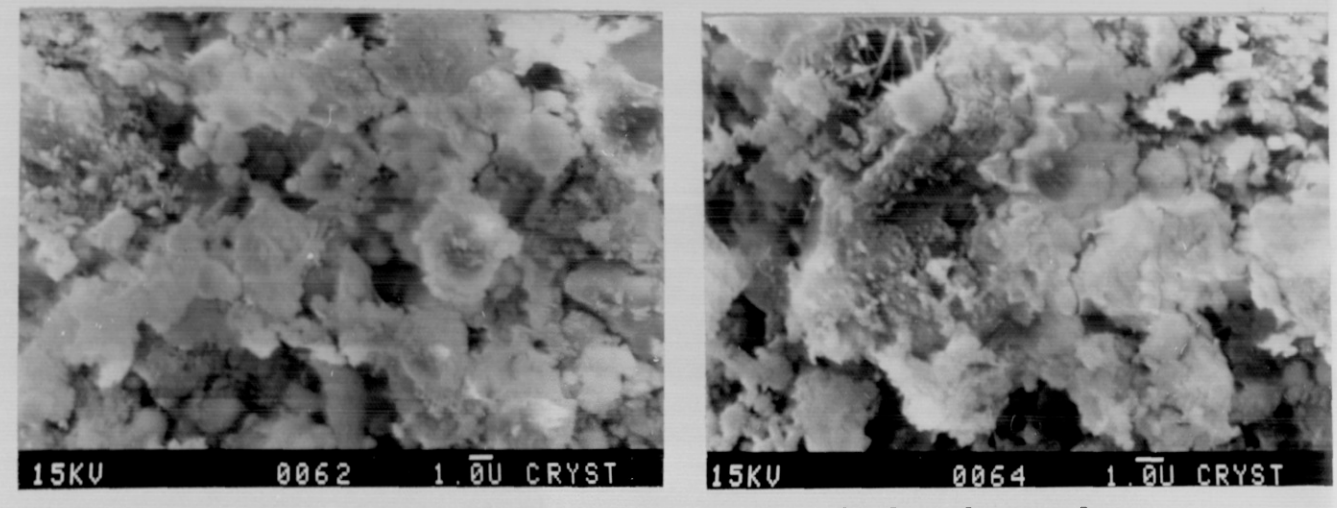


Figure 5.19 Micrographs of the 3 day leached Sealosafe sample.

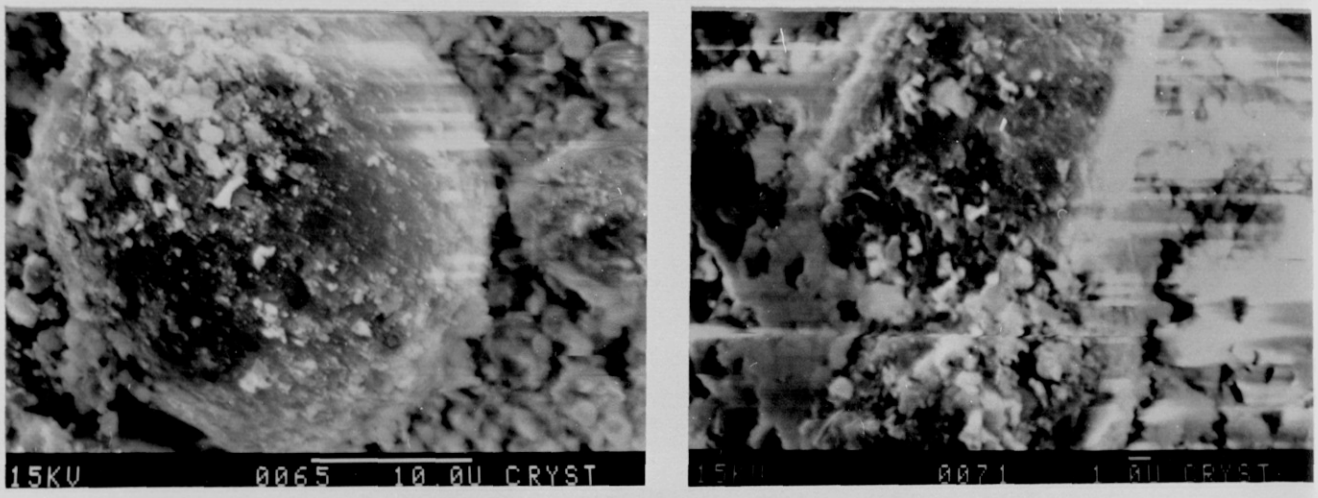


Figure 5.20 Micrographs of the 4 day leached Sealosafe sample.

undergone considerable leaching with an increased area of the gel type structure visible with high Si counts. In addition, a relatively small amount of the AFt phase was visible as compared to the 1 day sample. The EDAX analysis demonstrated that relatively large amounts of Ca had been leached from the matrix and that the approximate amounts of Ca and Si were similar in the sample.

After 4 day's leaching the sample had been modified to a further extent by the hydrolysis action of the leaching fluid. In Figure 5.14 rods of the AFt phase were no longer identifiable and the hydration products that were on the cement grain had been hydrolysed leaving a smooth surface with a semi-gel type structure. This structure had a high Si content as shown in the EDAX analysis.

The 5 day leached sample (Figure 5.15) shows that the structure of the cement grains had been destroyed leaving a mass of gel and amorphous structures. The Si peak from the EDAX analysis was demonstrably larger than the Ca peak.

Similar changes in the microstructure took place in the Sealosafe sample. Figure 5.16 shows that the 28 days OPC/PFA matrix had hydrated to give C-S-H, C-H, AFt and AFm. The PFA particles displayed signs of reaction with hydration products covering some of the grains. The EDAX analysis on the cement particles gave a Ca:Si ratio of 10:5 and on the PFA particles, a ratio of 2.5:10. It has to be pointed out that whilst the source of Ca was predominantly from cement the Si content derived from both cement and PFA. Micrographs of the 1, 2, 3 and 4 days leached samples are shown in Figures 5.17 to 5.20.

Figure 5.17 shows the 1 day leached sample indicating the effect of the leaching fluid on the PFA/OPC matrix. Calcium silicate hydrate was still observable but its structure was deformed. The AFt phase was identifiable both on the cement

and PFA particles. The surface of the cement particles was evidently etched although some hydration products were observed. The surface structure of the PFA particles was not significantly different from the pre-leached sample.

The 2 and 3 day leached samples are shown in Figures 5.18 and 5.19. Continued hydrolysis of the leaching fluid removed more C-S-H from the matrix, but ettringite (AFt) was still identifiable. However, no significant alteration was induced on the PFA surface.

The leached sample after 4 days is shown in Figure 5.20. No C-S-H was identifiable. The AFt phase had also disappeared leaving a massive gel product with high Si content.

5.2.3 Discussion

The dynamic leaching test was designed to provide an accelerated leaching environment in order to assess the capability of different materials to chemically stabilise selected pollutants. The crushed test procedure was designed to reduce - as far as possible - the physical barrier between the leaching fluid and the pollutants.

The results from the dynamic tests carried out on Chemfix and Sealosafe revealed that the retention of metals was of the order of Cd > Zn > Hg. This was probably due to the highly alkaline environment of the cement and PFA/OPC matrices rendering most of the Zn and Cd insoluble as complex hydroxides. The solubility products of $Zn(OH)_2$ and $Cd(OH)_2$ are 10^{-11} and 10^{-14} respectively. However $Zn(OH)_2$ is more soluble than would be expected from this constant owing to the equilibrium: (35)

$$Zn(OH)_2\ (s) \;=\; Zn(OH)_2\ (aq) \quad k = 10^{-6} \qquad (5)$$

Furthermore, $Zn(OH)_2$, being amphoteric by nature, readily redissolves in an excess alkaline environment to give zincate ions, probably of the type $(Zn(OH)_3(H_2O))^-$ or $(Zn(OH)_4)^{2-}$. This explains the higher concentration of Zn than Cd in both processes. Mercury, on the other hand, was incapable of forming a hydroxide and instead formed a partially soluble oxide in the alkaline environment (solubility 10^{-3} to 10^{-4} moll $^{-1}$ in water) which was readily leached from the matrices.

The use of two Hg salts in the study displayed the different mechanisms by which the stabilising agent reacts with the metal carrying different ligands. In the Chemfix sample, the $Hg(NO_3)_2$-dosed sample gave a much lower leachate concentration than the $HgCl_2$-dosed sample. This was probably due to the difference in chemical characteristics of $Hg(NO_3)_2$ and $HgCl_2$. Mercuric nitrate is largely ionic in nature and the main species in solution are $Hg(NO_3)_2$, $HgNO_3^+$ and Hg^{2+} together with the red precipitate of HgO due to hydrolysis. The retention of these species in an alkaline environment would probably be the result of the formation of HgO. Mercuric chloride, however, is largely covalent in nature and thus the extent of its reaction with the hydroxyl ion in solution was significantly less than that of the ionic species such as $Hg(NO_3)_2$.

This contrast in the retention of $HgCl_2$ and $Hg(NO_3)_2$ in Chemfix was not observed in Sealosafe, indicating that Hg was retained by different retention mechanisms in the cement/PFA blended system.

The retention of phenol by both processes was minimal. After 5 days' leaching 62% and 57% of all phenol in the Chemfix and Sealosafe samples respectively had been leached from the matrices. This indicates that cement, PFA and sodium silicate were incapable of chemically stabilising this organic pollutant.

Comparing the concentration of all three metals in Chemfix and Sealosafe, both processes produced low Cd concentrations. Sealosafe produced a lower Zn leachate concentration than Chemfix. This was probably because whilst the alkaline environment of cement immobilised the precipitated Zn in the form of a complex hydroxide, the pH in the Sealosafe leachate was not high enough to resolubilise the amphoteric Zn due to the replacement of part of the cement by non-alkaline PFA. In the Hg-dosed samples, Sealosafe released a much lower leachate concentration than Chemfix. This can be partly accounted for by the use of a higher solid content in the Sealosafe formulation. It should be noted that although both samples were crushed to pass through a 2 mm sieve in the dynamic test, the Sealosafe sample was still stronger in terms of strength and physical integrity than the Chemfix sample because of the much lower water to solid ratio (W/S) used. It is believed that the particle size and reduced surface area of the Sealosafe sample partially accounted for the lower leachate concentration. Chemical stabilisation of Hg by the PFA is an additional explanation of the reduced leachability. Thus, the leaching test results indicate that although the chemical stabilisation of $HgCl_2$ by cement was low, incorporation of PFA into the cement matrix increased the degree of stabilisation.

Static leaching tests, however, produced a rather different picture in the leachability of these three metals in both the Chemfix and Sealosafe matrices. Leachate concentrations of Zn and Cd from the Chemfix samples were both higher than, but Hg lower than the results obtained from the dynamic test.

The low pH encountered in the static test resulted from the insufficient dissolution of lime from the solidified mass. This was in contrast to the high pH environment produced by the physical breakdown of the cementitious matrix in the dynamic test.

In the static test, less surface area of the solidified material was exposed to leaching than in the dynamic test. Thus Zn and Cd which would have been rendered insoluble in the high pH environment of the dynamic test were subjected to leaching in the acidic environment of the static test. This was reflected by the close correlation between metal concentration and the pH values of the solution. It also provides an explanation as to why more Zn and Cd were released from the Sealosafe sample than from the Chemfix sample.

The static test resulted in lower Hg release from the Chemfix sample than did the dynamic test - a phenomenon contrary to that for Zn and Cd. This was due to the different mechanisms in operation for the retention of these metals in the solidified matrices. In the static leaching test where there was less Hg exposed to leaching, the near neutral chemical environment did not result in severe physical breakdown of the matrix. The Hg concentration of the Sealosafe sample in the static test procedure was higher than that in the dynamic test procedure. This was principally due to the physical breakdown of the weak solidified mass in the acidic environment by the hydrolysis action of acetic acid. This physical breakdown of the matrix was noticed as early as after 2 days' leaching. It was also reflected in the percentage of Ca released from the solidfied material which gave an indication of the dissolution of the matrices. 5.1% and 1.8% of the total Ca content was released from the Sealosafe and Chemfix sample respectively after 2 days. Therefore, the Sealosafe solidifed mass had undergone a considerable physical breakdown in the course of the leaching period. This physical breakdown exposed a much larger amount of Hg to the acidic leaching fluid, resulting in an increase in the Hg concentration in solution. Although this physical effect was also encountered in the dynamic test, the highly alkaline chemical environment in that case rendered most of the Hg insoluble.

The above interpretation of the results shows that all three metals were immobilised in the cementitious matrices by both physical and chemical mechanisms. However, chemical fixation was the main operative mechanism for retention of Zn and Cd and physical encapsulation the chief mechanism for the stabilisation of Hg.

Extended leaching studies on two Chemfix and Sealosafe samples (using different leaching fluids) produced more information regarding the mechanism of fixation and leaching.

As can be seen from Table 5.20 the breakthrough in Zn and Hg leachate concentrations occurred after approximately 55% of Ca was leached from the solidified product. The rate of Ca leached has also been shown to be dependent on the buffering index of the leaching fluids.

The initial pH of the leachate for all the leaching fluid used was high due to the alkalinity of the solidified product. The pH decreased gradually throughout the leaching experiment. The rate for such decrease in pH was highest with 0.5 M and followed by 0.3 and 0.15 M buffered acetic acid solution used. The data from the experiment seems to suggest that the breakthrough point for all three leaching fluids occurred only after the pH had dropped below 7. The significance of such a critical pH value is still unknown but it seems to correlate well with the consistence in the amount of Ca released from the matrix.

The use of SEM has elucidated in what form this leaching fluid acts on the cemenetitious material. In a pre-leached Chemfix sample with the simulated metal waste, normal hydration products of calcium silicate hydrates (C-S-H) calcium hydroxide (C-H), calcium aluminate hydrates (AFt and AFm phases) and unhydrated cement grains together with calcium-silicate gel were observed.

The SEM study showed that the most easily hydrolysed structure in the Chemfix was the C-S-H phase which was no longer observable after the 2 day' leaching period. However Zn and Hg leachate concentrations did not change appreciably indicating that C-S-H was unlikely to be involved in the fixation mechanisms.

Further leaching hydrolysed the matrix and was associated with continued Ca removal. Possible sources of Ca are AFt and AFm, calcium-silicate gel, calcium hydroxide and unhydrated cement grains. After 3 days, less AFt (the most identifiable phase) and AFm could be seen, although there was an increase in the calcium-silicate gel type structures. Concentrations of Si and Ca were similar at this stage. However, the AFt phase was no longer visible after the 5 day leaching period and this led to the subsequent dramatic rise in Zn and Hg leachate concentrations. This indicates that the disappearance of this phase marked the beginning of breakdown of the structures that "fix" the metal though there was no direct evidence to prove that this phase was directly responsible for such fixation.

The results from the Sealosafe matrix also showed that the hydrolysis action of acetic acid continued to remove Ca from the solidified material. This resulted in a largely gel-like product with a high Si content until breakthrough occurred. The most dominant structure, ettringite, was observed to be the breakthrough indicator. After this phase was hydrolysed the cementitious matrix had been sufficiently broken down for the fixed waste material to be easily leached. This occurred after approximately 55% of Ca removal. As noted previously, the degree of chemical fixation as opposed to physical entrapment was greater for Zn than Hg. It is evident from this study that these processes occurred in conjunction with each other as demonstrated by the simultaneous rise in Zn and Hg leachate concentrations.

Extended leaching of both Chemfix and Sealosafe matrices resulted in a drastic release of metals after a similar percentage of Ca was released from the matrices. This illustrates the important role of Ca in the stabilisation of both metals. However, this phenomenon occurred after a different number of elutions for the two matrices because of the different Ca contents in the solidified materials. Replacing cement by PFA lowered the total amount of Ca in the matrix as PFA contains little Ca. This led to an earlier breakthrough period in the Sealosafe matrix.

The leaching test results also demonstrated that the cement based stabilisation/solidification process was unable to retain phenol. High leach rates of phenol were obtained both for the Chemfix and Sealosafe processes. This was due to the inability of cement, PFA and sodium silicate to react with phenol, either through sorption or formation of insoluble compounds.

The fact that the two manganese salts (Mn^{2+} and MnO_4^-) displayed different leaching characteristics showed that ionic interactions between the cementitious matrices and the pollutant ions played an important role in the immobilisation. Positively charged ions such as Mn^{2+} were able to react with the -ve charged hydroxyl molecules forming insoluble hydroxide. The -ve charged MnO_4^- ion, however, was unable to react with the hydroxyl ions. Although the actual chemical reaction involved is believed to be more complex (Section 4) this simple mechanism explains the difference in the leach rate of Mn^{2+} and MnO_4^-.

5.3 Compressive Strength Measurement

One of the aims of the stabilisation/solidification process is to provide a waste form with adequate physical strength for easy handling. The possibility of using the solidified product as fill for land reclamination or other engineering purposes also requires adequate strength development. There are many methods for measuring the strength of a cementitious material including tensile, flexural, shear, penetration and compressive strength measurements. However the simplest and most reliable method, giving a direct indication of strength for the purpose of landfill conditions, is the compressive strength test.

5.3.1 Method

Physical strength measurements were performed in the compression mode to investigate the effect of heavy metals and other parameters on strength.

Three series of experiments were designed to determine:

(i) The effect of water/cement ratio (W/C) and silicate content on the strength of the Chemfix product.

(ii) The effect of W/C, and PFA/OPC ratio on the strength of Sealosafe product. The effect of adding sodium silicate to this PFA/OPC blended system was also investigated.

(iii) The effect of heavy metals on the strength development of Chemfix and Sealosafe products.

The effect of sodium silicate on the setting rate which indicates the initial thickening (setting) of the slurries was measured by a pocket penetrometer. Mixes prepared for the study are presented in Tables 5.21 to 5.23.

Table 5.21 Strength data of Chemfix without metal addition

Mix	W/C	Si/C	Strength (Nmm^{-2}) 1 day	7 day	28 day
1	0.32	-	17.89	48.15	61.50
2	0.70	0.04	3.30	10.54	15.87
3	0.875	0.05	2.01	6.41	9.44
4	1.00	0.04	0.97	3.73	5.65
5	1.00	0.05	0.99	3.12	5.59
6	1.00	0.06	1.23	5.09	7.18
7	1.00	0.08*	1.40	4.54	6.87

*Si/C = 0.08 is the maximum amount of sodium silicate added to produce a workable paste for the given W/C.

Table 5.22 Strength data of Chemfix/Sealosafe without metal addition

Mix	PFA/OPC	W/S[+]	Si/S	Strength (Nmm^{-2})			
				1 day	7 day	28 day	90 day
8	3.0	0.5	-	0.57	2.35	4.03	12.09
9	3.0	1.0	0.06	0.15	0.23	0.62	1.25
10	3.0	1.0	0.08	0.29	0.57	1.29	2.24
11	3.0	1.0	0.10	0.28	0.81	1.54	2.22
12	1.0	1.0	0.06	0.32	0.80	1.69	3.11
13	0.33	1.0	0.06	0.58	2.16	3.28	6.20
14	0.33	1.0	0.08	1.10	3.03	4.64	7.05
15	0.33	1.0	0.10	1.32	3.02	4.71	7.16

[+]S = PFA + OPC

Table 5.23 Strength data of Chemfix and Sealosafe with metal addition

Mix	Additive	Strength (Nmm^{-2}) 1 day	7 day	28 day
		Chemfix (W/C = 1.0 Si/C = 0.05)		
5	-	0.99	3.12	5.59
16	2% Zn	n.d.	n.d.	2.95
17	2% $HgCl_2$	1.34	4.92	6.02
18	2% $Hg(NO_3)_2$	0.52	3.49	5.04
19	2% Cd	0.27	1.70	3.61
		Sealosafe (PFA/OPC = 3.0 W/S = 0.5)		
8	-	0.57	2.35	4.03
20	2% Zn	n.d.	n.d.	0.22
21	2% $HgCl_2$	0.57	-	5.42
22	2% $Hg(NO_3)_2$	0.48	2.16	4.00
23	2% Cd	0.20	1.21	2.68

Table 5.24 Initial strength data measured by pocket penetrometer

Mix	W/C	Si/C	Penetration strength (psi) 3 h	4 h	6 h	7 h
1	0.32	-	>700	>700	>700	>700
2	0.70	0.04	100	270	700	700
3	0.875	0.05	0	100	360	540
4	1.00	0.04	0	15	160	400
6	1.00	0.06	30	100	280	520
7	1.00	0.08	100	124	400	540

Mixes were prepared first by mixing water/waste solutions and cement/PFA in an ordinary rotating pan concrete mixer with paddles to produce homogenous slurries. This was followed by the addition of 40% sodium silicate solution as required and the slurries were further agitated to produce homogeneous pastes. The resulting pastes were cast into 51 mm cube moulds in two layers and were compacted using a vibrating table.

Figure 5.21 Pocket penetrometer for measurement of initial set rate.

The cubes so prepared were allowed to cure at room temperature. After 24 hours the cubes were removed from the moulds. Except for those to be tested after one day, the cubes were then submerged in a water tank until immediately prior to compressive strength testing. Compressive strengths were tested at intervals of 1, 7 and 28 days using a standard compression test instrument conforming to BS 4550. The setting rate which indicates the initial thickening of the slurries was measured by a pocket penetrometer (Figure 5.21).

5.3.2 Results

Results of the compressive strength measurements for series i, ii and iii are presented in Tables 5.21, 5.22 and 5.23 respectively. Table 5.24 shows the initial strength data measured by a pocket penetrometer for series i.

Graphical presentation of the relationship between strength on W/C and Si/C, PFA/OPC and Si/S are presented in Figures 5.22 to 5.26.

Figure 5.22 illustrates that the compressive strength of the solidified products decreased exponentially with W/C or W/S ratios. This illustrates that the W/C ratio is the most important parameter in governing strength. The effect of different PFA/OPC ratios on strength is given in Figure 5.23 and shows that compressive strength decreased with increase in PFA content.

The effect of adding sodium silicate on the initial stength development of Chemfix and Sealosafe are illustrated in Figures 5.24, 5.25 and 5.26. The initial stength of all samples increased with Si/C ratio but the silicate contributed little to the final strength of the Chemfix sample.

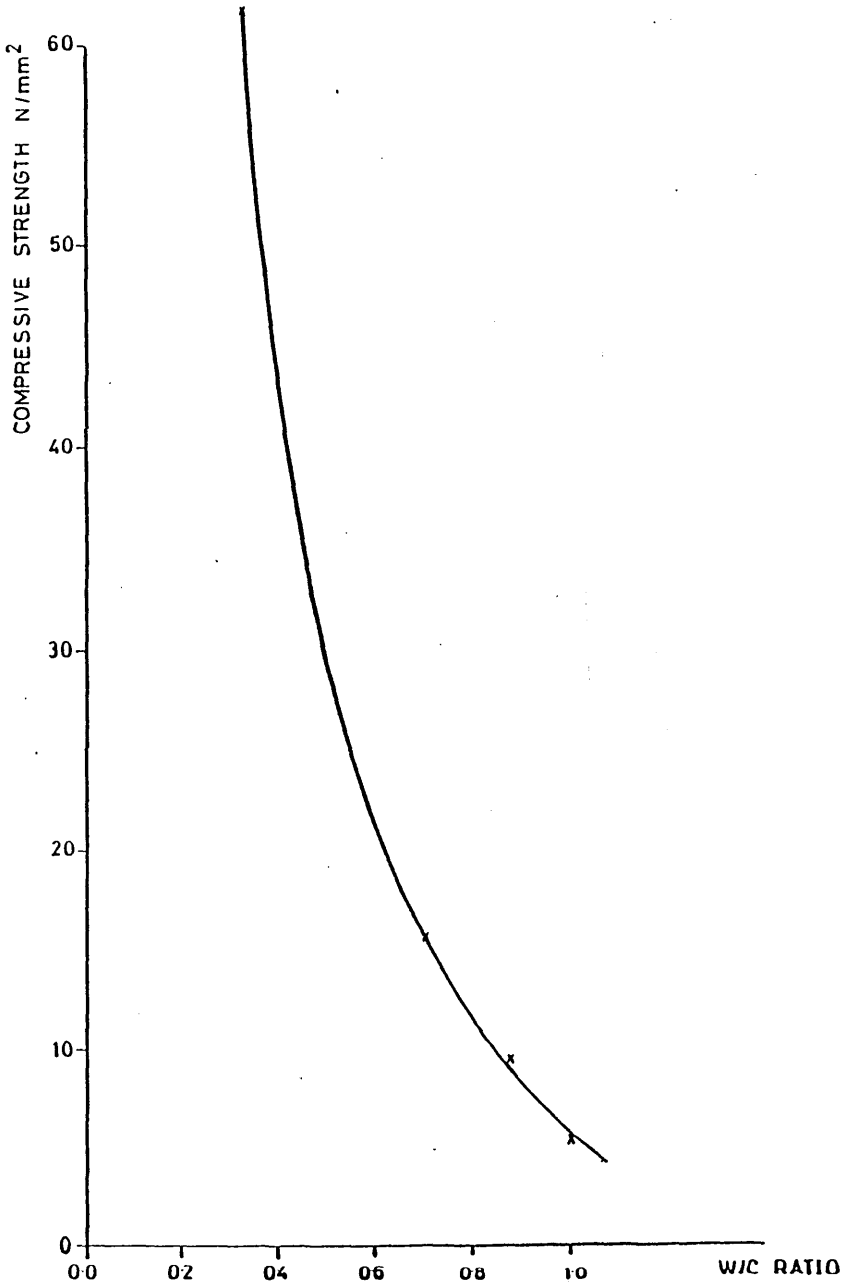


Figure 5.22 Compressive strength v. W/C for Chemfix sample at 28 days.

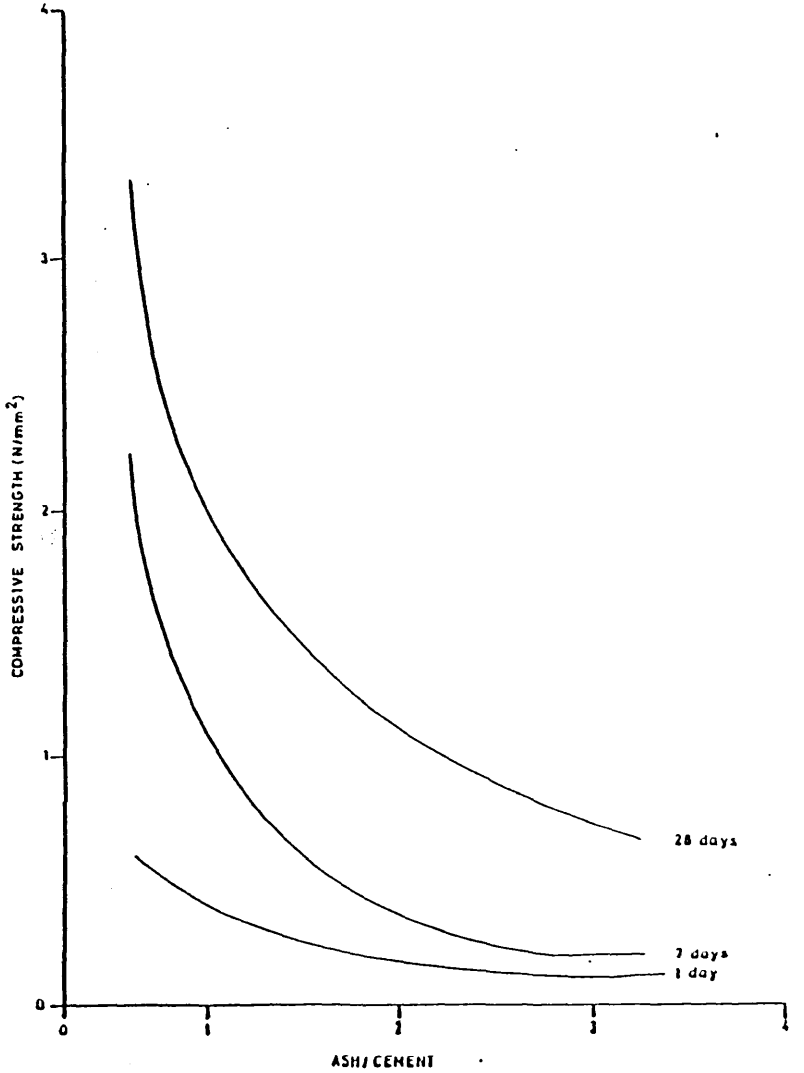


Figure 5.23 Compressive strength v. ash/cement for Sealosafe samples.

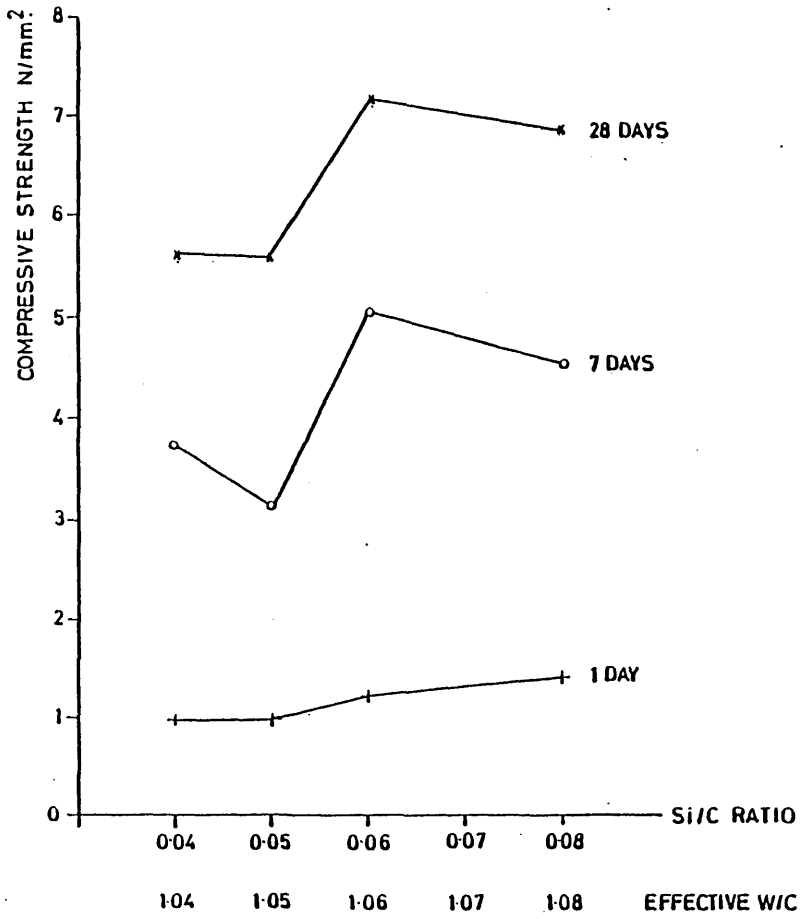


Figure 5.24 Compressive strength v. silicate/cement and effective water/cement ratios.

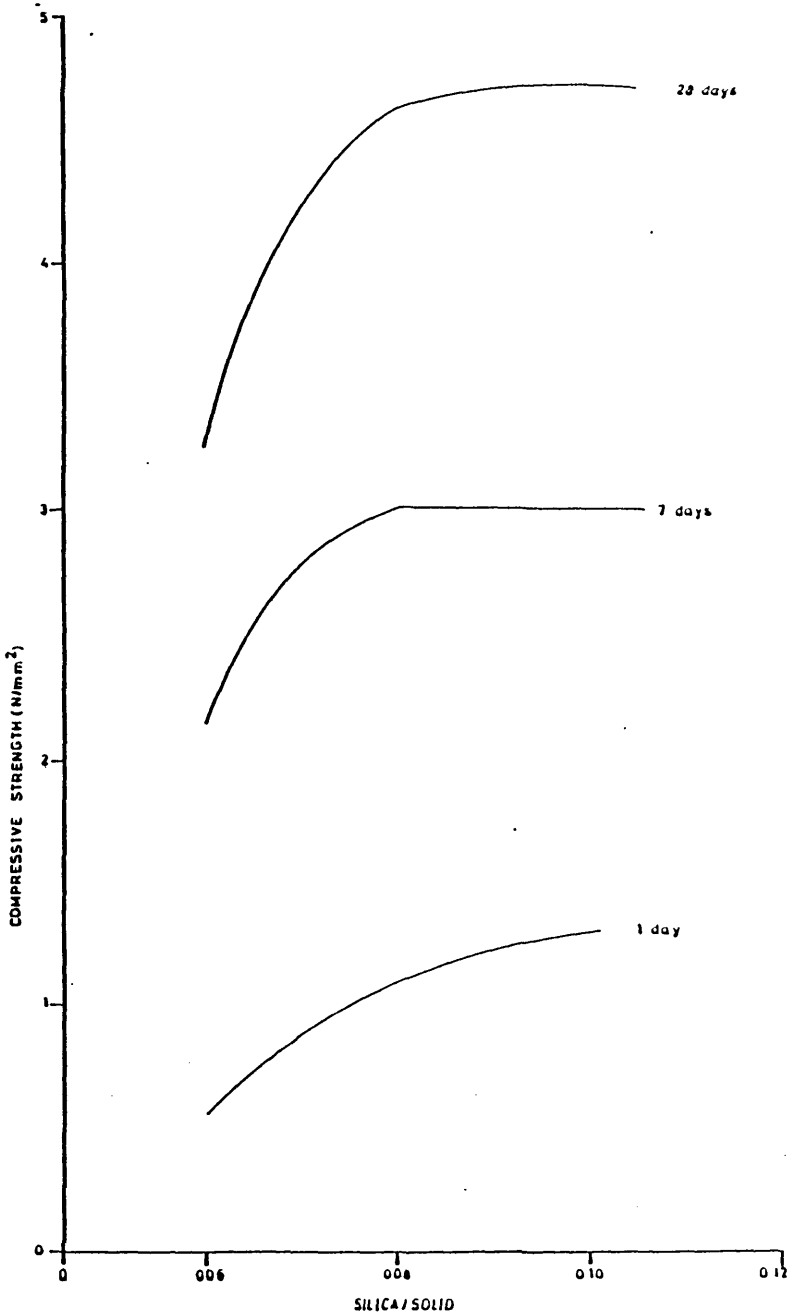


Figure 5.25 Compressive strength v. silica/solid for sample with ash/cement = 0.33

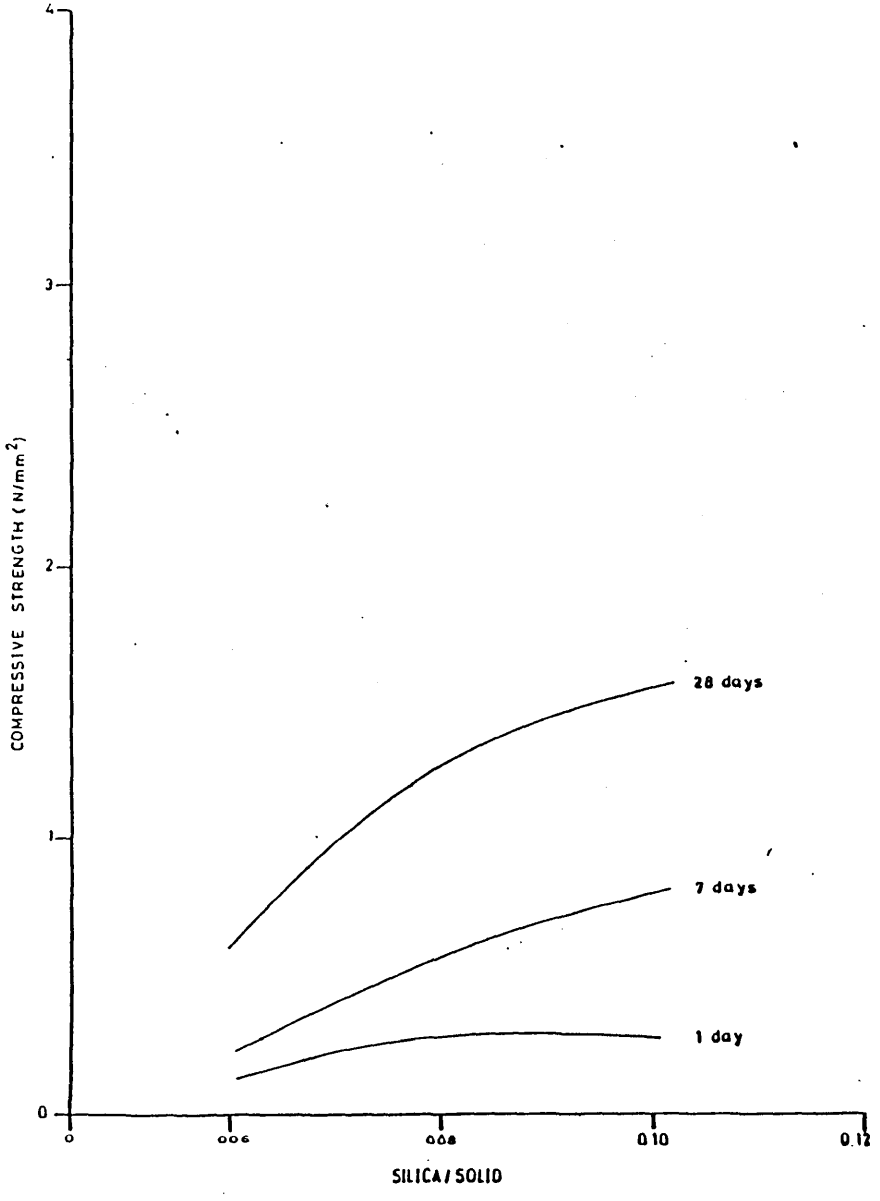


Figure 5.26 Compressive strength v. silica/solid for sample with ash/cement = 3.0

The effects of adding metal-containing simulated waste to the cementitious mixes, can be illustrated by the strength values presented in Table 5.23 . A similar trend was observed for both solidification processes. In both, the strength values were in the order of

$$Zn < Cd < Hg(NO_3)_2 < Water < HgCl_2$$

5.3.3 Discussion

Mixes 1 and 2 exhibited the highest initial strength due to the low W/C ratios (0.32 and 0.7 respectively). The initial strength development of mixes 4, 6 and 7 which have the same W/C ratio show that the initial strengh increased with Si/C ratios. This effect was confirmed by the one-day strength in Figure 5.24. In comparing the initial strength of mix 3 with that of mixes 6 and 7, it is interesting to note that mix 3, which has a lower W/C and Si/C, gave a very low initial strength value at 3 hours compared to mixes 6 and 7. However the strength gradually built up to exceed that of mixes 6 and 7 after 7 hours. This result was confirmed by the strength values obtained after 1, 7 and 28 days (Table 5.21). The effect of the Si/C ratio on strength development for mixes with the same W/C ratio (mixes 4, 5, 6 and 7) is illustrated in Figure 5.24. After 1 day, compressive strength increased with increasing Si/C ratio (i.e. silicate content). However the role of sodium silicate at 7 and 28 days was not as clear. There appears to be an optimum dosage for sodium silicate corresponding to Si/C = 0.06 for W/C ratio of 1.00. This can be explained by the change in effective W/C ratio on the addition of an aqueous solution of sodium silicate, i.e. the strength improvement due to the addition of sodium silicate was counterbalanced by the reduction of strength due to the increased W/C ratio.

Figures 5.25 and 5.26 illustrate the effect of sodium silicate content on strength with different PFA/OPC ratios. Generally, the addition of sodium silicate increased the strength of the Sealosafe mixes. For the samples with PFA/OPC = 0.33 the greatest increase in strength was detected at 7 days with very little improvement from 7 days to 28 days. This contrasted with results from the samples containing PFA/OPC = 3.0 in which there was progressive improvement over the whole 28 days.

It should be noted, however, that the strength values of the mixes with PFA/OPC = 0.33 were higher than those for the samples containing PFA/OPC = 3.0. This was so at all curing times and for all silicate contents. This showed that by replacing cement with PFA in the Sealosafe system the strength of the solidifed product was reduced. It also showed that PFA did not significantly contribute to the strength development - at least in the mixes with a high W/S ratio (i.e. 1).

The contribution of sodium silicate to the Sealosafe system was probably different to that of the Chemfix or other similar systems having a high cement content. When alkaline sodium silicate was added to PFA/OPC the Ca concentration in solution was greatly depressed - possibly by the common ion effect (with NaOH) but principally by the formation of insoluble calcium silicate gel:

$$Na_2X + Ca(OH)_2 \longrightarrow CaX + 2NaOH \qquad (10)$$

X denotes the monomeric or polymeric silic acid radical. The availability of NaOH accelerated the attack on the PFA particle's silica and alumina surface to form soluble silicate and aluminate. Since the PFA particle surface was acidic, eventually neutralisation of the free alkali by reaction with PFA reduced the pH and permitted the Ca ion from the cement to go into solution. This led to the formation of calcium silicate and calcium aluminate hydrates near the Si- and Al-rich PFA particle surface. These reactions were kinetically

slow and took a considerable time to occur, particularly in systems with a low cement content.

In contrast, in the pure Chemfix (cement/sodium silicate) system, calcium-silicate gel was precipitated immediately after the addition of sodium silicate. The gel formed differed from the calcium silicate hydrates normally found in cement hydration as the latter formed under specific conditions through a different mechanism. The elevated alkali content, however, continued to suppress the Ca within cement from going into solution. The further precipitation of calcium silicate hydrate in cement hydration was retarded. The overall effect of the addition of sodium silicate was to produce a gel which accelerated the setting but contributed little to the long term strength. This result is in accord with the findings of Nelson and Young (63).

The fact that mixes with a higher PFA content showed a progressive increase in strength with increase in silicate content indicated that this reaction between Ca and PFA proceeded over an extended period. In mixes with a lower PFA content this reaction terminated after 7 days as little improvement of strength was detected after further additions of sodium silicate.

Comparing the strength values of the Chemfix and Sealosafe samples, Chemfix samples had higher strength values. It should be noted that a W/C = 1 and a 100% cement content were used in all Chemfix mixes whereas the Sealosafe samples were made up with a W/S = 0.5 and 33% cement content. This fact illustrates that cement content was the principal factor governing strength (at least up to 28 days values) in the solidification systems studied. The low strength values encountered in the Sealosafe system were probably due to the high percentage (64%) of cement that was replaced by PFA. In normal engineering practice, 25-30% cement was replaced by PFA and coupled with a much lower W/S produced concrete with comparable strength results to those obtained with normal OPC concrete.

The fact that the Zn-dosed samples in both solidification systems did not give any determinable value even at 7 days demonstrated that the early hydration reaction was seriously retarded. However, the material was able to solidify (i.e. form an aggregate with definite shape) and this was due to the gelling action resulting from Zn reacting with cement or PFA, and the calcium silicate gel formed in the cement/silicate system.

Cadmium retarded the strength development of both Chemfix and Sealosafe. The extent of such retardation was less than Zn. This demonstrates the different effects of Zn and Cd on the hydration of cement and cement/PFA blended systems despite their similar chemical properties.

Although $Hg(NO_3)_2$-dosed systems produced strength values less than that of the control, the retardaton was small when compared to Zn and Cd-dosed samples. Mercuric chloride, on the other hand, improved the strength development in both solidification processes, probably due to the acceleration effect of chloride on the hydration of cement (64).

The fact that both Hg salts did not significantly retard the strength developement showed that the hydration of cement and PFA/OPC blended systems were not inhibited by Hg.

The similar trend in the way in which different metal solutions affected the Chemfix and Sealosafe processses shows that similar mechanisms were operating in affecting the strength development of both cementitious matrices.

5.4 Permeability Measurement

The permeability of a solidified waste to water (or leaching fluid encountered in landfill environment) is one of the most important properties of the solidified material and governs two interrelated properties namely, durability and leachability. Durability addresses the long term stability of the treated material and leachability indicates the amount of pollutant mobilised with respect to time.

There is no standard procedure for measuring the permeability of solidified materials. Recent permeability data submitted by companies marketing stabilisation/solidification processes (32) makes no mention of the method adopted, curing regime used, ratio of waste additives being tested. Therefore the end product reflects the initial variation in experimental parameters and in consequence, comparision of results is impossible.

In engineering or hydrogeology, water permeability measurements using either a triaxial cell or hydraulic head apparatus are standard test methods. However, on application to cementitious systems three disadvantages arise. First, the time taken to achieve steady flow regime is extensive (8-10 days (65)). Second, the micro-structure of the cementitious matrix may be changed during measurement due to further hydration. Third, the effect of leaching of cementitious materials and/or encapsulated pollutant is enhanced which would also modify the flow regime of water through the matrix.

Gas permeability measurement is devised to overcome these difficulties although at present it has its inherent limitations; for example, there is no established relationship between the gas and water permeabilities though the latter is the more important parameter in affecting the properties of solidified materials. However, with a relatively fast rate of measurement (hours, instead of days/weeks), improved

reproducibility and a true indication of the micro-structural property for gas flow, the gas permeability technique can serve to provide a quick and straightforward indication of the physical quality of the solidified material.

The technique utilises a combination of Darcy's Law and the Poiseuille Equation for the determination of the permeability coefficient K which can be expressed as (66).

$$K = \frac{2 q l \nu P}{(P_2^2 - P_1^2)A} \quad \text{where} \qquad (11)$$

q = flow rate ($m^3 s^{-1}$)
l = thickness of specimen (m)
ν = viscosity of gas used (poise)
P_1 = outlet pressure (bar)
P_2 = inlet pressure (bar)
A = X-section area of specimen (m^2)

Take $\nu = 2.02 \times 10^{-4}$ poise for oxygen
$P_2 = 1$ bar

Then $$K = \frac{2 Q l \times 2.02 \times 10^{-16}}{(P_2^2 - P_1^2) A} \quad \text{where} \qquad (12)$$

Q = flow rate ($cm^3 s^{-1}$)

The unit of K is in m^2

K has a dimension of L^2 and is a measure of the intrinsic permeability of the porous medium. This intrinsic permeability can be interpreted approximately as the unique pore area governing the flow of fluid through the porous medium. It is governed by properties such as grain diameter, grain shape, porosity and pore size distribution of the porous medium (66). It differs from the hydraulic conductivity D which has a dimension of LT^{-1}. D depends on both the intrinsic properties and the characteristics of the fluid used for measurement.

It has been shown that K and D are related by the following (66).

$$D = K\frac{\gamma}{n}$$

where γ = specific weight of the fluid
n = viscosity of the fluid

For oxygen, at normal pressure and at 20°C

$$D = 6.5 \times 10^{5} K$$

Theoretically, hydraulic conductivity (D) for any fluid can be computed when the intrinsic permeability of the medium is known. However because the velocity of a gas layer in the immediate vicinity of the surface of the grains has a finite value - a phenomenon known as "gas slippage", the hydraulic conductivity of the porous medium computed from gas would overestimate the actual permeability to a liquid. However, the method was used to provide a quantitative assessment of the physical quality of the solidified materials.

5.4.1 Method

Mixes that have been made up for oxygen permeability measurement are presented in Table 5.25. System I simulated the Chemfix formulation using Ordinary Portland Cement (OPC) and sodium silicate solution. System II simulated the Sealosafe formulation which used Pulverised fuel ash (PFA) and OPC. Systems II, IV and V were intended to investigate the effect of incorporating solid particles in the form of sand and the variation of solution/cement/sand ratio and curing conditions on permeability.

As before, four heavy metal solutions were used to simulate industrial waste streams.

Table 5.25 Formulation and curing regimes of mixes for permeability measurement

System I	
Chemfix (OPC + sodium silicate solution)	
Solution/OPC	0.5
Silicate/OPC	0.02
curing = 14 days in water, 14 days at 20°C and 58% RH	
System II	
Chemfix + Sand (1)	
Solution/OPC	0.5
Silicate/OPC	0.02
Sand/OPC	1.0
curing = 14 days in water, 14 days at 20°C and 58% RH	
System III	
Sealosafe (OPC + PFA)	
PFA/OPC	3.0
Solution/Solid (PFA + OPC)	0.5
curing = 14 days in water, 14 days at 20°C and 58% RH	
System IV	
Sealosafe + Sand	
PFA/OPC	3.0
Solution/Solid (PFA + OPC)	0.5
Sand/Solid	1.0
curing = 14 days in water, 14 days at 20°C and 58% RH	
System V	
Chemfix + Sand (2)	
Solution/OPC	0.7
Silicate/OPC	0.02
Sand/OPC	3
curing = 28 days at 20°C and 58% RH	
Five mixes were made up for each system using	
a, water	
b, 2% $Zn(NO_3)_2$	
c, 2% $HgCl_2$	
d, 2% $Hg(NO_3)_2$	
e, 2% $Cd(NO_3)_2$	

The resulting pastes were cast (in two layers) into 50 x 150 mm diameter specially prepared cylindrical moulds (with cling-film at the base to prevent mould oil from penetrating the paste) and were compacted using a vibrating table. Cubes (51 mm) were prepared at the same time for compressive strength measurements. Mixes were allowed to cure at 20°C and 58% RH in a temperature controlled room. After 24 hours, the pastes were removed from the moulds and cured under conditions presented in Table 5.25. Tests were performed on duplicate samples.

Oxygen permeability measurements were carried out using a permeability cell (Figure 5.27). The cell consisted of a circular steel base and top plate. The sample was positioned horizontally using an annular steel cylinder and vertically by means of a perspex base and top plate. The use of a soft PVC collar (which was pressed against the cylindrical surface of the specimen via an inflated inner tube) maintained a gas tight seal.

Compressive strengths were measured using a standard compression test instrument conforming to BS 4550.

5.4.2 Results

The results of the permeability measurements are presented in Tables 5.26 to 5.28.

No permeability measurement was made for System I because all samples developed micro-cracks which invalidated the measured data. System II was abandoned because all samples were found to have permeability values below the detection limit of the instrument. For systems III, IV and V the following trends were revealed. The Chemfix samples had lower permeabilities than the Sealosafe samples. Zinc-dosed samples had the highest permeability value in all mixes examined followed by Cd, $Hg(NO_3)$ and $HgCl_2$-dosed samples in succession . Determination of weight loss due to drying showed that samples containing Zn

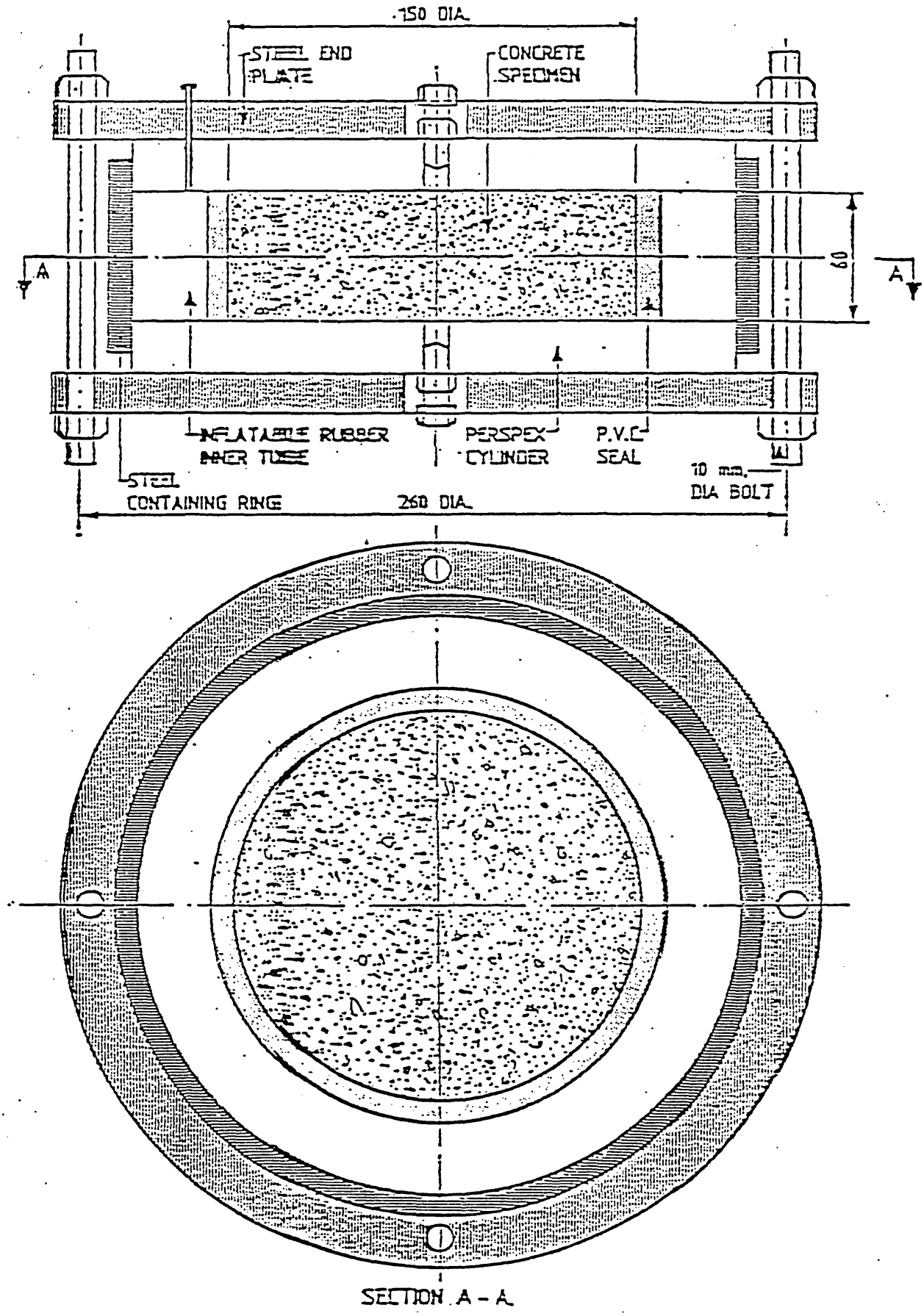


Figure 5.27 The oxygen permeability cell

Table 5.26 Permeability and compressive strength data of Series III (OPC + PFA)

Sample	K (m^2) at 28 days	Strength (Nmm^{-2}) 1 day	28 days	Density (gcm^{-3})	Moisture loss (%)
a, water	1.67×10^{-15}	0.57	4.03	1.33	20.1
b, Zn	2.03×10^{-14}	n.d.	0.22	1.24	25.9
c, $HgCl_2$	1.51×10^{-15}	0.57	5.42	1.34	21.3
d, $Hg(NO_3)_2$	3.75×10^{-15}	0.48	4.00	1.30	23
e, Cd	5.59×10^{-15}	0.20	2.68	1.35	21

Table 5.27 Permeability and compressive strength data of Series IV (OPC + PFA + Sand)

Sample	K (m^2) at 28 days	Strength (Nmm^{-2}) 1 day	28 days	Density (gcm^{-3})	Moisture loss (%)
a, water	2.23×10^{-15}	0.36	3.98	1.73	13.4
b, Zn	2.21×10^{-14}	n.d.	0.26	1.64	16.4
c, $HgCl_2$	1.09×10^{-15}	0.82	5.70	1.77	12.2
d, $Hg(NO_3)_2$	2.43×10^{-15}	0.69	4.12	1.72	12.2
e, Cd	4.62×10^{-15}	0.24	4.39	1.72	1.37

Table 5.28 Permeability and compressive strength data of Series IV (OPC + Silicate + Sand)

Sample	K (m^2) at 28 days	Strength (Nmm^{-2}) 7 days	Density (gcm^{-3})	Moisture loss (%)
a, water	4.97×10^{-16}	16.0	2.09	5.6
b, Zn	5.33×10^{-15}	1.64	1.99	10.8
c, $HgCl_2$	4.15×10^{-16}	16.6	2.12	5.9
d, $Hg(NO_3)_2$	4.00×10^{-16}	15.3	2.10	6.2
e, Cd	5.03×10^{-16}	14.6	2.08	6.2

lost more water than any other samples containing similar concentrations of contaminant. The remaining samples showed similar weight loss. Compressive strength measurements displayed a similar trend in which the values were in the ascending order: Zn < Cd < $Hg(NO_3)_2$ < water < $HgCl_2$.

5.4.3 Discussion

All the samples in System I (Chemfix) cracked after 14 days' curing period. The moisture loss (M.L.) was 4-5%. These cracks were believed to result from the stress induced by drying shrinkage common to cement pastes cured in a non-saturated environment. Consequently a series of mortar mixes were prepared to eliminate this problem. The fact that no flow was detected for any sample in System II showed that these samples had very low permeabilities at 28 days. This may have been because the pore spaces in the matrices were still saturated with water, inhibiting inflow of oxygen, or the permeabilities were below the detection limit of the cell used.

There was no visible cracks in the System III samples although the M.L. values were high. This indicated that the replacement of OPC by PFA reduced the stress induced by drying shrinkage. This was probably due to the ability of the PFA particle to relax some mechanical stress.

The addition of sand to the PFA/OPC blended system (System IV) reduced the M.L. There was no observable cracks detected in these samples.

System V was designed to overcome the difficulties encountered in Systems I and II and give valid permeability measurements. The reduction in cement content and increase in the proportion of sand in the mix restrained crack development. However, it also increased the permeability enabling flow to increase to a measureable value.

The metal solutions being investigated in Systems II, IV and V had a consistent effect on the permeability of the Chemfix and Sealosafe samples. Zinc-dosed samples had the highest permeability followed by Cd, $Hg(NO_3)_2$ and $HgCl_2$. Only the $HgCl_2$-dosed samples had a permeability value lower than that of the control. A similar trend was displayed in the compressive strength measurements at 28 days. It is probable that these two properties are inter-related and are governed by the similar micro-structure properties of the hydrated cementitious matrices.

The difference in the permeability of various metal dosed samples can be partly explained by considering the percentage of moisture loss. The Zn samples had the highest values but similar lower values were obtained for the other samples. These differences in moisture loss were related to the rate of drying and the degree of saturation of the pore space. However, the fact that the two Hg, the Cd and the control samples had similar rates of drying but produced different permeability values indicated that a mechanism other than that of drying was operative in governing the rate of oxygen flow through the sample.

It is evident that the micro-structure of the hydrated paste, especially the porosity, should play an important role in governing the permeability. Previous discussions in Section 4.1 have demonstrated the effect of adding different metal wastes to the micro-structure of the cementitious matrices. A good correlation was obtained between the micro-structure and the physical properties in terms of permeability and compressive strength.

The results demonstrate that the flow of oxygen through the cementitious matrices was governed by at least two mechanisms: the degree of saturation of the pore space with water and the micro-structure of the matrices governing gas flow.

Although there is no established relationship between the oxygen and water permeabilities the oxygen permeability value can be used to provide a quick assessment of the physical quality of the solidified product. As indicated earlier, the hydraulic conductivity of any fluid can be computed when the intrinsic permeability of the medium is known. Although this would overestimate the permeability to water due to "gas slippage", this overestimation can be regarded as an extra safety factor in the quality control of the solidified waste for landfill disposal.

6. DISCUSSION

6.1 Mechanisms of immobilisation of heavy metals in cementitious matrices

In the cement industry inorganic cations have been used as admixtures to facilitate mix design (64). The chemical and physical effects of metal electrolytes on cement or clinker hydration have been studied and are useful in evaluating the interaction between heavy metals and stabilising agents in the cement based stabilisation/solidification processes. These studies have therefore been reviewed.

As discussed earlier (Section 3.3), when cement is mixed and reacts with water, heat is given off and calorimetric methods can be used to follow the sequence of hydration. The effect of adding metal electrolytes have been studied using conduction calorimetry (67). The influence of any electrolyte on the early hydration and heat evolution of cement is threefold: the length of time of the induction period, the time of maximum rate of heat evolution, and the total heat evolution may all be altered (68). In general, an accelerator shortens the induction period and produces an early heat peak with a corresponding increase in height of the maximum rate of heat evolution. A retarder has the reverse effect. A ranking sequence of cations based on this calorimetric method has been compiled by Wilding et al. (69).

$$^1/_2Ca^{2+} > {}^1/_2Ni^{2+} > Ba^{2+},\ {}^1/_2Mg^{2+} > {}^1/_3Fe^{3+},\ {}^1/_2Cr^{2+} > {}^1/_2Co^{2+} > {}^1/_3La^{3+}$$
$$>> NH_4^+,\ K^+ > Li^+ > Cs^+ > Na^+$$
$$\longleftarrow \text{ acceleration}$$
$$^1/_2Cu^{2+} > {}^1/_2Zn^{2+} > {}^1/_2Pb^{2+}$$
$$\text{retardation} \longrightarrow$$

Also based on this calorimetric method Kando et al. (68) suggested that, generally, salts forming the least soluble hydroxides have the greatest retarding effect, while salts forming hydroxides of high solubility exhibit only a slight degree of retardation. The

alkali metal salts capable of forming soluble hydroxides, act as accelerators.

These studies demonstrated that the early hydration reactions of cement were modified by incorporating heavy metals. This has an important implication on the mechanism of immobilisation of heavy metal by cement based stabilisation/solidification processes.

Micro-structural studies using SEM, XRD and MIP have been used to identify the reactions and mechanisms taking place when metal solution is mixed with cement. In a study into the effect of $Pb(NO_3)_2$ on the early hydration of Portland cement, Thomas *et al.* (70) showed that after mixing with cement, Pb was rapidly precipitated from the aqueous solution. Furthermore they demonstrated that the precipitate was largely in a colloidal gelatinous form coating the surface of the cement grain. The composition of the coating was not simply a $Pb(OH)_2$ - as would be expected from an alkaline environment - but was a mixed basic Pb salt of variable stoichiometry, involving both nitrate and sulphate. It was postulated that this kind of colloidal membrane formation was typical of precipitation processes that occur within a narrow zone between two solutions with a high degree of supersaturation. It was further suggested that similar reactions would take place for cations with similar properties (*viz.* Cu, Zn, Sn, Cd). This coating did not completely stop the hydration of cement and water was able to diffuse through the membrane and be in contact with the cement. Therefore, the extent of retardation of different metals on the hydration depends not only on the fine structure of the coating but also on its chemical composition. Any changes in the structure of the coating (chemical conversion or crystallisation) could render it less effective and initiate further hydration of the cement.

Based on this study and some previous findings (71, 72) it was suggested that cement hydration was normally self inhibiting and the cement hydration largely controlled by diffusion through the protective colloidal coating around the cement grains (73).

Therefore the rate of reaction and the associated hydrate development will depend on the permeability and cohesion of the coatings. The addition of additives or admixtures would modify this coating to either a more open flocculated structure accelerating hydration or a dense coagulated layer resulting in retardation (Fig 6.1).

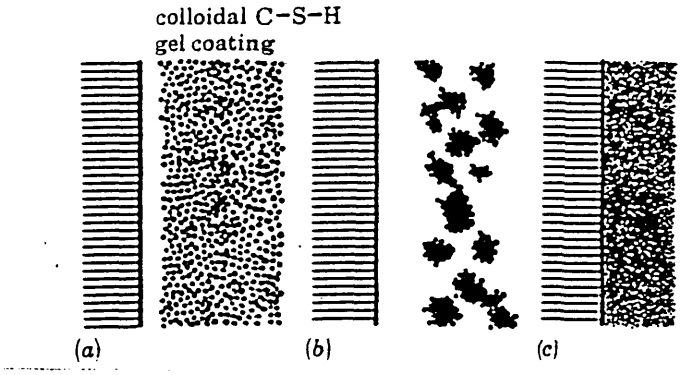


Figure 6.1 Schematic representation of possible changes in the colloidal structure of a C-S-H gel coating on a cement grain surface. (a) Normal protective gel coating, inhibiting hydration. (b) Flocculated, poorly adherent coating permitting accelerated hydration. (c) Dense, coagulated and strongly adherent coating causing retardation of hydration (73).

Corrobative evidence of the protective coating theory was provided by Stepanova et al. (74) for Cu and Zn cations. They attributed this coating to a complex formation between the additives and the components of cement giving a complex whose stability made a substantial contribution to the compressive strength of cement. They ranked the effectiveness of these additives in affecting the strength of cement in the sequence Mn<Co<Ni>Cu>Zn. This ranking corresponds to the variation of the enthalpies of complex formation and of the stability constants of complexes of the given metals with various ligands.

Separate studies had been conducted to investigate the effect of solid metal oxides and hydroxides on the hydration of individual clinker component of cement using differential calorimetry, SEM and XRD. Tashiro and co-workers (75, 76) concluded that Cr_2O_3, $Cu(OH)_2$ and ZnO retarded the hydration of C_3A through the formation of cubic calcium aluminate hydrate. Lead oxide, however, only retarded the initial reaction and then accelerated the hydration after a few minutes. On adding gypsum to the C_3A system the same authors found that the addition of these metal oxides and hydroxides promoted the crystal growth of ettringite and produced a significant change in the micro-structure hence affecting the physical strength of the hydrated paste. Therefore an additional effect of adding heavy metals to the cementitious matrices is to promote the formation of calcium sulphoaluminate hydrates (77). The increased production of crystalline AFt and AFm phases expanded the pore structure and resulted in an increase in total pore volume. This has an important implication on the physical properties of cement.

The study into the effect of $Pb(NO_3)_2$ on the physical properties of cement (78) showed that the reaction between Pb and cement produced vast quantities of gel with a complex composition. This gel was intrinsically weak with little mechanical strength. It was observed to cause micro-cracking in the hydrated cement resulting in increased porosity and reduced compressive strength.

The interest in using cement and other similar materials to encapsulate radioactive waste also initiated some studies on the mechanism of immobilisation of radioactive elements, especially Sr and Cs in cement. Komarneni and Roy (79) found that generally cement alone does not exhibit any sorption capacity for Cs and Sr but immobilises these metals upon carbonation by forming carbonates:

$$2CsCl + Ca(OH)_2 + CO_2 = Cs_2CO_3 + CaCl_2 + H_2O \quad (15)$$

$$SrCl_2 + Ca(OH)_2 = SrCO_3 + CaCl_2 + H_2O \quad (16)$$

This has been attributed to the inability of Cs and Sr to form insoluble hydroxide within the alkaline environment of cement. This lack of sorption ability of cement on Cs was also found by Glasser et al. (80). However, the use of other materials such as silicas, zeolites, kaolin and titania improved the retention of Cs through sorption in the cementitious matrix.

The above discussion demonstrates that the hydration reaction of cement is strongly influenced by the addition of different types of cations. The normal hydration of cement is retarded by metals which are capable of forming complex hydroxides within the alkaline environment resulting in the modification of the micro-structure of the cementitious matrix. However, little sorption or precipitation reactions can take place for metals which have high solubilities in the alkaline cement environment.

The possible use of pulverised fuel ash (PFA) to retain heavy metals had been studied by a few workers. Panday et al. (81) found that PFA was able to remove Cr(VI) from solution. The maximum removal was observed at pH 2.0. It was suggested that absorption was first governed by diffusion followed by surface compound formation. The absorption of anions, however, decreased as the pH of the solution increased. Papachristou (82) studied the retention of Pb by PFA and attributed the retention partly to the physical adsorption capability of the PFA and partly to chemical reactions between Pb ions or ions of other heavy metals and the CaO, Al_2O_3, SiO_3, MgO, $CaSO_4$ present in PFA.

The retention of fluoride by PFA has also been demonstrated by Tasitouridou et al. (83). The mechanism was found to be due to the absorption and chemisorption of fluoride by active alumina in the PFA which causes a positive charge in the acidic environment. The above studies show that PFA is able to act as sorbant for heavy metals in the cement based stabilisation/solidification process.

The aqueous chemistry study conducted in the present study on OPC, PFA, PFA/OPC and PFA/OPC/Silicate with water and different metal solutions provided an understanding of the initial chemical reaction involved in the stabilisation/solidification. The most important conclusion drawn from these results is that while the hydration of OPC results in an alkaline aqueous solution, PFA results in a neutral or slightly acidic solution. The replacement of PFA by OPC increases the alkalinity of the aqueous PFA/OPC environment. Accompanying the liberation of lime from the systems is the dissolution of the anhydrous clinker phase of cement releasing Ca. The implication of these findings is that the alkaline environment of the OPC and PFA/OPC systems would render insoluble many of the polyvalent metal ions in the early minutes of the reaction. This is confirmed by the findings in the experiment with Zn and Cd. The concentration of Cd - which form hydroxides of very low solubility - dropped to a low level immediately after mixing. A similar study on Pb by Thomas et al. (70) corroborates this result. Zinc, which forms a precipitate with the hydroxyl ion but possesses an amphoteric nature, also decreased rapidly to a low value but the concentration was slightly higher than those for Cd. A point to note is that the PFA/OPC system immobilised more Zn than the pure OPC system. This was due to the PFA providing a buffer which lowered the pH, preventing the resolubilisation of Zn.

For metals which do not form insoluble hydroxides (e.g. Hg and Cs) the exact concentration profile depends on the specific chemical reaction between the metal and OPC or PFA. Cement has been shown to be incapable of immobilising Cs (80), due to the strong positive charge of the Cs^+ ion, but PFA has been demonstrated to be able to adsorb Cs (80). Mercury, on the other hand has been demonstrated in this present study to show a progressive decrease in concentration in the OPC and PFA/OPC systems probably due to the precipitation of the HgO and adsorption onto the PFA particles.

However, it has been pointed out (80) that the sorptive properties of the PFA particles would be effectively reduced with time once

cement is introduced into the system due to (i) the reaction of the PFA with $Ca(OH)_2$ leading to a decrease in the amount of both and (ii) possible competition for the "active" sites responsible for the uptake of heavy metals in the waste and the alkali metals in the cement pore fluids.

Because of the variable nature of both the composition and mineralogy of PFA, it is difficult to generalise the mechanisms of the reaction between heavy metals and PFA or PFA/OPC blended systems. However, as discussed earlier, for typical British flyash which has a very low lime content, the results in the present research, indicate that PFA possessed little retention potential for Zn, Cd and $HgCl_2$ in the early hours of the reaction. This is due to the low lime content of the PFA and its inability to form hydroxyl compounds rendering the heavy metals insoluble. Microscopic evidence (Fig 4.8) confirmed that there were no precipitation or gel formations on the PFA particles. Mercuric nitrate, however, was retained which is thought to be due to cation exchange in the slightly acidic medium.

Chemfix is a solidification process utilising Ordinary Portland Cement and sodium silicate solution as stabilising agents. The normal procedure is first to mix the waste pollutants with cement producing a homogenous slurry (25), followed by the addition of sodium silicate solution. The aqueous chemistry studies have demonstrated that most of the polyvalent ions which are capable of forming insoluble hydroxides (e.g. Zn, Cd) in the alkaline aqueous cement environment would be precipitated rapidly. The actual metal concentration in solution after precipitation was low. This reaction lowered the pH of the solution due to the removal of the hydroxyl ion and hence increased the Ca concentration. Later addition of sodium silicate, therefore, would only be able to react with the small proportion of these heavy metals still remaining in solution, forming complex metal hydroxide-silicate as described

earlier (Section 3.5). The main effect of the sodium silicate therefore, was to react with the abundant Ca^{2+} concentration in solution forming calcium-silicate gel as revealed in the SEM study (Section 4.1). This gel has a high affinity for water but a very low intrinsic strength (63). Therefore addition of sodium silicate accelerated the setting of the initial paste and increased the water demand with the result that more waste solution could be incorporated into a fixed amount of solid. This is useful in reducing the material cost, but has a penalty in reducing the final strength - as described previously (Section 5.3) that the final strength is dependent on the water/cement ratio.

It has been suggested that when heavy metals are added to cement, a protective coating will be formed around the cement particle. This coating inhibits further hydration of the cement grain. The EXAFS study on Zn supported this theory by identifying a clearly defined 4 co-ordinated oxygen shell around the Zn atom. Although the local environment beyond this first shell could not be identified it can be postulated that the second shell consisted of a mixture of O-H and Si atoms. The fact that the EXAFS results of the pure cement system did not differ significantly from those of the cement/silicate (Chemfix) system supported the theory that sodium silicate did not contribute to the reaction with the metal.

As far as stabilisation of waste is concerned, the stability of this complex coating is important. The chemical bonding retains the metal pollutant in the matrix and this can be demonstrated in the dynamic leaching tests. However, the penalty of forming this stable structure is to inhibit the normal hydration of cement producing C-S-H which is responsible for the strength development of the cemenetitious system. The results from the compressive strength and oxygen permeability measurements illustrate this.

For metals which do not form complex precipitates with cement, this coating theory implies that they will not interfere with the normal hydration of the matrix. This is indeed confirmed in the study on Hg salts in the form of $HgCl_2$ and $Hg(NO_3)_2$. SEM, XRD and porosity

studies all showed that the microstructure of the hydrating matrices was not significantly affected by Hg addition. Confirmation of this was given by the EXAFS study which showed that Hg was incapable of forming a definite local environment in the cementitious matrices. This resulted in comparable compressive strength and permeability values to that of the control as the hydration was not retarded. It also explains the relatively high leachability in the dynamic leaching tests - which were designed to test the chemical stabilisation potential of the matrices to the pollutants.

In a PFA/OPC (Sealosafe) blended system, the reaction between OPC and Zn and Cd is likely to be similar to the pure cement system although the pH of the former system may be lowered by the buffering effect of the PFA. This was confirmed by the micro-analysis by SEM, XRD, porosimetry and EXAFS. However, the dynamic leaching tests on the solidified material demonstrated that the blended system immobilised more metals than the OPC system. The replacement of OPC by PFA immobilised more Zn due to the lower pH value which prevented resolubilisation of the amphoteric Zn in the alkaline environment. The amount of $Ca(OH)_2$ in solution was lowered - as detected by the XRD - due to reactions between Zn and Cd cations with hydroxyl ions released from the cement. This removal of $Ca(OH)_2$ from solution reduces the extent of an early pozzolanic reaction between lime and PFA unless an additional source of lime is present. In addition, the observed mechanical properties of the Zn and Cd-dosed PFA/OPC (Sealosafe) samples were also poor due to retardation effect of these two metals on hydration and resultant modification of microstructure. The incorporation of PFA therefore, will not improve the physical properties of the solidified material.

A combination of alkaline oxide precipitation and cation exchange is thought to be responsible for the retention of Hg in the PFA/OPC system. This was confirmed in the sorption experimental study which illustrated that the PFA was able to take up Hg from solution despite the acidic environment. In addition, the two Hg salts

gave slightly different sorption and desorption characteristics in the PFA systems. These reactions, however, did not interfere significantly with the normal hydration of cement and PFA as revealed in the SEM, XRD, EXAFS and porosimetry studies. The resulting physical properties were comparable to the control in terms of compressive strength and permeability.

The static leaching test, which was designed to assess the physical retention potential of the cementitious matrices, showed that Hg was mainly physically immobilised and that the stronger Chemfix matrix retained more Hg than the weaker Sealosafe matrix. Zinc and Cd however, were mainly chemically fixed in the matrices and mobilistion of these two metals took place after the leaching environment became acidic.

Generally, a good correlation between Macro (leaching, strength and permeability) and Micro (SEM, XRD, porosity and EXAFS) was found. It has been shown that metals such as Zn and Cd which retarded the hydration of cement and PFA modified the microstructure of the matrices and produced a weak product with high permeability. Dynamic and leaching tests indicated that these metals were retained in the alkaline environment of the matrices. Metals which did not retard the hydration of cement and PFA (e.g. Hg) produced a microstructural environment very similar to that of the control. The mechanical properties in terms of compressive strength and permeability were comparable to the control sample. However, the chemical stabilisation of these metals by cement and PFA was much smaller, as indicated in the dynamic leaching tests.

As far as the immobilisation of metal wastes is concerned, the stability of the complex coating around the cement grain is important to fully exploit the chemical fixation potential. However, promotion of this coating would seriously inhibit the normal hydration and result in a physically poor product. This has an important implication for those metals relying on the physical means of stabilisation.

It should be noted that the aim of the solidification/stabilisation processes is to reduce the leachability and to improve the physical properties of the solidified waste in terms of mechanical strength and permeability. Therefore, not only the reaction between the hazardous components of the waste with the stabilising materials, but the normal hydration of OPC, PFA, OPC/PFA are important. The latter affects the mechanical properties and the long term performance of the solidified material.

Generally, there is a direct relationship between porosity, strength and permeability. However, it should be noted that this relationship holds only within matrices of similar characteristics (i.e. within the Chemfix or Sealosafe processes). Although the Sealosafed products in the study had lower porosity, the physical properties in terms of strength and permeability were poor when compared to the Chemfix samples. This is because the contribution of PFA to strength occurred only at a later period of hydration. In addition, the use of PFA lowered the water demand of the mix and often resulted in the production of a layer of supernatant after all the solid had been settled (illustrated in Fig 6.2). This production of supernatent can be a major source of pollution as surface runoff to a nearby watercourse. It is therefore recommended that the exposed surface area of freshly placed Sealosafe products should be kept to a minimum and sedimentation ponds or trenches should be constructed to collect the runoff discharge from the landfill area.

The problem of poor physical properties and initial surface runoff can be overcome by using a low waste/cement or waste/solid ratio. This parameter has been demonstrated to be the most important in governing setting and strength. However, as material cost, especially cement, is the most significant item in the process, the increased use of cement in the solidification process will make the process even less competitive against alternative disposal methods. The use of sodium silicate in Chemfix has been demonstrated to accelerate the initial setting and improve the initial strength. The calcium-silicate gel produced was also a powerful sorbant for

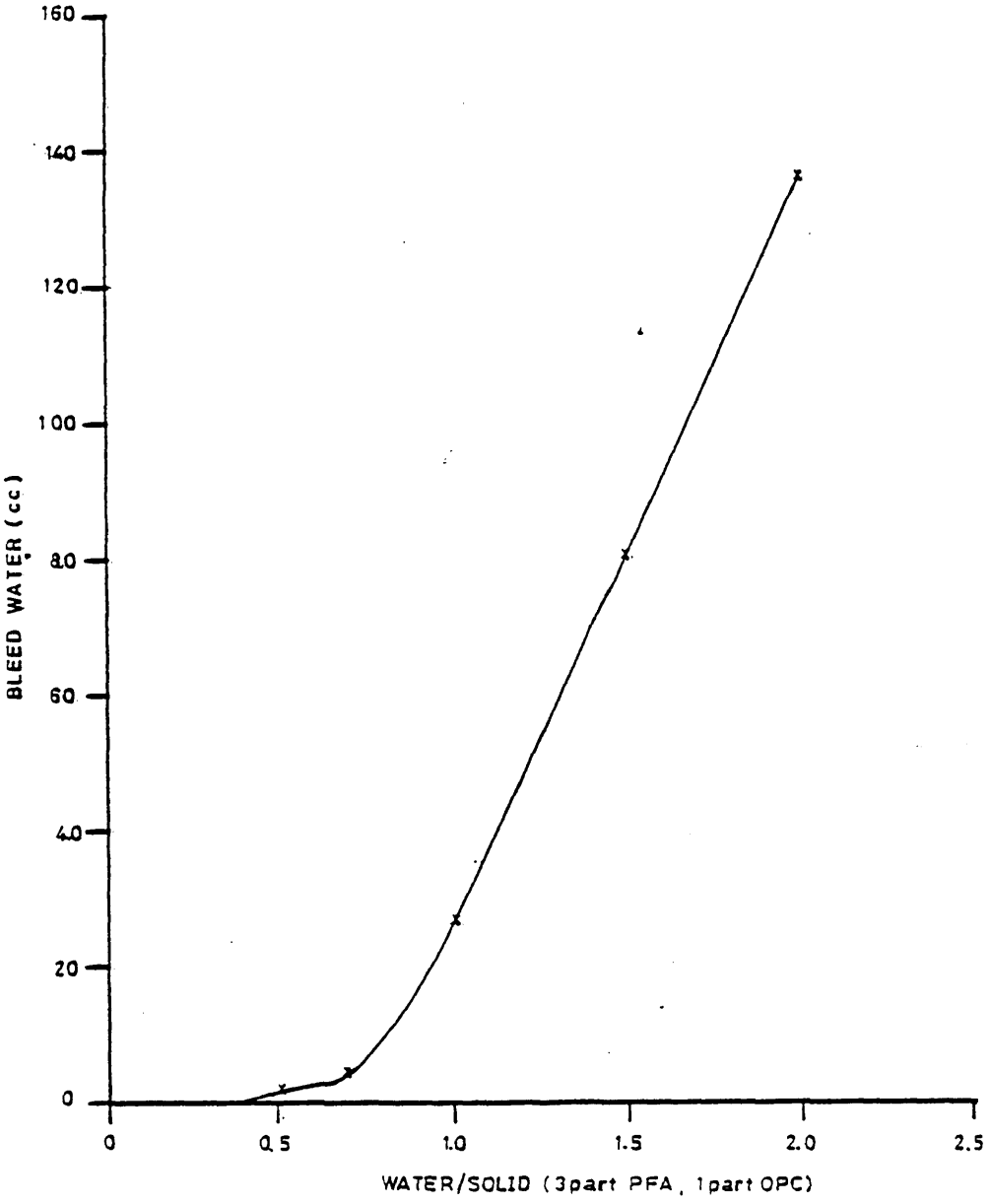


Figure 6.2 Relationship between bleed (supernatant) water and water/solid ratio

water thus increasing the water demand, although the long term strength was not improved. However experimental results of the PFA/OPC/silicate system demonstrated that sodium silicate not only increased the initial setting, but also contributed to the final strength. Therefore the selective use of sodium silicate in the PFA/OPC blended solidification process should overcome the problem of supernatant formation and promote long term strength. However, increased doseage of sodium silicate will increase the amount of calcium-silicate gel formed. It has been shown that this gel has very poor physical properties and the most damaging effect was due to shrinkage. This resulted in extensive cracking in some of the solidified products (Figure 6.3) and has important implications on the long term stability of the material, especially when used with highly alkaline waste.

The use of PFA has been shown to facilitate the retention of certain metals through sorption and/or chemisorption. However, due to the variability of the characteristic of PFA, a generalised concusion is not appropriate. It is probable that almost all PFA can be used as stabilising agents at some level without significant loss of performance. But with the present paucity of knowledge of the relationship between PFA characteristics and PFA performance, it is necessary to produce a guideline for the use of these materials in the stabilisation/solidification processes.

Regarding the mechanisms of immobilisation of hazardous pollutants by the stabilising materials Lubowitz et al. (84) suggested that most fixatives in current practice stabilise metal contaminants through microencapsulation rather than through chemical fixation. They further suggested that a truly chemically 'fixed' product which needed high operating pressure and temperature was unlikely to be produced in current practice under the normal processing conditions. They proposed that the stabilising agents (e.g. cement, silicate and PFA) reacted with the heavy metal contaminants and caused precipitation of insoluble microscopic and macroscopic particles that were microencapsulated in the solidified cementitious matrix.

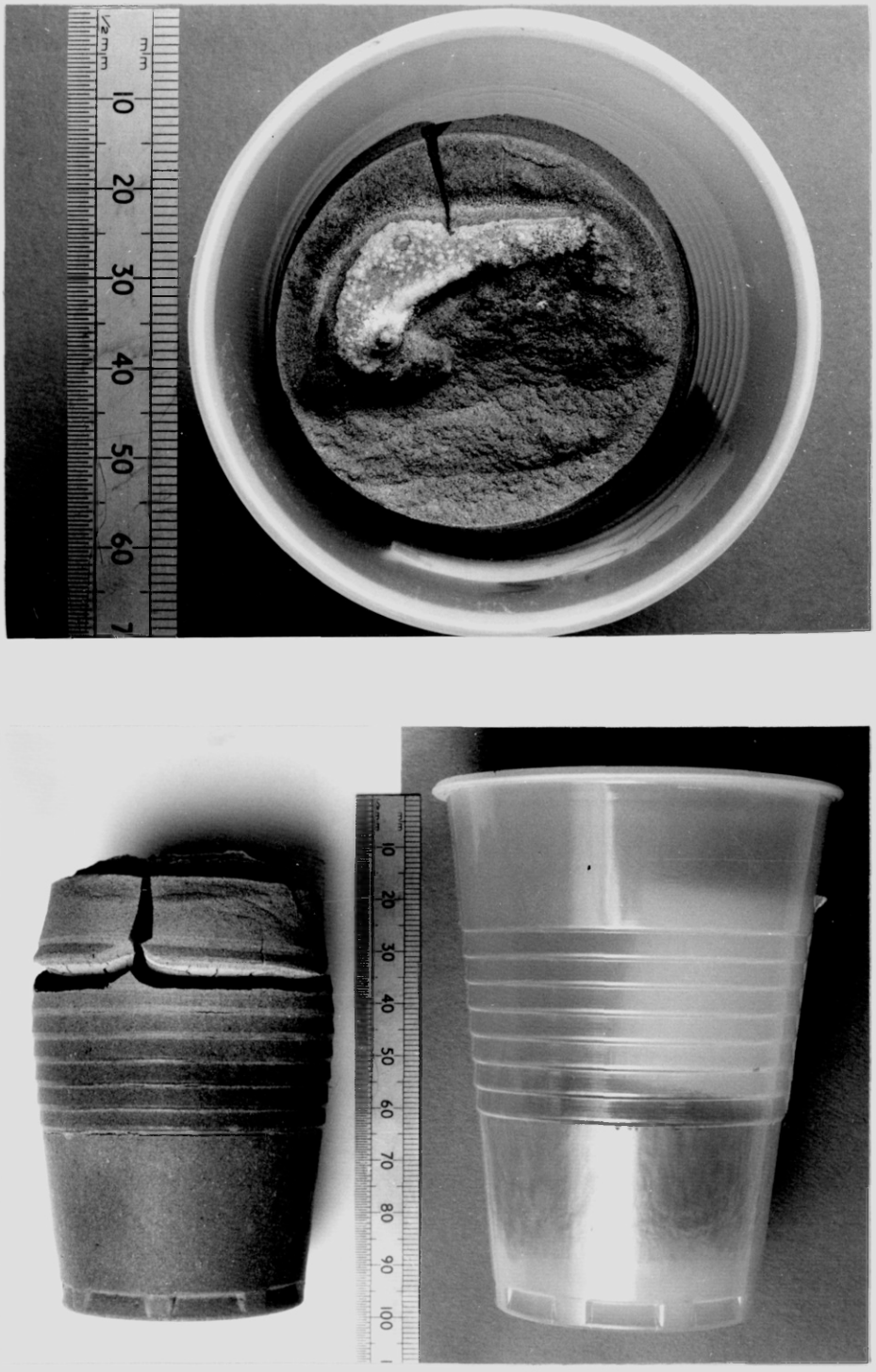


Figure 6.3 Photographs showing the extensive drying shrinkage and cracks resulted when excess sodium silicate solution was used in solidification.

However, the definition of the term "chemical fixation" must be clarified before any discussion on the ability of the solidification processes to chemically "fix" any metal pollutants. One must distinguish between the chemical precipitation reaction forming an insoluble chemical compound and the crystal substitution chemical reaction in which the metal species is incorporated into the chemical structure and the crystal lattice of the raw and hydrated matrices. The latter process has been shown in the present research to be unlikely to occur. Other research work, especially on radioactive waste, indeed showed that crystal stabilisation only occurred at elevated pressure and temperature (85, 86) (e.g. at clinkering temperature in the production of Portland cement). However, the simple precipitation and sorption reactions between metals and cement and PFA have been demonstrated to occur in the alkaline environment. The EXAFS study produced evidence that Zn was chemically bonded to the oxygen in a complex hydroxide-silicate structure.

Thus a strong chemical bonding with high dissociation energy can be realised in the simple precipitation reaction. Furthermore, it has been demonstrated by the SEM study that the microstructure and the physical quality of the cementitious matrix was seriously affected by the incorporation of some heavy metals (e.g. Zn, Cd). This implies that the physical means of microencapsulated proposed by Lubowitz _et al_. for these metals are not valid. However, the leaching test study showed that these metals were well immobilised by the cement based stabilisation/solidification systems.

Little chemical stabilising has been shown to take place for metals like Cs with negligible chemical reaction with the stabilising agents (80). It has been demonstrated that the main immobilising mechanism for these metals in the cementitious matrix was the physical barrier between the waste solution and the leaching fluid. As supporting evidence the workers reported that most of the Cs was present in the pore fluid.

For Hg and other similar metals which form a partially insoluble compound in the alkaline environment but do not modify the microstructure of the cementitious matrix the microencapsulation theory may be appropriate to describe the immobilising mechanism. However, this is actually a combined effect of the above two mechanisms.

The above discussions illustrate that there are three levels in immobilisation of waste by the cement based stabilisation/ solidification process under normal processing conditions: (i) a chemical reaction; (ii) a physical barrier between the leachate and pollutant imposed by the bulk solidified waste and (iii) a combined effect which can be described as microencapsulation.

Two fundamental mechanisms can thus be identified in the immobilisation of heavy metals in the cement based stabilisation/ solidification processes.

(i) A chemical fixation mechanism which involves the formation of insoluble compounds between the waste components and the stabilising agent. Several chemical mechanisms take part in the reaction - involving precipitation, sorption and chemisorption. The immobilisation of Zn and Cd is mainly accounted for by this mechanism.

(ii) A physical encapsulation mechanism in which the solidified matrices provide an impermeable barrier between the leaching fluid and the waste pollutant. This impermeable barrier relates to the physical properties of the solidified materials in terms of strength and permeability. These two properties are determined principally by the porosity of the matrices. Metals such as Hg and Cs are immobilised mainly by this mechanism.

These findings invalidate the claimed mechanisms by which both processes are operative for the immobilisation of waste:- It is claimed that the Chemfix process is based on a three dimensional

network of newly formed crystals similar to pyroxene structure (25) while the Sealosafe process is claimed to be based on a crystal capture mechanism (26). It has been shown that in order to substantiate crystal chemical substitutions of waste ions into cement or any other cementitious hydrates, high pressure and elevated temperatures are necessary. This substitution of metal ions into the crystal lattice is unlikely to be achieved at the normal processing conditions for both Chemfix and Sealosafe processes.

6.2 Review of field practice of cement based stabilisation/ solidification processes

The approach used in this research was to examine the mechanisms of the solidification in a carefully controlled laboratory experiment. The scope of the study did not allow field experiments to be conducted. However two field monitorings of the actual practice of Chemfix and Sealosafe processes have been carried out by the Department of the Environment and the United States Environmental Protection Agency. These findings have been reviewed and are presented below.

The Chemfix process was used in the Haigh Quarry landfill operation in Yorkshire during 1970-1972. A field investigation was carried out in 1977 into the solidified product from the landfill site (87). Ground water analysis yielded concentrations of leachates similar to those claimed by the operating company on the basis of their laboratory tests. For wastes with a zinc content up to 2,000 ppm, copper up to 150 ppm, chromium up to 350 ppm and lead up to 270 ppm, containment appeared to be good. Containment of highly acidic waste and phenolic wastes was less satisfactory. Because of the alkaline environment generated by the Chemfix process many metals did not enter solution and concentrations of heavy metals in Chemfixed leachates were low. It was suggested that one horizon of acidic waste within a much larger mass of alkaline Chemfix would be buffered to alkaline conditions by the surrounding Chemfix.

The United States Environmental Protection Agency has conducted an extensive investigation into the Sealosafe process being operated at West Thurrock, Essex (88). Using their Extraction Test Procedure, they found that lead, chromium, arsenic, barium, cadmium and nickel were generally immobilised by the Sealosafe matrix but selenium was consistently leached from the solidified mass. Groundwater samples collected from the eighteen monitoring wells at the disposal site generally gave little indication of toxic metals leaching from the solidified material. Cyanide, however, at levels higher than the drinking water standard were present in a number of monitoring wells. It was suggested that cyanides should be completely destroyed before solidification.

High metal concentrations were detected in the surface water samples collected from the ponds at the base of the disposal area. It was suggested that this contamination probably resulted from drainage of the excess water used in the solidification reaction or from leaching of the uncured material.

Analysis of the geological samples directly below the site showed no consistent pattern that could be related to leaching from the solidified material. This indicated that the inorganic constitutents in the waste were generally immobilised by the solidification process.

The Hazardous Waste Inspectorate (9) in their recent study into the landfilled Sealosafe product commented that some solidified material still had a consistency of "porridge" after some months of treatment. This suggests a closer quality control is needed for successful use of the process.

The above discussion demonstrated that, generally, cement based stabilisation/solidification processes are capable of immobilising heavy metals in field conditions which is in accord with the findings of the present study. However, the cement based stabilisation/solidification processes are incompatible with organic and inorganic cationic wastes as their leaching potential under field conditions is significant. Supernatant water and surface runoff are of great concern with the Sealosafe process and this problem has been demonstrated both in the laboratory and field conditions. The suggested use of other additives (Section 5.3) such as sodium silicate in the Sealosafe process should be further investigated to minimise this problem. The findings of the Hazardous Waste Inspectorate illustrated the importance of the physical quality of the solidified product which has been demonstrated (Section 5.3) to be dependent on several parameters. Poor products are often resulted from reducing the doseage of stabilising material, especialy cement, during solidification. Therefore adequate quality test procedure should be imposed to safeguard malpractice.

6.3 Long term prediction of leaching characteristics

It has been pointed out (56) that a real life leaching procedure to simulate the actual landfill environment is not practicable because such a test requires extensive experimental effort and would take a long time to complete. To provide a time-based prediction of the long term leaching characteristics of pollutants from solidified waste two approaches can be adopted: (A) by an accelerated laboratory leaching study. This is accomplished using more vigorous leaching conditions e.g. higher temperature, more stringent solution pH, buffering and redox conditions and higher flow rate (faster leachate renewal rate for batch tests). This approach assumes that leaching under the real life and accelerated conditions are controlled by the same mechanisms.

An acceleration factor (Af) can be defined as the ratio of the test duration under the real life condition (tr) and the accelerated condition (ta) yielding the same cummulative fraction of pollution release (89):-

$$Af = \frac{tr}{ta} \qquad (17)$$

The results from the accelerated test can then be used to extrapolate the long term behaviour of the solidified waste in the landfill environment.

(B) by a modelling approach using mathematical leaching models which are either based on empirically derived formulae based on laboratory test data or analytical models based on the mass transport theory and other leaching mechanisms.

An empirical model that can be used is (89)

$$F(t) = a + bt^{1/2} + ct \qquad (18)$$

Where $F(t)$ = cumulative fraction leached

t = time

a, b, c = coefficients

The first term, 'a' represents the initial wash out of pollutant from the specimen. (a -ve 2 term indicates a delay of release). The second term, 'b', represents a square root, time dependent effect for bulk diffusion. The time dependent third term 'c' represents the other controlling leaching mechanisms, including a kinetically controlled chemical reaction and an interface mass transfer resistance.

Leaching mechanisms that have been commonly associated with solidified materials include bulk diffusion, chemical dissolution and interface mass transfer (89). All these mechanisms can be modelled by the mass transport theory. On application to solidified waste this theory suffers from an inherent limitation because a simple analytical solution for the model must be based on an assumption that no chemical interaction between the leachate and the waste form occurs, which would change the leaching environment with time (89). This assumption is essential to model the transfer of chemical species from the solid to the liquid phase due to the difference in concentrations in a constant aqueous chemical environment. This limitation with regard to solidified waste will be discussed later.

A leaching behaviour that is solely represented by bulk diffusion can be represented as: (89)

$$\frac{\Sigma C}{Co} = \left(\frac{2A}{V}\ \frac{De}{\pi}\right)^{1/2} \qquad (19)$$

where $\frac{\Sigma C}{Co}$ = Cumulative fraction leached

$\frac{A}{V}$ = Specific surface

De = Diffusivity constant.

A simple chemical dissolution term can also be incorporated in this equation. The modified expression can be represented as

$$\frac{\Sigma C}{Co} = \left(\frac{2A}{V}\right)\left(\frac{De't}{\pi}\right)^{1/2} \quad (20)$$

$$\text{where } De' = \frac{De}{1+Kd} \quad (21)$$

$$Kd = \frac{C\ (\text{immobile})}{C\ (\text{mobile})} \quad (22)$$

The mathematical expressions describing other chemical reactions have also been derived (89) but the solutions are too complex to be incorporated in the general diffusion expression.

Cote and Hamilton (90) have found that leaching of certain heavy metal waste from the solidified matrices follows this diffusion model. The conclusion drawn from this interpretation is that leaching is governed by a concentration differential dependent diffusion process.

However, in the extended leaching studies (Section 5.2), the leaching mechanisms of Zn and Hg have been identified as being related to the micro-structure of the solidified matrices which could not be accounted for by any diffusion theory. It can be argued that the short term leaching characteristics of the solidified waste follow the diffusion model, as part of the pollutant concerned is immobilised by the physical process. Some chemical dissolution can be accounted for incorporating a Kd term. However a major part of the pollutant is chemically bonded to the stabilising agents and their release is governed by their specific fixation mechanisms. In both the Chemfix and the Sealosafe products, there was a sudden surge in both the Zn and Hg concentrations after a certain period of leaching. This release was related to the percentage of Ca released from the matrices and to the buffering indexes of the leaching fluid used. The release of Ca and the changing pH environment in both the dynamic and static leaching tests showed that the leachate environment was being continually modified by the leaching process. This is contrary to the assumptions made in the mass transfer model. This mechanism of release is thought to be related to the breakdown of

the microstructures responsible for the retention of metals. Although this breakthrough may take a long time to actually take place in a true landfill environment it demonstrates that the bulk diffusion model cannot truly represent the long term leaching behaviour.

Since there is a unique relationship between the percentage of calcium released, the microstructure of the leached solid and the release pattern of the pollutants a model can be used to predict the time duration when this percentage of calcium is released from the matrix.

It is suggested that any leaching test can be used to establish the particular percentage of calcium released from the matrix with a particular mix design for a specific waste stream. After this percentage is obtained a more realistic pilot scale column test can be conducted. The data obtained for the calcium concentration can then be used to model the time scales involved for the same percentage of the calcium that would be leached before the breakthrough. The short term results obtained for the pollutant concerned can be used to interprete the suitability of the solidification processes for that particular waste. For the types of waste which are well retained in the matrices, this breakthrough may never occur in a real landfill environment. If the occurrence of this breakthrough is found likely, however, the waste in question should not be treated by a solidification process. For pollutants which are not well retained but are attentuated by the solidified matrices, careful interpretation must be applied to determine whether this breakthrough occurs before the time when most of the pollutants will have leached out.

A mass-transport model based on 1st or 2nd order diffusion equations is thought to be inappropriate to model the calcium leachate concentration. This is because the cementitious matrix is continually being hydrolysed by the leaching fluid. The rate of this hydrolysis depends on the pH, or more importantly on the buffering capacity, of the leaching fluid. Consequently, an empirical approach based on experimental data should be used.

6.4 Economics and practical application of cement based solidification processs

The cost of using solidification processes for the treatment of waste prior to ultimate land disposal is high when compared to the straightforward mono-or co-disposal of waste to landfill. This is due to the high processing costs in terms of materials and equipment. The greater volume and weight also increase the basic cost of landfill after treatment. A comparision of costs for the various treatments and disposal methods is given in Table 6.1.

Table 6.1 EEC chemical industry: Cost range of engineering waste by different methods (DM/tonne)* (5)

Controlled engineering to land	3-30
Disposal to land in a site lined with plastic sheet	17-75
Underground disposal by dropping into old wells or mines	30-300
Underground storage e.g. in salt caverns	170-400
Land disposal after encapsulation either by mixing the waste with cement or other agents or by incarcerating whole drums in cement	17-150
Coastal sea dumping from ships or barges	6-25
Deep-ocean dumping beyond the continental shelf	190-300
Simple incineration (without significant heat recovery)	50-180
Incineration with alkaline stack scrubbing	200-600
Incineration on board ship at sea	100-600
All types of chemical treatment and in particular:	
destruction of cyanide by hypochlorite	500-900
reduction of chromic acid	170-500
destruction of cyanide (catalytic)	350-40

*£1 = DM 4 (1985)

The total cost of any solidification process can be divided into three components: (i) pretreatment, (ii) the solidification process and (iii) the ultimate disposal to land.

(i) Pretreatment

Certain wastes received for solidification require some form of pretreatment prior to the solidification process. The most common pretreatment operations are neutralisation of acids or alkali, lime treatment for the precipitation of heavy metals, oxidation of cyanide and reduction of chromium (VI). This requires additional capital and reagent costs.

(iii) Solidification

The most expensive item in cement based solidification processes is the cost of the stabilising reagents, especially Ordinary Portland Cement. In the Chemfix process OPC and sodium silicate are priced at £60 and £80 per tonne (1984 figures). Although the PFA used in the Sealosafe process is relatively cheap (£5 per tonne), the overall reagent cost including OPC can represent a large proportion of the final market price. It is understood that the reagent costs contribute over 50% of the cost of Chemfix (91).

The actual amount of reagent required for the solidification process also depends on the nature of the waste material. For waste with a high solid content, such as contaminated soil and wastes that contain small quantities of substances that inhibit the hydration of the cementitious material, less material is required. The plant requirements for the cement based stabilisation/ solidification processes are relatively unsophisticated with the major elements being mixing tanks, reagent feeds and pumping plant. Capital costs are obviously lower than those for, say, incineration. Running costs in terms of manpower and energy are also not high in relation to other chemical treatment techniques, but are higher than the requirements for landfill disposal.

(iii) Landfill

This element of cost depends on several parameters including: the volume and character of the waste to be disposed of, the availability of landfill capacity and the transportation of raw and solidified materials.

One of the most important advantages of stabilisation/solidification techniques is that disposal of the treated waste can take place at a greater number of sites than would otherwise have been the case. This is an obvious advantage in regions where hazardous waste producers are at a financial and practical disadvantage by not being able to dispose of certain wastes efficiently through lack of landfill space. In the UK it is not unknown for particularly unpleasant wastes to be transported several hundred miles and under these circumstances chemical stabilisation/solidification on the site by mobile treatment plants or treatment at a local fixed plant could provide an attractive alternative.

A cost comparision (Table 6.2) of the different inorganic solidification processes applied to a simulated waste has been carried out based on a model developed by Cote and Hamilton (90). It should be noted that the Chemfix process (cement + sodium silicate) is more expensive than the Sealosafe (cement + PFA) process for liquid sludge without dewatering. However, these two processes have comparable costs after dewatering although PFA is much cheaper than sodium silicate. This is due to the difference in cost in the pretreatment, processing material doseage and volume and waste of the final products needed to be disposed of.

This economic analysis also shows the advantages of pretreating the waste prior to solidification. The cost of pretreatment by precipitation with lime and dewatering can be offset by the saving resulting from the decrease in waste volume for solidification. However, the exact processing procedure, with or without pretreatment should be carried out on a case by case basis, depending on the size of the project and the availability of processing facilities.

Table 6.2 Total annual cost ($ 1982)* to dispose of 1 m^3 of the synthetic solution through different pretreatment and solidification alternatives (90)

	Solidified as:		
	Solution	Liquid Sludge 8.2% TS	Dewatered Sludge 23.5% TS
Cement	-	109	-
Fly ash	-	49	-
Fly ash - lime	130	50	35
Fly ash - cement	133	54	37
Bentonite - cement	194	81	47
Soluble silicates - cement	184	67	38

*£1 = $ 1.8 (1985)

Note: The calculated costs are based on the model and include pretreatment, solidification and landfilling costs.

Based on the results of this present research, a more economic approach to solidification processes has been devised by using a combination of Chemfix and Sealosafe. Since the chemical (leaching) behaviour of Chemfix and Sealosafe are similar for most heavy metal wastes, a comparision of the reagent costs with respect to the physical quality is estimated and is presented in Table 6.3.

Table 6.3 Material cost comprison of Chemfix, Sealosafe and combined systems

	Strength (Nmm^{-2})		
	1 day	28 days	cost (£/tonne)*
Chemfix (cement + silicate) W/C = 1; Si/C = 0.05	0.99	5.59	64
Sealosafe (cement + flyash) W/S = 0.5; PFA/OPC = 3	0.57	4.03	36
Combined (cement + flyash + silicate) W/S = 1; Si/S = 0.1; PFA/OPC = 0.33	1.32	4.71	50

*For simulated solution waste, real waste may contain a higher percentage of solids which would reduce the amount of processing material needed.

The above cost comparison illustrates that the combined system is more expensive than the Sealosafe process but is less expensive than the Chemfix process. However, it should be noted that the Sealosafe process uses nearly twice as much stabilising agents than the other two systems (i.e. Sealosafe W/S = 0.5, other W/C = 1.0) which will increase its transportation and final disposal costs.

Although the strength values at 28 days are in the order of Chemfix > combined system > Sealosafe. The 1 day strength values show that, the combined system achieved the highest rate of setting. This is important as far as the early chemical and physical qualities of the solidified product are concerned as the initial stage after solidification is often the most critical period in the whole treatment operation.

The use of PFA in the combined system also exploits the sorption capacity of the PFA particles for certain inorganic waste pollutants. This substantiates the immobilisation potential of the ordinary cement/silicate matrix.

The major factors affecting the use of cement based solidification processes in the waste disposal industry are environmental acceptability and economics.

The long term stability of the solidified products in a landfill environment has been the major concern in using the solidification process. While it is generally promoted by the vendor companies that the treatment process is capable of producing a monolithic solid with reduced leachability, until there is adequate scientific evidence and field validation of these claims, extensive application of the process will not be possible. Many of these processes have been operated purely in an empirical manner with varying degrees of success so that public confidence in their use has been reduced. The approach being used in this research, employing micro and macro analysis, has provided an understanding of the fundamental mechanisms involved in the solidification processes. More research is needed to establish the long term leaching behaviour of the solidified material, especially on the suitability of its use for solid waste in the dilute-and-disperse landfilling strategy practiced in the UK.

It is evident that the solidification process is much more expensive than conventional practiced landfill (3-5 times) and it is therefore likely to be economically attractive only in areas where there is a shortage of landfill sites licensed to accept hazardous and/or special waste. But the findings of the Hazardous Waste Inspectorate (9) illustrate the problems of conventional landfill disposal of hazardous waste. The "Best Practicable Means" strategy of waste disposal generally adopted in the UK does not suggest a "cheapest tolerable means" approach generally practiced in the waste disposal industry. It has been suggested that the indiscriminate use of direct landfill as the major disposal route for hazardous waste should be corrected in order to provide economic incentives for a high quality truly professional waste disposal industry.

With growing environmental pressure and changing legislation, especially within the EEC and the US there may soon be a case for the extensive use of solidification procedures. There are a number of economic factors which would positively influence the use of the solidification process and these are summarised below:

i) More selective use of high quality landfill for special wastes for which there are no simple alternative treatment/disposal options.

ii) Increased restriction on transport of problem waste encouraging the use of on-site treatment.

iii) Setting up a centralised plant for hazardous waste treatment and incorporating the solidification process as an integrated part of the treatment options.

Furthermore, it has been put forward by the process operators that the solidified material can be used as fill or construction material. If enough scientific and engineering evidence is obtained for the long term physical behaviour of the solidified material to uphold these claims, the soldification process would have an extra cost advantage over landfill. However, more research is needed in order to establish this benefit.

6.5 Proposed quality control test procedure for solidification process

The most important factor affecting the use of solidification processes is the long term stability of the product in a normal landfill environment. Public confidence as well as that of the waste producers and waste disposal controlling agencies cannot be achieved unless there is a thorough understanding of the mechanisms affecting the stability of the solidification product. There is still no consensus on the testing method to assess the physical and chemical properties which would give an indication of the long term performance of the product. A recent study by Rushbrook et al. (92) has attempted to define empirically these characteristics by a simple cone penetrometer test (conforming to BS 1377:1975). They have suggested that the performance of the solidified waste can be monitored by measuring the penetration depth of the cone. They defined a satisfactory mix design should have a penetration depth of less than 1.5 mm after 7 days and 0.5 mm after 28 days. They found a reasonable correlation between the setting behaviour measured by the penetrometer with the leaching behaviour as defined by the Waste Research Unit leaching procedure (93).

However, in this present study, two mechanisms have been identified for stabilising hazardous pollutants in the cementitious matrices; namely - chemical fixation and physical encapsulation. Types of waste which are stabilised by either of these processes have been identified. Generally, inorganic cationic wastes are stabilised by chemical means while inorganic anionic and organic substances depend on a physical barrier to prevent contact with the leaching environment. Therefore it is unlikely that a simple cone penetration test which is designed to measure the physical properties will be able to indicate the long term performance of the solidified waste. (Furthermore, the cone penetrometer results are too susceptible to surface effects such as drying, shrinkage and carbonation).

Testing methods should be devised to assess the chemical and physical capabilities of the cementitious matrices to prevent leaching. A standardised leaching test based on the one developed by the Waste Research Unit at Harwell (Appendix C) can be used to assess the chemical potential of stabilisation. A strength testing method based on the pocket penetrometer method (Section 5.3) could be used to assess the physical integrity of the solidified mass. A ranking system can then be developed based on the results from these tests to define the quality of the solidified waste.

A large scale column test designed to simulate the actual landfill condition should then be conducted to validate the ranking system developed. This would give the assurance and scientific knowledge needed to test the suitability of any solidified waste for landfill disposal. Once this assurance is established, the simple ranking system can be used as the quality test procedure.

6.6 Recommendations for further work

1. The full advantages of using Ordinary Portland Cement, pulverised fuel ash and sodium silicate in a combined solidification procedure should be evaluated. Attention should be paid to the development of an optimum mix design for a specific compatible waste stream so as to reduce the leaching potential and improve the short and long term mechanical properties. A detailed economic appraisal should be conducted for the alternative procedure.

2. Long term prediction of the leaching behaviour of the solidified waste based on the understanding of the leaching mechanism from this research should be conducted. Parameters other than the buffering capacity and pH which would affect the leaching characteristic should be investigated.

3. The ranking system proposed for the quality control of the solidified waste should be further developed. This system should be validated by at least a small scale field monitoring exercise.

4. Further work is also required to establish the relationship between the gas and water permeabilities for the solidified material.

5. Development of stabilisation agents for the immobilisation of organic wastes as cement, pulverised fuel ash and silicate possess little retention for organic materials. However, these stabilisation materials should be compatible with the cementitious systems and should not induce significant deterioration to the physical properties of the solidified matrices.

7 CONCLUSIONS

7.1. The fixation mechanisms of heavy metals is related to the microstructure of the cementitious matrices. A good correlation was obtained between the macro properties (leaching, strength and permeability) and micro properties (morphology, pore structure, crystalline constitutents and local chemical environment) of the solidified products examined by scanning electron microscopy, x-ray diffraction, mercury intrusion porosimetry and extended x-ray absorption fine structure.

7.2. Two immobilisation mechanisms have been identified for the retention of heavy metals in the cementitious matrices, namely: chemical fixation and physical encapsulation. Zinc and cadmium were immobilised mainly by the chemical fixation mechanism and mercury was retained by a combination of the two mechanisms.

7.3. A similar chemical mechanism was responsible for the immobilistion of zinc and cadmium. Both metals retarded the hydration of the cementitious matrices by forming a coating on the cement particles. The degree of retardation depended on the stability of this coating. The hydration retardation resulted in a deterioration in the physical properties of the solidfied products in terms of strength and permeability.

7.4. The addition of mercury in the form of mercuric nitrate and mercuric chloride did not significantly interfere with the hydration of cement. Two different chemical reactions were operative in retaining mercury in the Chemfix and Sealosafe processes. A pure chemical precipitation took place in the Chemfix process but a combination of precipitation and sorption/ chemisorption occurred in the Sealosafe process.

7.5. Pulverised fuel ash was able to take up mercury from solution by sorption and/or chemisorption but showed little retention for zinc and cadmium.

7.6. Zinc was able to form a definite local environment in the cementitous matrices. This was related to the retarding effect of the metal on cement hydration. In contrast, the local environment of mercury was highly disordered which explained why mercury did not interfere with the normal hydration of cement.

7.7. The retarding effect of metals on the physical properties of the solidified products was in the descending order of

$$Zn > Cd > Hg(NO_3)_2 > Control > HgCl_2$$

7.8. The precipitated product of zinc in the cementitious matrices was not a simple zinc hydroxide or zinc silicate but was of complex composition with a 4-oxygen co-ordinated first shell.

7.9. The addition of zinc and cadmium increased the proportion of calcium sulphoaluminate hydrates (ettringite and monosulphate) in the solidified matrices and resulted in a more open pore structure.

7.10. The results of the study invalidated the mechanisms of immobilisation proposed by the companies who market the processes.

7.11. The results of the dynamic and static leaching tests demonstrated that the leach rate of pollutants of the solidified wastes depends on a particular leaching test procedure. Therefore careful interpretation is needed to assess any leach test result provided by vendor companies.

7.12. The leach rate of zinc and cadmium was low when compared to mercury in the dynamic leaching test.

7.13. The cement based solidification process is incapable of chemically immobilising phenol.

7.14. The buffering index of the leaching environment has been identified as one of the most important parameters in affecting the leaching behaviour of the solidified products.

7.15. The use of pulverised fuel ash provided a buffer to the highly alkaline cement pore fluid and reduced the leach rate of certain heavy metals which are amphoteric in nature.

7.16. The static leaching test results demonstrated the importance of the physical properties of the solidified product in relation to leaching. Soldified products with poor physical properties degraded easily in the leaching environment and resulted in a high leach rate.

7.17. The leaching mechanism of the solidified waste was related to the microstructure. The ettringite phase was identified as an indicator of the degree of deformation to the structure responsible for the retention of pollutants. The breakdown of the microstructure was related to the percentage of calcium released from the matrices.

7.18. The most critical parameter governing strength of the solidified product was the water/cement or water/solid ratio. This was also related to the porosity of the hydrated matrices. However, the cement content was also important in governing the strength and permeability of the Sealosafe process.

7.19. Sodium silicate formed a gel with the calcium released from the cement. This gel greatly accelerated the setting of the matrix and increased the water demand. However, the gel contributed little to the long term strength of the solidified product.

7.20. The use of pulverised fuel ash in the Sealosafe process reduced the water demand and the setting rate. This resulted in the occurrence of supernatant water. The strength development of the Sealosafe blended system was slow when compared to Chemfix.

7.21. Adding sodium silicate to the Sealosafe process accelerated the setting rate and contributed to the long term strength of the solidified matrix.

7.22. Extensive drying shrinkage resulted when too high a dose of sodium silicate was used to increase the water demand.

7.23. Oxygen permeability test methods provided a quick and reliable assessment of the physical quality of the solidified waste.

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APPENDIX A

Categories of substances subject to the Control of Pollution (Special Waste) Regulations 1980

1. Acids and alkalis.
2. Antimony and its compounds.
3. Arsenic compounds.
4. Asbestos (all forms).
5. Barium compounds.
6. Beryllium and its compounds.
7. Biocides and phytopharmaceutical substances.
8. Boron compounds.
9. Cadmium and its compounds.
10. Copper compounds
11. Heterocyclic organic compounds containing oxygen, nitrogen and/or sulphur.
12. Hexavalent chromium compounds.
13. Hydrocarbons and their oxygen, nitrogen and/or sulphur compounds.
14. Inorganic cyanides.
15. Inorganic halogen-containing compounds.
16. Inorganic sulphur-containing compounds.
17. Laboratory chemicals.
18. Lead compounds.
19. Mercury compounds.
20. Nickel and its compounds.
21. Organic halogen compounds, excluding inert polymeric materials.
22. Peroxides, chlorates, perchlorates and azides.
23. Pharmaceutical and veterinary compounds.
24. Phosphorus and its compounds.
25. Selenium and its compounds.
26. Silver compounds.
27. Tarry materials from refining and tar residues from distilling.
28. Tellurium compounds.
29. Thallium and its compounds.
30. Vanadium compounds.
31. Zinc compounds.

APPENDIX B

Table B1. Aqueous chemical experimental data for cement

Time (mins)	a	b	c	d	e
			pH		
1	12.5	11.3	12.3	12.5	12.1
3	12.6	11.8	12.5	12.5	12.2
5	12.6	12.1	12.5	12.5	12.2
10	12.7	11.8	12.5	12.5	12.3
15	12.8	11.8	12.5	12.5	12.3
20	12.8	11.8	12.6	12.6	12.4
50	12.9	12.3	12.8	12.8	12.5

Time (mins)	a	b	c	d	e
			Ca Concentration (ppm)		
1	1005	1426	1123	1038	993
3	1125	1644	1312	1238	1146
5	1300	2071	1607	1326	1395
10	1275	1892	1553	1291	1361
15	1300	1607	1553	1326	1395
20	1300	916	1560	1326	1381
50	1400	734	1517	1430	1361

Time (mins)	b(Zn)	c($HgCl_2$)	d($Hg(NO_3)_2$)	e(Cd)
		Metal concentration (ppm)		
1	4.87	164	159	nd
3	11.07	153	150	nd
5	23.37	149	169	nd
10	4.63	149	198	nd
15	3.63	137	183	nd
20	3.45	137	154	nd
50	2.22	138	176	nd

* (a) water
(b) $Zn(NO_3)_2$
(c) $HgCl_2$
(d) $Hg(NO_3)_2$
(e) $Cd(NO_3)_2$

Table B2 Aqueous chemical experimental data for pulverised fuel ash

Time (mins)	a	b	c	d	e
			pH		
1	5.8	5.5	6.2	5.5	5.5
3	6.2	5.5	7.0	6.0	5.5
5	7.0	5.5	7.0	6.2	5.8
10	8.5	5.5	7.0	6.4	5.8
15	8.6	5.5	7.2	7.0	5.8
20	9.0	5.5	7.5	7.0	5.8
50	9.0	5.5	7.6	7.5	5.8

Time (mins)	a	b	c	d	e
			Ca Concentration (ppm)		
1	220	295	257	452	260
3	287	350	377	460	322
5	312	370	530	520	325
10	322	440	455	480	325
15	335	375	485	520	345
20	340	420	600	556	395
50	347	430	530	520	415

Time (mins)	b(Zn)	c($HgCl_2$)	d($Hg(NO_3)_2$)	e(Cd)
		Metal concentration (ppm)		
1	1578	1183	30	1428
3	1600	1050	25	1350
5	1500	650	20	1350
10	1600	483	30	1250
15	1580	277	98	1250
20	1500	185	166	1300
50	1300	115	335	1100

Table B3 Aqueous chemical experimental data for Chemfix

Time (mins)	a	b	c	d	e
			pH		
1	12.3	11.3	12.3	12.3	12.1
3	12.5	11.8	12.3	12.5	12.2
5	12.3	12.0	12.1	12.1	12.3
10	12.5	11.8	12.1	12.1	12.1
15	12.5	11.8	12.3	12.3	12.3
20	12.5	12.0	12.3	12.3	12.3
50	12.8	12.5	12.6	12.8	12.5

Time (mins)	a	b	c	d	e
			Ca Concentration (ppm)		
1	1005	1426	1123	1038	993
3	1125	1644	1312	1238	1146
5	525	950	675	575	500
10	35	215	40	40	35
15	20	170	25	20	25
20	20	175	35	20	25
50	80	160	155	166	145

Time (mins)	b(Zn)	c($HgCl_2$)	d($Hg(NO_3)_2$)	e(Cd)
		Metal concentration (ppm)		
1	3.78	164	159	nd
3	5.88	153	150	nd
5	10.50	112	100	nd
10	1.06	62	75	nd
15	0.33	75	62	nd
20	0.30	62	62	nd
50	0.61	75	70	nd

Table B4 Aqueous chemical experimental data for Sealosafe

Time (mins)	a	b	c	d	e
			pH		
1	11.1	5.9	11.1	11.2	6.0
3	11.4	6.0	11.5	11.4	9.0
5	11.6	6.0	11.6	11.6	9.0
10	11.7	6.0	11.7	11.8	10.0
15	11.8	9.0	11.8	11.8	11.0
20	12.0	10.0	11.9	11.9	11.6
50	12.1	11.0	12.0	12.0	12.1

Time (mins)	a	b	c	d	e
			Ca Concentration (ppm)		
1	393	750	731	753	675
3	450	1062	893	874	900
5	415	1287	900	875	950
10	412	1175	925	825	937
15	480	1500	760	875	950
20	530	1425	890	937	1000
50	600	1050	900	875	1125

Time (mins)	b(Zn)	c($HgCl_2$)	d($Hg(NO_3)_2$)	e(Cd)
		Metal concentration (ppm)		
1	866	251	268	255.0
3	662	240	238	21.5
5	260	236	203	0.4
10	142	231	194	0.1
15	30.4	185	185	nd
20	2.23	208	189	nd
50	2.69	208	194	nd

Table B5 Aqueous chemical experimental data for Chemfix/Sealosafe

Time (mins)	a	b	c	d	e
			pH		
1	11.1	5.9	11.1	11.2	6.0
3	11.4	6.0	11.5	11.4	9.0
5	11.8	6.3	11.5	11.5	11.0
10	12.1	10.3	12.0	11.8	11.2
15	12.1	10.4	12.1	11.9	11.5
20	12.2	11.0	12.1	12.1	11.6
50	12.4	11.5	12.2	12.1	11.7

Time (mins)	a	b	c	d	e
			Ca Concentration (ppm)		
1	393	750	731	753	675
3	450	1062	893	874	900
5	30	365	102	90	147
10	5	15	5	7	7
15	5	10	7	6	6
20	6	11	5	5	5
50	5	27	7	6	4

Time (mins)	b(Zn)	c($HgCl_2$)	d($Hg(NO_3)_2$)	e(Cd)
		Metal concentration (ppm)		
1	866	251	268	255
3	662	240	238	21
5	121	143	143	1.94
10	18.4	175	69	0.2
15	0.7	56	56	0.3
20	0.3	56	50	0.2
50	0.2	68	50	0.3

APPENDIX C

Experimental Procedure for the Waste Research Unit Laboratory Leaching

Equilibrium shaker test (duration 4 to 80 hours)

1. Place a suitable sample of waste (e.g. 50 to 100 cm^3) into a 500 ml wide-necked flask.

2. Add one bed volume* of model leachate from a measuring cylinder, this should be about 30 to 100 mls. Two model leachates are suggested; for mono-disposal of the waste, distilled water should be used as a simulation of rainfall, but if co-disposal with domestic refuse is considered, 500 ppm acetic acid buffered to pH5 with sodium hydroxide should be used, to simulate landfill leachate.

3. After adding the model leachate, stopper the flask and shake on a mechanical flask shaker for one hour. The shaking should be vigorous enough to thoroughly mix the contents of the flask, about ten cycles per second for a mechanical shaker.

4. After one hour a suitable quantity of the liquid needs to be recovered for analysis. This should preferably be no more than 10% of the volume of model leachate added in step 2. In order to recover this liquid it will usually be necessary to filter a portion of the flask's contents. A Whatman No. 541 filter paper inserted in a Buchner funnel, with a side-arm test tube or vacuum flask, connected to a suction device is suitable for this purpose. Particularly intractable wastes such as some sludges may require centrifuging before attempting to filter, and millipore apparatus may be used to remove small particles from solution, if the initial filtering does not give a reasonably clear solution.

*"The volume of liquid required to just cover and render mobile a given sample of waste".

5. Apart from the liquid sample, the entire contents should be replaced in the flask together with enough model leachate to replace the volume extracted for sampling.

6. The procedure outlined in steps 3, 4 and 5 should be repeated at hourly intervals until four samples have been collected. It is then suggested that the flask is shaken for the rest of the day (e.g. another four hours) and that analysis of the samples collected so far should proceed.

7. If no equilibrium is apparent from the first day's samples, further samples should be taken after shaking for 24, 32, 48, 56, 72 and 80 hours (i.e. morning and afternoon for three days).

8. Analysis

Suitable analysis will depend on the species of interest for the particular waste which is under test. However it is suggested that pH and conductivity give a good general guide and that only very important toxic species and easily determined species are analysed individually at this stage. For example, only one or two metal species if a sludge from an electroplating shop is being tested. An atomic absorption spectrophometer is a suitable tool for rapid analysis of metals, which require very little sample.

9. Interpretation

Many wastes will be found to give steady values of pH, conductivity and species in solution within a few hours of shaking. A shaking time which is sufficient to allow equilibrium to be established with the waste should then be selected for the repetitive shaker test. A period of two to four hours is most usual. A small number of wastes will require up to 80 hours before the samples taken are found to give consistent results indicating equilibrium. For these wastes, a longer repetitive shaking time will be required, and for this reason the test procedure will take an extended time to complete. A maximum shake time of 80 hours is suggested, not only

due to the practical problems of such an extended test, but also because percolation rates in a landfill would not normally allow establishment of equilibrium conditions, if that cannot be achieved within 80 hours in a vigorous shaking test. For such wastes the leaching will be controlled by kinetic factors and the determination of an accurate equilibrium time is not necessary. In order to maintain a worst case under these circumstances, a repetitive shaking time should be chosen which corresponds to the maximum concentrations observed in the model leachate during the 80 hour equilibrium test.

10. The repetitive shaker test can now be carried out.

Repetitive shaker test (Time required normally 2 to 9 days)

1. Set up flask as for the equilibrium test, so that it contains the sample of waste and one bed volume of suitable model leachate.

2. Shake for the time determined by the equilibrium test.

3. After shaking the leachate needs to be separated for analysis. Normally the flask's contents can be successfully vacuum-filtered through a Whatman No. 541 filter paper. As with sampling during the equilibrium test, this may be supplemented by prior centrifuging of the flask's contents and secondary filtering through millipore equipment when necessary.

4. Return as much of the filtered waste as is practical to the flask. If the experiment is to be left overnight it should be at this stage before the next bed volume of model leachate is added.

5. The next bed volume of model leachate should be added to the waste. In most cases this will be the same volume as used originally, but for wastes which are highly soluble or undergo substantial physical changes it is advisable to use the criteria of just covering the waste returned to the flask, instead of automatically adding the same volume again. This approach can also be used to allow

continuation of the test if some of the waste is lost during the filtering operations. The volume of model leachate added at each stage should be recorded so that total releases of contaminant can be calculated from the concentrations in the leachate samples.

6. Steps 2 to 5 should be repeated so that a leaching over a total of five bed volumes is carried out. After separating the fifth bed volume of leachate, a quantity of the waste equivalent to only one tenth of that originally used should be returned to the flask.

7. Ten bed volumes should be added to the waste in the flask, which will normally mean adding the same volume of model leachate as was done for the first bed volume. As before, wastes which have undergone obvious physical changes should have their bed volumes redetermined at this stage, especially since ten, rather than one bed volumes are added. The flask should then be sealed and shaken as before. After shaking, the contents should then be separated and the waste returned to the flask.

8. The leachate collected after this stage represents the average leaching over six to fifteen bed volumes, and can be considered as giving an estimate of the leaching after 10 bed volumes. It is now advisable to analyse the six samples collected at this stage, together with any fluid removed from the waste during the preparation stage.

9. If further monitoring over a longer period of leaching is required, step 7 can be repeated to give samples indicative of leaching after 20, 30, 40 etc, bed volumes.

10. Analysis

The solutions obtained can be analysed for any species or properties likely to be of concern. Since a much larger volume of liquid is retained than in the equilibrium test, a more

comprehensive analysis may be carried out and it is these results which may be used to predict the suitability of the waste for landfill disposal. With many wastes the leaching over ten bed volumes will be found to have reduced all species to insignificant levels, but longer term leaching can be carried out by repeating step 7 for as long as is thought necessary.

11. Interpretation

The result may be expressed as a plot of concentration against bed volumes leached if the maximum concentration of the contaminant in the leachate is required. Alternatively, the total release may be significant, and a histogram of absolute releases in mg/kg of waste is then most appropriate. In order to plot the latter the volume of each bed volume is required to convert concentrations to absolute quantities of contaminant (see stage 5). Any interstitial fluid recovered from the waste during prepration may be plotted as that leached after zero bed volumes, i.e. before any leachate has interacted with the waste.

Attentuation factors may be calculated as the ratio of the concentration in the waste as deposited to the maximum concentration in the leachate. These may then be used in conjunction with other attentuation factors appropriate to the particular landfill site to decide whether deposition of the waste is going to adversely affect the leachate quality. The concentration factors can be also used to estimate the quantity of waste which can be tolerated at the site to keep the leachate quality within target objectives.

APPENDIX D

Table D1: Extended leaching test results of 0.15 M buffered HAC leachate of Chemfix with Zn and Hg

Elution		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
pH		11.8	11.6	11.2	11.0	10.9	10.3	9.8	9.0	8.0	8.3	7.3	7.3	7.0	6.7	6.1
Zn	(ppm)	1.3	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.4	5.4	27.5	68.85	111.6
Hg	(ppm)	42	32	27	16	16	14	8	6	4	3	4	5	6	5	11
Ca	(ppm)	1143	2237	2462	2087	2600	2925	3825	4125	4187	3362	3750	3112	3087	3037	2675

Table D2: Extended leaching test results of 0.3 M buffered HAC leachate of Chemfix with Zn and Hg

Elution		1	2	3	4	5	6	7	8	9	10	11
pH		11.6	11.2	10.7	10.1	9.4	8.7	8.2	7.0	6.7	5.4	5.0
Zn	(ppm)	2.4	0.1	0.1	0.1	0.2	0.9	0.1	87.2	175.0	254.0	135.0
Hg	(ppm)	60	56	35	20	15	11	10	14	39	83	116
Ca	(ppm)	3437	5325	5500	6675	6375	4800	4650	4350	5570	3175	1150

Table D3: Extended leaching test results of 0.5 M buffered HAC leachate of Chemfix with Zn and Hg

Elution		1	2	3	4	5	6	7	8
pH		11.5	11.0	10.1	8.7	8.0	6.7	5.6	4.8
Zn	(ppm)	1.0	0.6	0.1	0.1	0.2	63.6	298.0	134.0
Hg	(ppm)	50	41	19	15	11	31	84	112
Ca	(ppm)	4287	4700	8050	7575	7350	5850	5425	4750

Table D4: Extended leaching test results of 0.15 M buffered HAC leachate of Sealosafe with Zn and Hg

Elution		1	2	3	4	5	6	7	8	9	10	11
pH		11.8	11.4	10.9	10.4	9.9	9.6	8.8	8.3	7.7	6.5	5.5
Zn	(ppm)	0.13	0.05	0.05	0.05	0.04	0.04	0.28	0.03	0.26	23	85
Hg	(ppm)	3.7	1.5	1.0	1.5	1.5	1.0	0.6	0.9	0.7	0.9	2.7
Ca	(ppm)	2556	1929	1911	1911	1185	2450	2541	3458	3489	3229	2386

Table D5: Extended leaching test results of 0.5 M buffered HAC leachate of Sealosafe with Zn and Hg

Elution		1	2	3	4	5	6
pH		11.2	11.1	9.26	6.0	5.0	4.8
Zn	(ppm)	0.05	0.01	0.12	164.5	80.0	29.8
Hg	(ppm)	25	10	6	56	35	11
Ca	(ppm)	6600	7200	10368	10900	2200	600

APPENDIX E

Assessing the leaching characteristics of stabilised toxic waste by use of thin layer chromatography

Principle of method

The reagents forming the basis of the particular solidification technique under examination are mixed and spread onto a thin layer chromatography plate. Two alternative procedures are then possible. The toxic components can be spotted onto the plate immediately following its preparation and a suitable period for solidification and ageing allowed. Alternatively the toxic components can be introduced to the plate following the ageing period and immediately prior to development of the plate. The procedure is intended for aqueous components of the waste stream. For sludges containing solid, a filtering procedure is required before operation. Development of the plate is carried out in the normal way by standing in a suitable solvent which travels through the thin layer thus simulating leaching action.

Materials which are well retained by the fixation process would be expected to show little or no movement through the thin layer while components which are not well retained would be expected to travel a further distance.

Experimental

The initial work has been carried out using the standard Chemfix formulation which is a material based on cement and sodium silicate. Forty grammes of cement was added to 200 ml of distilled water and mixed. To this, 8 ml of a 40% sodium silicate solution was then added and well mixed. The resulting slurry was spread on to glass thin layer plates using a standard spreader. To prevent too rapid drying of the mix and subsequent shrinkage and cracking of the thin layer the plate was allowed to cure in a tank with a relative humidity of 86% for 28 days to allow cement hydration and normal ageing. Following this the toxic components were spotted on and the plates were transferred to a thin layer

chromatography tank and processed in the normal way using distilled water as the eluent. In some cases the progress of the solvent front could not be readily observed and it was found better to allow the solvent to run the full length of the plate by leaving it in the tank for a standard time.

The toxic components selected for initial evaluation were the cations copper, nickel, zinc and mercury, chromate and manganate anions and phenol. Detection of the free metal ions was by spraying with a dilute solution of dithiozone in carbon tetrachloride and phenol was detected by spraying with a dilute solution of 4 aminophenozone followed by a dilute solution of potassium ferricyanide. Chromate and manganate were self-indicating.

The extent of fixation of these toxic components was also evaluated by a standard column leaching test using distilled water as the eluent. The leachate was collected in 100 ml fractions and analysed for metals by atomic absorption spectrophotometry and for phenol by gas chromatography.

In a series of tests activated carbon and zeolite (type A) additives were incorporated into the standard Chemfix formulation and the retention characteristics evaluated by both methods.

Results and discussion

A set of typical results from column leaching tests on these materials treated by this process is presented in Table E1. This shows that the concentration of heavy metal ions which were well retained remained fairly constant throughout the leaching test whereas those components which were poorly stabilised had peak concentrations during the initial stages of elution and tend to a limiting value after 400 ml of water had passed through the sample. The proportion of components leached out at this stage is represented in terms of the leachate factor (L_f) where;

$$L_f = \frac{\text{sum of contaminant leached in the first four fractions (mg)}}{\text{total weight of contaminant present (mg)}}$$

Table E1

Column leaching tests and thin layer chromoatography data

Constituent	Total Content	Leachate No.* 1	2	3	4	5-10	Leachate Factor L_f	Thin Layer R_L Value
Copper	200	<0.005	<0.005	<0.005	<0.005	<0.005	<0.01	0
Nickel	200	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0
Zinc	200	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0
Mercury	200	15	11	7	9	9	0.21	0.06
Chromate	200	26	11	3	2	-	0.21	0.48
Manganate	200	32	25	5	5	-	0.33	0.75
Phenol	10	5.6	0.9	0.3	0.2	0.1	0.70	0.47

All results in mg

(*) Each leachate number represents 100 ml

The developed thin layer chromatography plates showed that the components had travelled on the plates as streaks rather than spots which are usually obtained in thin layer work, and normal R_f values therefore have little significance. The movement through the thin layer has therefore been normalised with respect to the distance travelled by the solvent front such that;

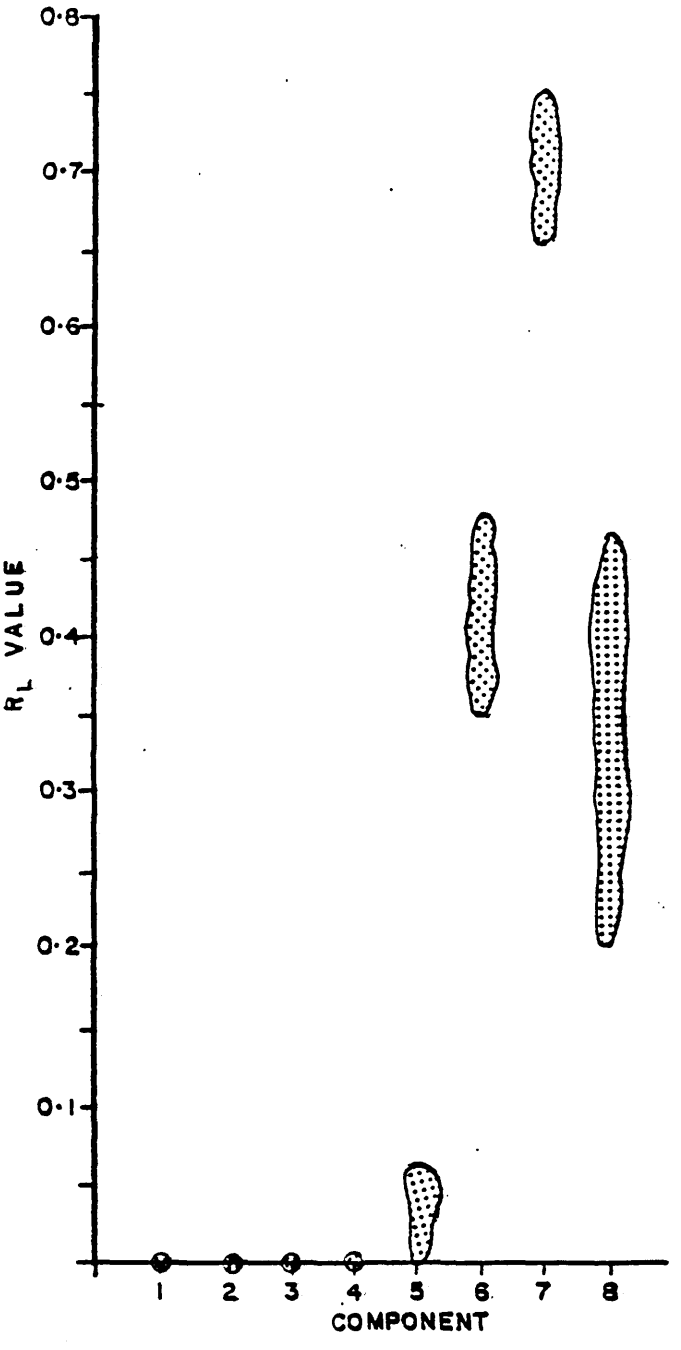
$$R_L \text{ value} = \frac{\text{maximum distance travelled by component}}{\text{distance travelled by solvent front}}$$

The normalised retention values, R_L, and the leachate factor, L_f, presented in Table E1 follow similar trends for the toxic constituents tested. A more illustrative means of comparison is given in Figure E1 which shows a copy of a typical thin layer chromatogram (a) and a histogram of the column leaching results (b). Those materials which were well retained by fixation processes showed no movement through the thin layer; mercury which was released slowly from the mix was seen to move a short distance while phenol, chromate and manganate were not retained at all well and showed pronounced movement.

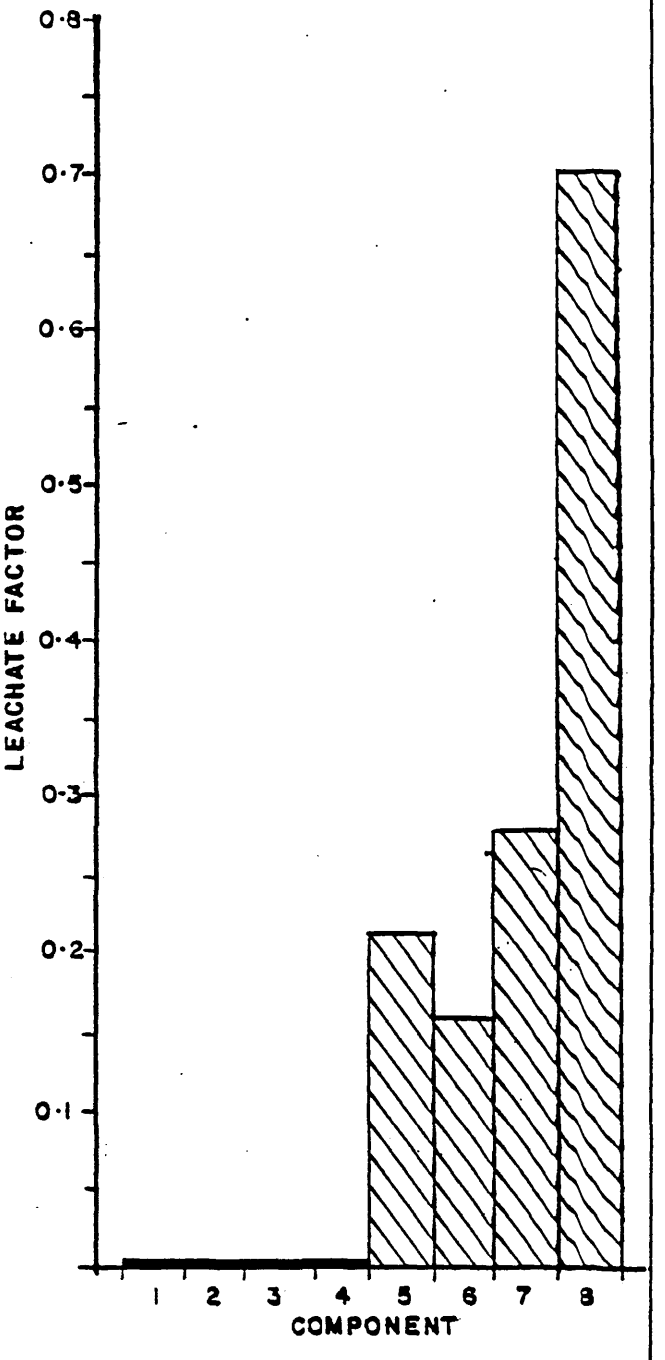
A particular feature of stabilisation processes is the use of selected materials which when incorporated in the solidification process reduce the mobility of toxic components. The effect of adding activated carbon and zeolite (type A) to the standard formulation which may be expected to influence the retention of toxic components in the mixture was therefore investigated by both test procedures and the results are represented in Table E2. These show the improvement in retention characteristics, particuarly for phenol and mercury, by these additives and further illustrates the application of this thin layer chromatography procedure for the assessment of toxic waste stabilisation processes.

It is important to note that the TLC technique measures the mobility of soluble ions within the solidified matrix and not leaching from the matrix itself. The column leaching test and the TLC method presented are therefore distinct. The former gives an indication of the leachability

a) TYPICAL THIN LAYER RESULTS



b) HISTOGRAM SHOWING LEACHATE FACTOR FROM COLUMN LEACHING TESTS



COMPONENT (2) COPPER Cu^{2+} (3) NICKEL Ni^{2+} (4) ZINC $^{2+}$

(5) MERCURY $H^{2+}g$ (6) CHROMATE CrO_4^{2-} (7) PERMANGANATE MnO_4^- (8) PHENOL

$$R_L \text{ VALUE} = \frac{\text{Maximum distance travelled by component}}{\text{Distance travelled by solvent front}}$$

$$\text{LEACHATE FACTOR} = \frac{\text{Sum of contaminant leached in first four fractions (mg)}}{\text{Total weight of contaminant present (mg)}}$$

Figure E1 Thin layer Chromotography results

Table E2

Effect of various additives on the retention of toxic components in soldified material.

Constituent	Addition to Normal (+) Mix	Concentration in Raw Sludge mg/l	Leachate Factor L_f	Thin Layer R_L Factor
Phenol	NONE	100	0.70	0.47
	1.0% Active Carbon	100	0.14	0.19
Chromate	NONE	2000	0.21	0.48
	5% Zeolite	2000	0.16	0.35
Manganate	NONE	2000	0.33	0.75
	5% Zeolite	2000	0.23	0.31
Mercury	NONE	2000	0.23	0.06
	5% Active Carbon	2000	N.D.	0.0

N.D. Not determined

(+) Normal Chemfix 200 ml waste + 40 g cement + 8 ml sodium silicate (40% solution)

of material from the cement matrix involving a two stage process; the initial solubilisation of toxic component or the products of reaction with pozzolanic and silicate material follwed by movement of the material through the solidified matrix contained within the column. The TLC method on the other hand measures only the mobility of material through the uncontaminated solidified cement/sodium silicate matrix. This measure of mobility is the common feature of the methods and one which forms the basis for comparison of these two techniques. It should be noted that the properties of Chemfix in the column procedure will be altered by the addition of metal or organic material compared to the pure cement/silicate mixture of the TLC plates. It is not known whether this difference in structure has any effect on the mobility of material through the matrix. This factor may be the cause of the observed variability in results between these two tests.

Conclusion

There is a fair degree of correlation between this method and the traditional column leaching test although in the particular case of phenol the movement through the thin layer is less than expected. The reason for this is unclear but it is evident that the method can be useful for assessing leachability of toxic components from stabilised wastes. The method is rapid, requiring no tedious chemical analysis, only colour development on the plate and gives a good visual indication of the retention or otherwise of the toxic components under consideration.

The method is currently limited to qualitative or semi-quantitative applications. Some refinement to the method is necessary and the effect of many variables needs to be examined such as the thickness of the thin layer, its water content, the effect of spotting on toxic components at different stages of solidification, detection limits and the effect of spotting real sludge samples on plates. All these factors will need thorough evaluation before the application of thin layer chromatography as a quantitative method is established. However, it is believed the method will be useful to waste disposers and companies offering inorganic

fixation processes as a rapid screening technique to determine whether particular wastes are suitable for treatment. Moreover if further work shows that there is a direct correlation between movement of components through the matrix and the degree of stabilisation, thin layer chromatography may become a useful tool for evaluating the kinetics of leaching. The rapidity with which the tests can be completed and the visual nature of the results will clearly aid research and development into solidification techniques especially where the effect of different additives on the retention of toxic components is to be evaluated.

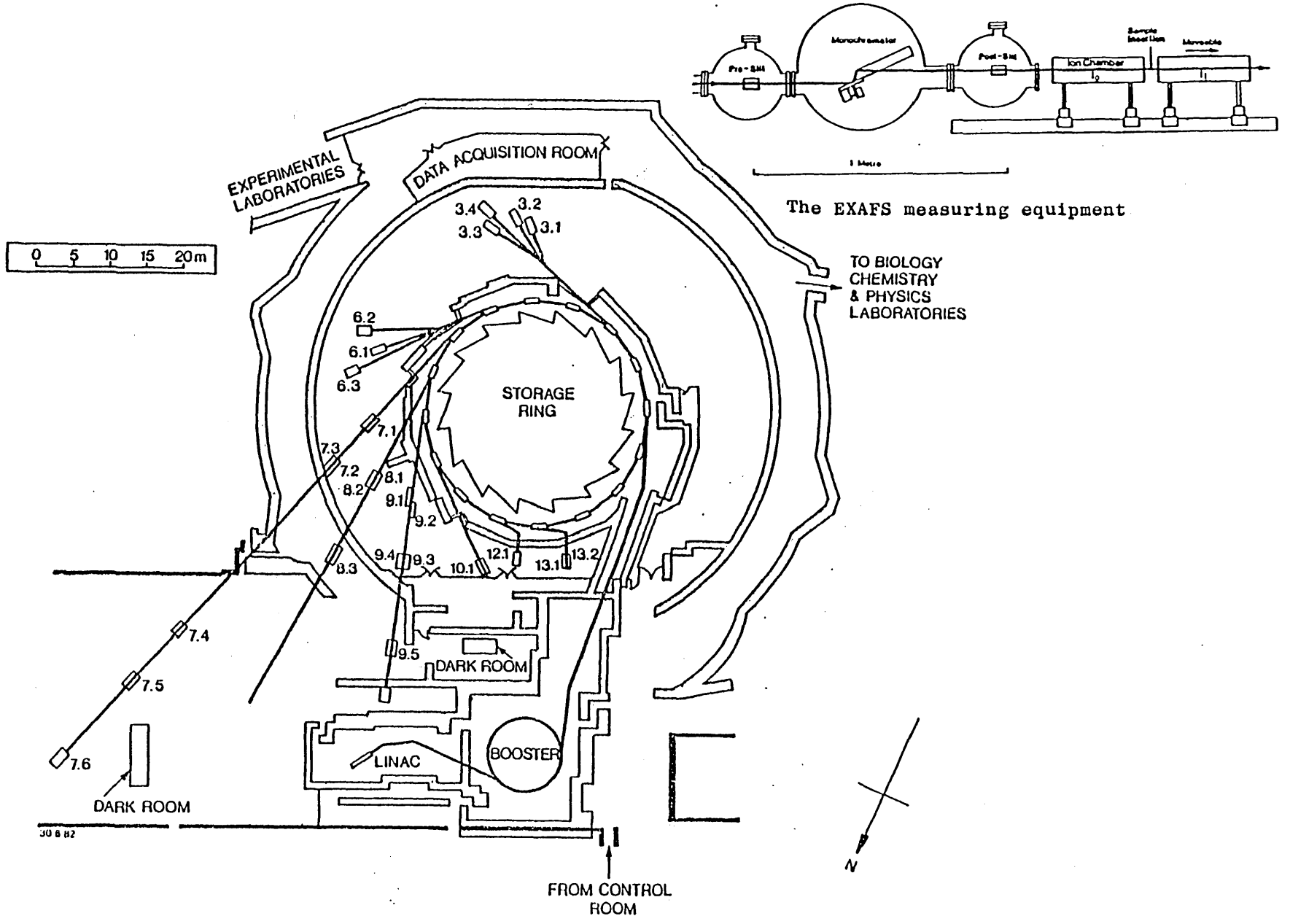


Figure F1 Schematic representation of the experimental layout at Daresbury Laboratory (Source SERC Daresbury Laboratory)

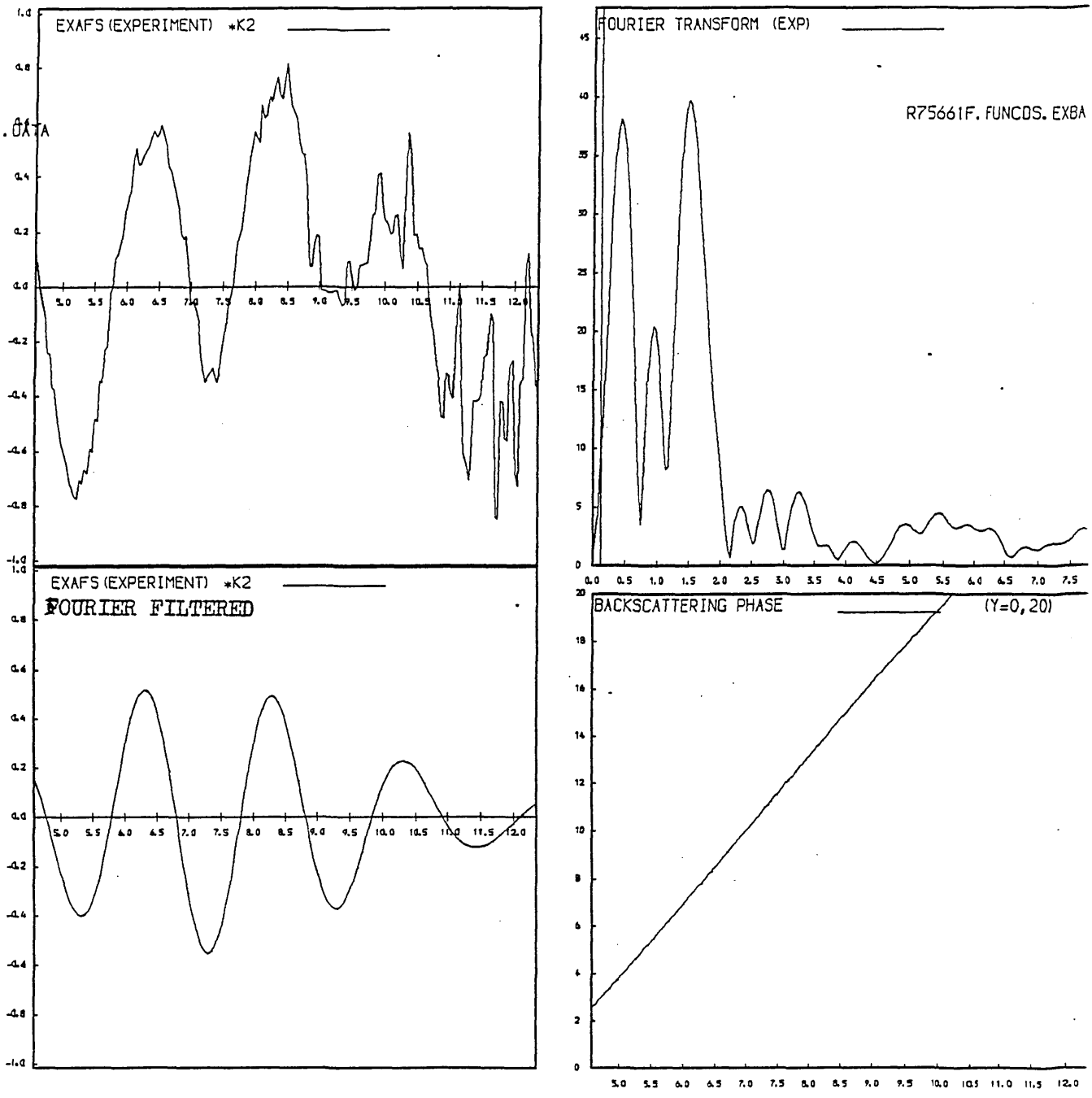


Figure F2 An example of a detail analysis of the EXAFS spectrum
a) Fourier Filter to obtain a modified spectrum of selected energy range

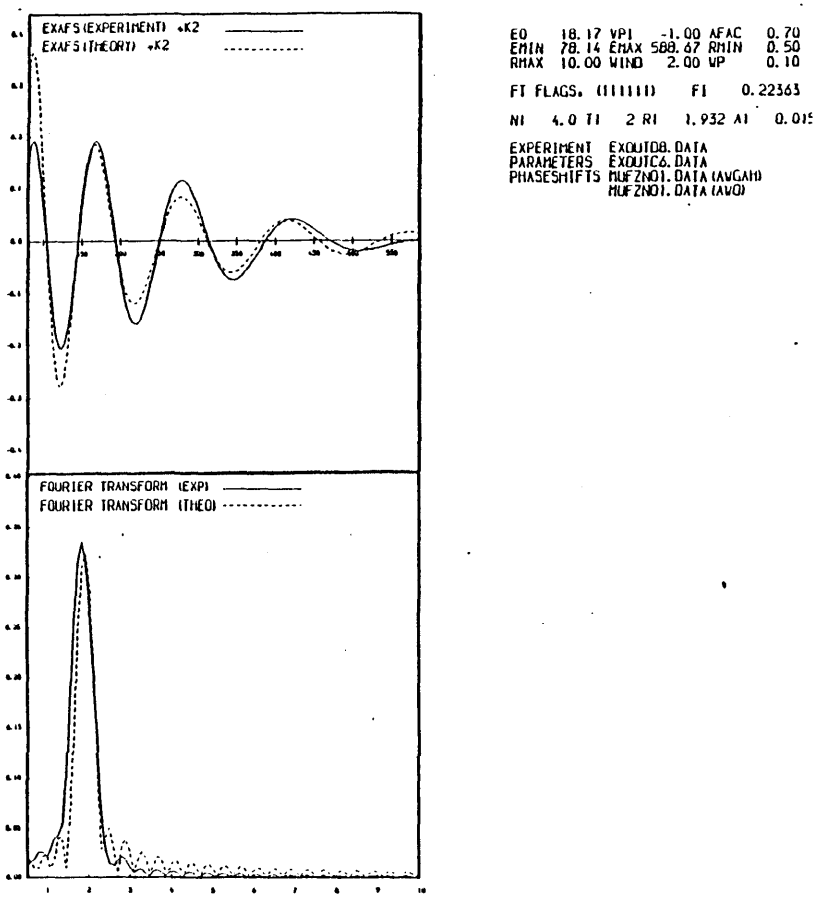
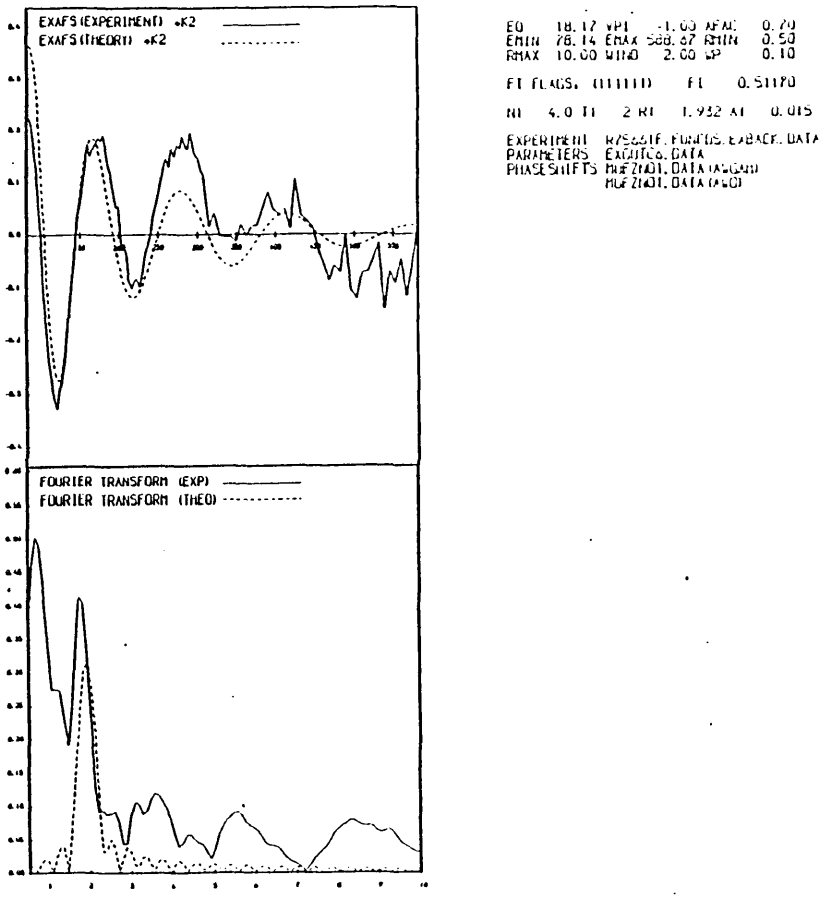


Figure F2 Cont'd

b, least square curve fitting of the filtered spectrum to obtain structural parameters



c, Back substitute the obtained parameters to the original spectrum.

APPENDIX G

Possible use of cement based stabilisation/solidification process for organic wastes

Although it is generally accepted that the cement based stabilisation/solidification process is not suitable for immobilising organic waste organic chemical admixtures have been frequently used in concrete technology as retarders, plasticisers and water reducers. The chemical compositions range from simple aliphatic hydroxycarboxylic acids to complex hydrocarbons and polysaccharides. The most commonly used organic admixtures are Ca, Na or NH_4 salts of lignosulphonic acids, or hydroxycarboxylic acids (64). The lignosulphonate molecule is a complex structure; average molecular weight of about 20,000 to 30,000 and is a phenyl propane unit with a carboxyl, hydroxyl, methoxy and sulphonic acid groups. The hydroxycarboxylic acid contains (OH) and (COOH) groups and examples of those used include citric acid, tartaric acid, and malic acid (64).

The water reducing and retardation mechanisms are related to adsorption and dispersion of the organic admixtures in the cement-water system. The retardation is primarily attributed to their effect on the hydration of C_3S phase, although some effect on the C_3A may also be important.

The nature of bonding between the organic admixture and the hydrating cement is not completely understood. It is suggested that (OH) groups in the admixture are attached to the oxygen atoms of the cement compounds through hydrogen bonding. It is also possible that the organic chemicals form bonds through the carbonyl, sulphonate and (OH) groups with the Ca or Al ions on the surfaces of the cement hydrate. Adsorption and desorption studies have indicated that it is the hydrated rather than the unhydrated cement constituents that irreversibly adsorb the organic molecules by forming a complex on the hydrated grain surface (64). Wilding *et al.* (69) studied the retardation of a range of organic admixtures on cement hydration by calorimetry. They devised a ranking system which is presented in Figure G1.

With the aliphatic acid there is a general increase in retardation with mass and number of carboxylic group. It has been suggested that the most important factor governing retardation is the presence of α or β hydrocarboxylic groups that are capable of strongly chelating with calcium. The number and position of the hydroxyl group in the aromatic series is important and may be related to their complexing capabilities with cement. The stability of the organic complex with calcium is the most important consideration in assessing the retardation of the saccharides. The general conclusions from these studies were that the chemistry of precipitation of C-S-H gel was altered by preferential complexation of organic molecules with calcium and/or silicon either in solution or by incorporation into the precipitated gel.

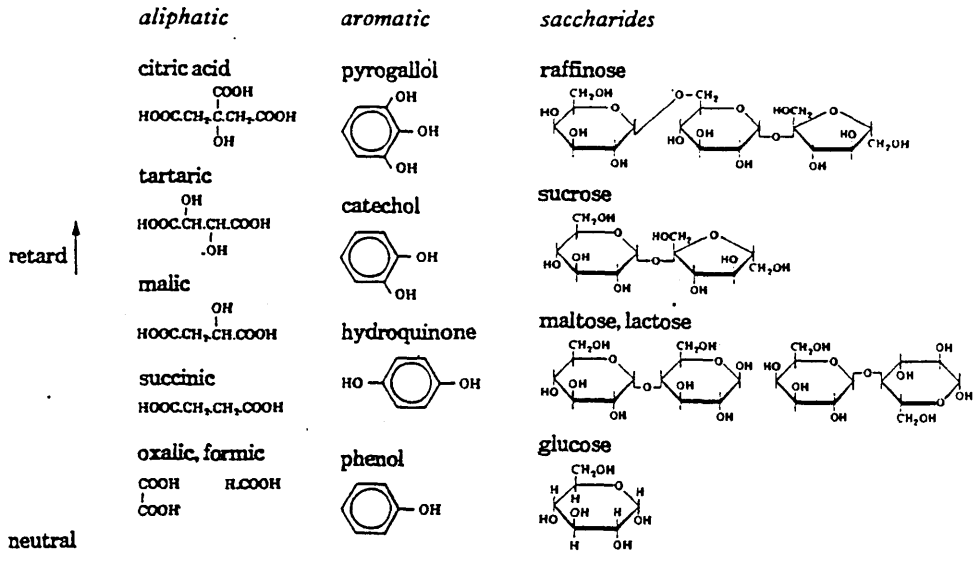


Figure G1 Retarding effect of organic compounds on cement hydration (69)

The above discussion demonstrates that organic materials have been incorporated in the cement matrices as chemical additives to facilitate mix design so as to achieve high workability with lower water/cement ratio. The chemical reaction involved is mainly complex formation between the organic admixture with the calcium on the hydrated cement surface. The extent of this complexing reaction depends on the chemical nature of the organic molecules. Adsorption studies showed that some of

the organic molecules are permanently bonded to the cement hydrate. Therefore, the full potential of using the cement based stabilisation/ solidification system for the disposal of organic waste should not be underestimated, especially when considering the possibility of sorption of chlorinated aromatics on the cementitious hydrates. Incorporation of other materials such as clays or silica may also facilitate the retention of organic compounds in the cementitious matrix.