THE IMMOBILISATION OF RADIOACTIVE WASTES

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SUMMARY

THE IMMOBILISATION OF RADIOACTIVE WASTES

Section 1 of this thesis identifies the principles of radioactive waste management and describes the sources and categories of waste generated in the nuclear fuel cycle. The practices presently used in the UK are described and the rates of production of the different categories of waste are given. The areas where research is needed to satisfy environmental considerations and public concern are identified.

Section 2 reviews the choice of cement as the immobilisation system for low and intermediate level wastes. The desire to improve cement based characteristics is discussed and the technique of incorporating polymers is reviewed. The importance of leaching characteristics is highlighted and methods of measurement are compared.

Section 3 describes experimental studies concerned with the incorporation of polymers, the polymerisation of monomers and the production and testing of composites. The preferred technique of polymerising monomers within the cement matrix during the wet cure phase of setting to form a composite is described in detail.

In Section 4, the results are discussed, conclusions are drawn and areas where further work would be beneficial are identified.

Research described in this thesis is the subject of patent applications in the United Kingdom and overseas.

KEYWORDS

Radioactive waste
Immobilisation
Leaching
Cement composites
Organic Polymers

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DEFINITIONS AND NOMENCLATURE

S.I. units of measurement are used throughout this thesis except where data are quoted from other published work. In such cases the units used by the quoted author are used.

1 Bequerel = 1 Bq = 1 disintegration per second

1 Curie = 3.7×10^{10} disintegrations per second

1 Bq = 2.703×10^{-11} curies

1 rad = energy absorption of 100 ergs per gram in any particular medium

1 Gray = 1 Gy = energy absorption of 100 joules per kilogram in any particular medium

1 rad = 0.01 Gy

1 rem = absorbed dose (rad) x quality factor

1 Sievert = 1Sv = absorbed dose (Gy) x quality factor

quality factor = 1 for X-ray, γ and β

3 for thermal neutrons

10 for α and fast neutrons

Abbreviations

AGR = Advanced gas cooled reactor
PWR = Pressurised water reactor
SGHWR = Steam generating heavy water reactor
HLW = High level wastes
ILW = Intermediate level wastes
LLW = Low level wastes

$$\frac{Wa}{Co} = \frac{\text{weight of aqueous solution (simulated waste)}}{\text{weight of organic polymers}}$$

$$\frac{Wa}{C} = \frac{\text{weight of aqueous solution (simulated waste)}}{\text{total weight of all cementitious components}}$$

$$\frac{Co}{C} = \frac{\text{weight of organic polymer}}{\text{total weight of all cementitious components}}$$

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SECTION 1.

THE PRODUCTION AND MANAGEMENT OF RADIOACTIVE WASTES IN THE NUCLEAR POWER INDUSTRY.

1.0 THE PRINCIPLES AND OBJECTIVES OF RADIOACTIVE WASTE MANAGEMENT

The fundamental objective in the management of radioactive waste is to ensure that neither the process operators involved nor the public at large receive radiation doses in excess of their respective dose limits. The dose must be kept as low as is reasonably achievable in accordance with the general principles of radiological protection. Four alternative approaches can be identified:

1. Dilution and dispersion to the environment.
2. Delay and decay.
3. Concentrate and store.
4. Disposal of wastes where practicable.

United Kingdom practice is based on the policies originally proposed in 1959 by a Government White Paper, Cmnd 884. The radiological objectives were:

1. To ensure, irrespective of cost that no members of the public will receive more radiation than the relevant International Commission on Radiological Protection (ICRP) dose limits for individual members of the public.
2. To ensure, irrespective of cost that the whole population of the country shall not receive an average dose of more than 1 rem per person in 30 years.

3. To do what is reasonably practicable having regard to cost, convenience and the national importance of this subject to reduce the doses far below these levels.

The Radioactive Substances Act 1960 implements these controls in the UK and provides for the control and disposal of radioactive waste and the control of the handling and storage of wastes at places other than major nuclear sites. Under the provisions of the Act authorisations are needed to hold, use and discharge radioactive materials to the environment in gaseous and liquid form and to dispose of solid wastes. The Nuclear Installations Act 1959 provides for the control of safety matters including waste handling and storage at licensed nuclear sites.

2.0 THE DISCIPLINES OF WASTE MANAGEMENT

All industrial processes inevitably produce waste products which have no realisable value. Society has tacitly accepted this fact for many generations yet today there is world-wide concern about pollution and environmental damage because many wastes and effluents have not been properly dealt with in years gone by. Legacies of long term hazards from the disposal of mercury, toxic heavy metals, hydrocarbons and insecticides are now apparent.

3.0 THE CLASSIFICATION OF WASTES

The categories of radioactive waste encountered in the nuclear industry are shown in Table 1.

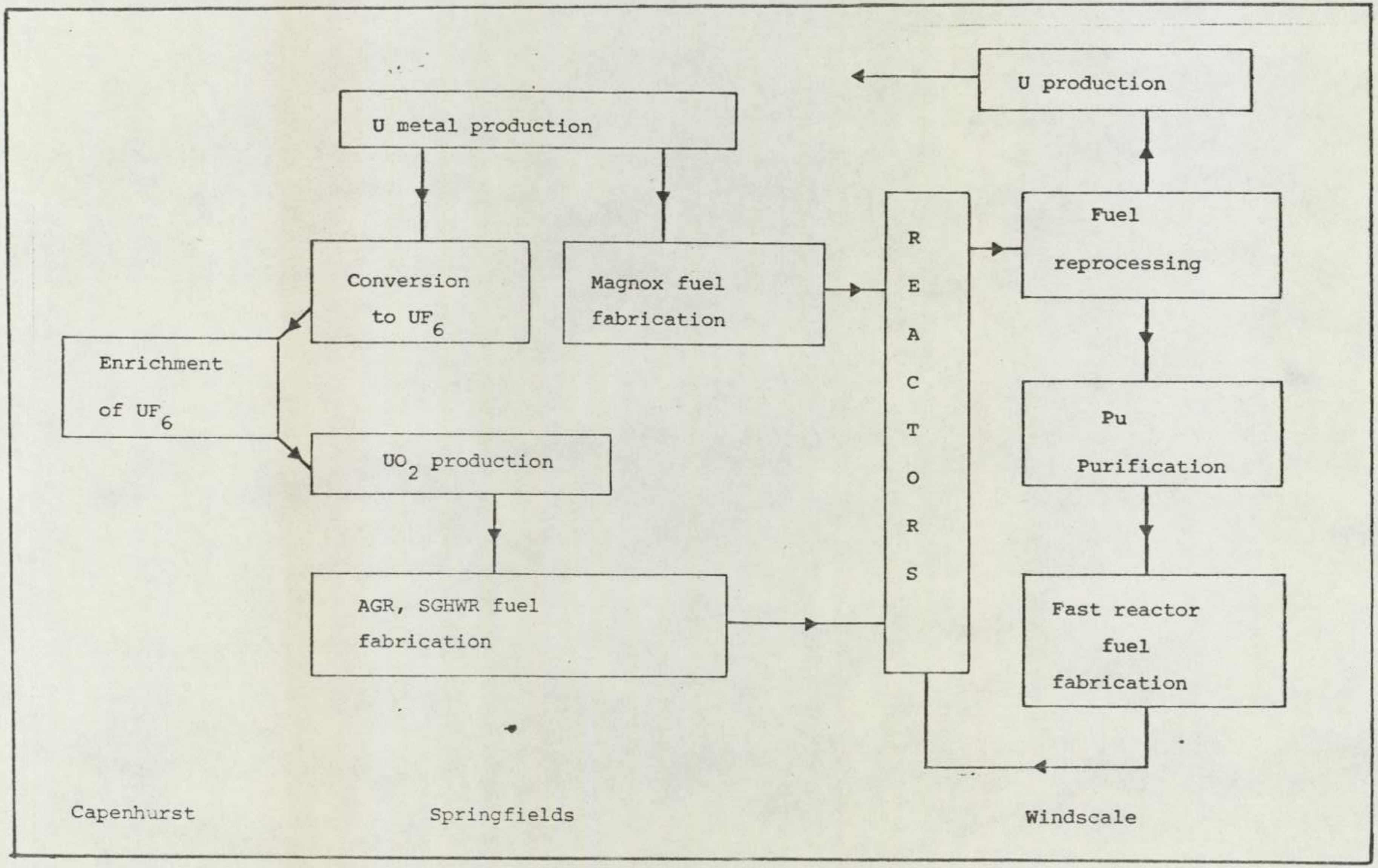


Fig. 1. THE NUCLEAR FUEL CYCLE.

Table 1 Classification of Radioactive Wastes

Waste Category as generated	Gross Radioactivity $Ci\ m^{-3}$ (upper limit)
Low (LLW)	10^2
Intermediate (ILW)	10^4
High (HLW)	10^7

4.0 THE NUCLEAR FUEL CYCLE

Fig. 1 shows the main features of the Nuclear Fuel Cycle.

4.1 Uranium Mining, Milling and Refining

Uranium is found in such minerals as Carnotite, a potassium uranium vanadate and Autunite, a hydrous phosphate of calcium and uranium, in sandstone formations in North America, Western Europe, Australasia, Latin America, Africa and India. There is no uranium mining in the United Kingdom.

After crushing, the ore is wet ground in rod mills to a slurry containing 65% solids. This is then leached with sulphuric acid and an oxidant. The slurry passes through hydrocyclones and thickners and the tailings pumped to a tailings pond to which, ultimately, 97% of the ore is discharged. The leach liquid contains the uranium which is extracted by counter current washing with an amine/kerosene solvent. The solvent is then washed with ammonium sulphate solution and the uranium is precipitated by addition of gaseous ammonia, washed and dried. The product, commonly called yellow cake, is packed into steel drums and is imported in this form into Britain.

The disposal of the tailings is a considerable waste management problem since the total weight of waste solution accompanying the sand and slimes to the tailings ponds represents 150% of the weight of the ore used. The slimes contain the radionuclides ^{230}Th and ^{226}Ra and their daughter nuclides at a concentration of about 3.7×10^5 Bq l^{-1} (10^{-5} Ci l^{-1}). One of the decay products of ^{226}Ra is ^{222}Rn. Since radon is a noble gas it is free to diffuse from the tailings and escape into the atmosphere. Macbeth et al (1) has estimated that about 20% of ^{222}Rn produced escapes from the tailings. At the present time there are over 10^8 tonnes of mill tailings stockpiled in the USA alone and Rogers (2) forecasts that by the end of the century the stockpiles will reach 1.7×10^9 tonnes. Sears (3) and Cohen (4) report that a typical pile of mill tailings from producing fuel for a 106 reactor year of 1000 MW in a Light Water Reactor (LWR) would extend over some 250 acres.

4.2 Enrichment, Conversion and Fabrication

Imported yellow cake is processed at Springfields in two main streams; the purification and chemical conversion of the uranium and the manufacture of metal and oxide powder into fuel elements. The chemical process gives rise to normal chemical effluents of negligible radioactivity and the main hazards arise from the generation and use of fluorine and hydrofluoric acid. The product, UF_6, a white solid at room temperature and a gas above 56°C, is transported to Capenhurst for ^{235}U enrichment by gaseous diffusion or high speed gas centrifuge.

The enriched uranium is returned to Springfields for the manufacture of UO_2 and uranium fuel elements. Magnox reactors generally employ fuel elements consisting of uranium metal encased in Magnox cans and some later designs use uranium dioxide bonded into small pellets, heat treated, ground and inserted into stainless steel or zirconium alloy tubes which are filled with inert gas and sealed.

4.3 Nuclear Power Stations

Fuel elements are loaded into and removed from reactors by means of a charge machine. The intensely radioactive spent fuel elements are transferred by means of a heavily shielded chute into a water filled cooling pond. The cooling ponds are about 6 metres deep and contain racks in which the fuel elements are stored. The water, which provides shielding as well as cooling, is chemically treated but corrosion of the fuel element cladding occurs and fission products pass into the water phase. Sedimentation and ion-exchange resins are used to remove the fission products from the aqueous phase.

Fig. 2. shows the decay heating characteristics of typical Magnox fuel elements. It is normal to allow

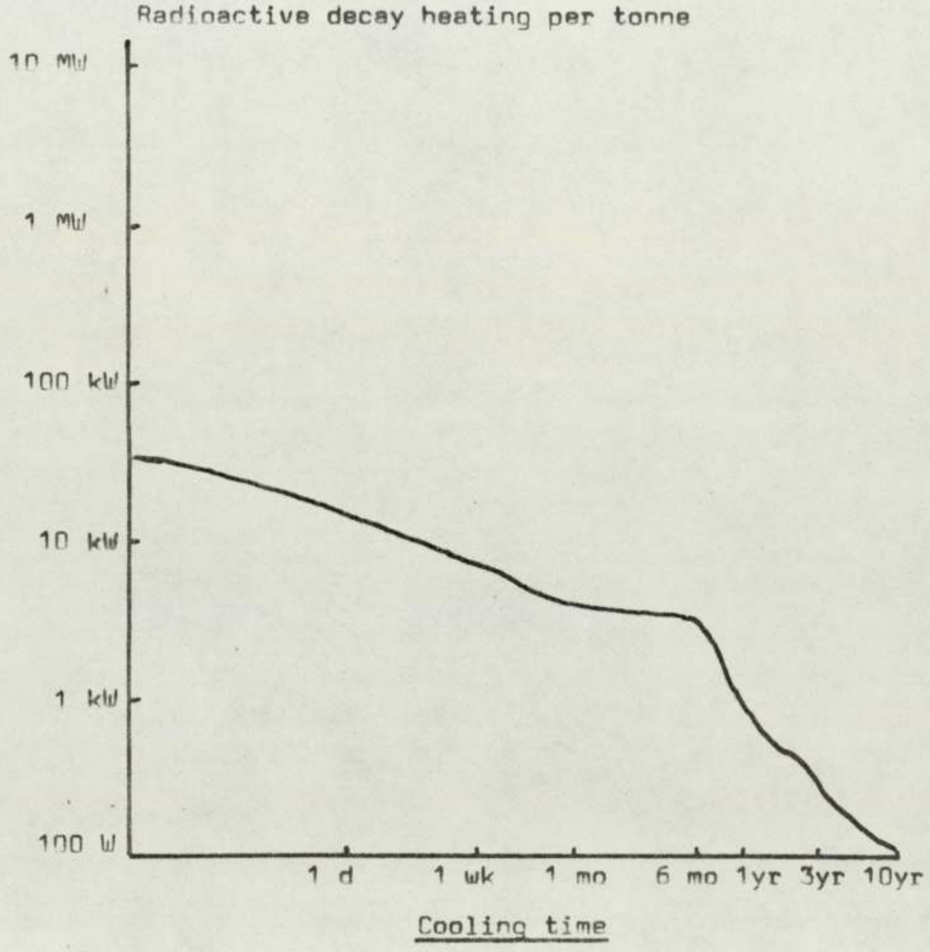


Fig. 2. THE VARIATION IN RADIOACTIVE DECAY HEATING IN DISCHARGED REACTOR FUEL FROM 4000 MW d/t MAGNOX REACTOR

Source: Reference 7

at least six months cooling before sending a discharged fuel element for reprocessing and during this time the shorter-lived radioisotopes such as ^{131}I (half life of 8 days) have decayed away. Magnox fuel elements are quite cool after this time but Fast Breeder Reactor (FBR) fuel elements would still require further cooling.

The spent fuel elements are loaded under water into 50 tonne steel flasks and transported to the reprocessing plant at Windscale.

4.4 Reprocessing

Reprocessing is undertaken to recover uranium and plutonium. The fuel is mechanically decanned before being dissolved in nitric acid. A solvent based on tributyl phosphate is used to extract the uranium and plutonium which leaves the majority of fission products dissolved in the aqueous phase with a resulting specific activity of about 3×10^{12} Bq l^{-1} (80 Ci l^{-1}). The liquid contains entrained solvent which is removed by steam distillation and small amounts of metal salts. To reduce their bulk, these high level wastes are concentrated in evaporators giving a final specific activity exceeding 3.7×10^{13} Bq l^{-1} (10^3 Ci l^{-1}). These liquids are stored in water cooled tanks awaiting treatment and disposal.

4.5 Decommissioning

All industrial processes have a finite life-time and the processes described above will eventually be superseded. Each operation within the Nuclear Fuel

Cycle is performed in plant and machinery that will one day become defunct either through malfunction, reduced efficiency or alternative technology development. Consideration therefore has to be given to the problems associated with decontaminating, dismantling, removal and disposal of the components and the eventual re-use of the site of a nuclear installation.

5.0 NUCLEAR WASTE MANAGEMENT PRACTICES IN BRITAIN

5.1 Gaseous Emissions

The principal gaseous discharges from the nuclear power industry consist of the inert gases and iodine. Iodine is a volatile fission product which escapes by leakage from some fuel elements. ^{131}I has a half-life of 8 days and two main pathways have been identified which affect man; the first by direct inhalation and the second by digestion of contaminated milk. Both pathways cause a radiation dose to the thyroid gland in which iodine concentrates. Whereas routine discharges are small causing a maximum annual thyroid dose of only a few mrems, release of ^{131}I would be expected to be a major source of radiation under accident conditions. Inert gases disperse more widely into the atmosphere. The irradiation of cooling air in Magnox stations produces ^{41}Ar, a β emitter with a half-life of 110 minutes. The annual discharge from each station is in the range of 10^{14} to 10^{16} Bq (3 to 150 x 10^3Ci) (5). Clarke (6) has estimated the collective dose to be 250 man rems from this source which is considered to be an insignificant hazard to the public.

Generation of ^{85}Kr occurs at reprocessing plants during spent fuel element de-cladding. About 3.7×10^{16} Bq y^{-1} (10^6 Ci y^{-1}) of ^{85}Kr is discharged to atmosphere at Windscale through an absolute filter which is included to remove fine particulate matter. The discharge also includes 5×10^{14} Bq y^{-1} (12×10^3 Ci y^{-1}) of ^3H and 10^{13} Bq y^{-1} (250 Ci y^{-1}) of ^{14}C as carbon dioxide. The radionuclides are widely dispersed in the atmosphere and result in about 1 mrem per year skin dose for people living near to the plant. This merits careful monitoring over a long period of time.

5.2 Low Level Liquid Wastes

Low level liquid waste arisings within the industry stem from the drainage of plant areas and floor drains, coolant gas dryers, laundry, wash basins, etcetera, and these effluents are generally filtered before mixing with uncontaminated cooling water and discharging to surface waters. The activity is present in the form of miscellaneous activation products such as ^{60}Co, ^{59}Fe and fission product ^{137}Cs. Discharges from Magnox stations contain ^3H in water amounting to 6×10^{11} to 10^{13} Bq y^{-1} (15 to 310 Ci y^{-1}) but Advanced Gas-cooled Reactor (AGR) stations would be expected to produce greater quantities.

The second main source of these wastes stems from the underwater storage of spent fuel elements at the power stations prior to their removal for reprocessing. The cladding of Magnox fuel elements corrodes leading to the contamination of the water with ^{35}S, ^{45}Ca and ^{55}Fe. Corrosion can lead to the penetration of the cladding and subsequent release of fission product ^{90}Sr and ^{137}Cs into solution. The stainless steel cladding used in AGR fuel elements is expected to be more resistant to corrosion. These radioactive aqueous wastes are treated by sedimentation, flocculation and ion exchange prior to discharge to surface water.

5.3 Low Level Solid Wastes

Wastes within this category arise at all stages of the nuclear fuel cycle. Materials such as packaging, protective clothing, electric cabling, paper and scrap metal are included. Small quantities are incinerated at their source but the major portion is transported to Drigg, near Windscale in Cumbria, where it is buried in engineered trenches. The specific activity of this waste is limited to 7.4×10^{8} Bq m^{-3} (20×10^{-3} Ci m^{-3}) and the β activity to 2.2×10^{9} Bq m^{-3} (60×10^{-3} Ci m^{-3}). The dose rate from unshielded waste must not exceed 7.5×10^{-3} Gy h^{-1} (0.75 rad h^{-1}) (beta/gamma) and must be buried beneath at least 1 m of soil. The waste is buried in trenches based on glacial boulder clay above St. Bees sandstone. The trenches are drained to a stream which flows into the tidal reaches of the River Irt and which is monitored regularly.

The quantity of solid low level waste generated in the industry is difficult to establish with any degree of reliability because of the practice of storing these wastes at their source rather than ensuring regular disposal. Table 2 shows an analysis of these waste arisings.

Table 2 Rate of Production of Solid LLW

Waste type	Annual production m^3/year per 1000 MWe			
	Magnox	AGR	SGHWR	PWR
Non-combustible	50	30	50	50
Combustible suitable for incineration	400	400	750	750
Combustible unsuitable for incineration	10	10	20	20
Wet materials	10	5	250	100

Volumes refer to non-compacted storage space.

Source: Reference 11

The Royal Commission on Environmental Pollution 1976 (7) indicated concern at the quantities of solid low level waste accumulating at power stations and, although satisfied with operations at Drigg, expressed the need to develop a national disposal facility. More recently, an Expert Group reported (8) that certain action was necessary to 'optimise' practices on this site. It noted that the disposal trenches cut through sand and gravel which lies above the glacial clay and identified the possibility of lateral movement of radioactive leachate from the deposits. The group recommended that new alternative sites be found for such wastes in other parts of the country. Another landfill disposal facility exists at Dounreay and Ulnes Walton, Lancashire, also accepts some uranium contaminated wastes from Capenhurst and Springfields. Sea disposal of packaged low and intermediate level solid waste has been practised since 1949, in accordance with international regulations (9, 10), and managed by AERE Harwell. At the present time some 1000 - 3000 tonnes gross weight containing 300 tonnes of waste are dumped annually. The activity of this waste ranges from

8×10^{14} to 4×10^{15} Bq (2×10^{4} to 10^{5} Ci) ^{3}H,

4×10^{14} to 10^{15} Bq (10^{4} to 3×10^{4} Ci)

of other beta emitters and 2×10^{13} to 4×10^{13} Bq (500 to 1000 Ci) alpha activity mainly plutonium (5). The dumping site is 500 miles south west of Lands End in water which is 2.5 miles deep (8).

5.4 Intermediate Level Wastes

Intermediate level wastes generally contain fission products but do not require artificial cooling. Many of them contain γ emitters and therefore can not be packaged without external shielding.

Magnox reactors and AGR's produce some 2400 m^3 of intermediate level solid waste per station with an activity of 3×10^{15} Bq (80×10^{3} Ci) during a 25 year life. The major part of this activity is attributable to ^{60}Co produced by the neutron activation of steel components which must be stored in concrete silos within the biological shield. Storage of such waste for a decade reduces the activity by half. In 1976 the CEGB had in store some 7000 m^3 of such wastes and this had risen to 11,500 m^3 by 1979. The Royal Commission on Environmental Pollution (7) forecast waste production in this category as reaching 23,000 m^3 by 1985.

Concern has been expressed about current management practices of these wastes. An Electrical Power Engineers Association report (11) said that 'solid waste practices on current stations, while currently satisfactory from the radiological viewpoint, are not regarded as an optimum long term solution-------'

The Royal Commission (7) said that 'it was unable to discover any clearly formulated policy for the future disposal of this waste-------- The waste is quite secure at present, but presumably it will have to be removed eventually if the reactor sites are to be re-used.'

Wet intermediate level waste occurs in the form of water treatment sludges, filter cakes and spent ion exchange resins resulting from purification of cooling pond waters. Such material frequently contains ^{90}Sr and ^{137}Cs fission products which have half-lives around 30 years.

At Trawsfyndd (12) and Hinkley Point these wastes are solidified in cement in shielded steel drums and sent for ocean disposal.

Difficulty occurs with caesium bearing spent ion exchange resins since the cement products tend to fragment (13) and caesium leaches out very readily (14).

The development of new technology using composites of cement and synthetic polymers is described in this thesis and elsewhere (15).

The encapsulation of these wastes in bitumen is an alternative approach which is favoured in Europe. Hild (16) has described pilot plant work at Eurochemic for the treatment of intermediate level wastes. Active solutions are first subjected to batch-wise pretreatment such as hydroxide precipitation, sulphate precipitation, nickel ferrocyanide precipitation or fluoride precipitation which produces a series of slurries. The mixture is evaporated to drive off ammonia and reduce its volume. Bitumen is then fed to a twin screw self cleaning extruder evaporator which is heated by steam to 170°C. The waste slurry is also fed to the unit which is equipped with a battery of condensers which cool, condense and collect the evaporated steam. The bitumen to solids ratio is maintained at 1.2 to 1 typically. The bitumen products have softening points in the range 114 to 167°C and densities between 1.32 and 1.50 g cm^{-3}. Thermogravimetric studies show 1.6 to 3.4% weight loss at 320°C and 44 to 86.3% weight loss at 550°C. Radiation stability tests have shown volume changes of 0 to 24% (depending on bitumen/waste ratios) when subjected to 3 x 10^9 rads totally integrated dose.

Leach test data on these products have not been reported. Problems encountered during pilot scale operation have included serious build up of radioactive incrustations in the condenser systems. The technique suffers from several limitations including (17);
the high bitumen/waste ratios needed,
the necessity to precipitate radionuclides in a pretreatment step,
loss of radionuclides in the gas streams either during ammonia blow off or in the extruder,
fire and explosion hazards encountered due to the presence of nitrates,
and radiation stability limitations.

5.5 High Level Wastes

The mechanical de-cladding of fuel elements at Windscale produces high level solid waste. Magnox fuel elements produce a waste which is potentially inflammable and is stored under water in silos. The zircalloy sheaths from LWR's are also stored here and release considerable quantities of ^3H into the water. These silos also contain miscellaneous active hardware and other wastes with a very high specific activity. Future retrieval and packaging of this waste is likely to prove difficult (7) and the presence of considerable quantities of highly radioactive water represents a hazard. Accumulations of these wastes is expected to continue until about 1990 when packaging for deep sea disposal is scheduled to begin. The volume held in store at Windscale reached 19,000 m^3 by 1979 (18). About 0.25 to 0.6 m^3 of cladding waste is generated per tonne of fuel reprocessed. Processes for the decontamination and reduction in volume of these wastes are being developed.

The nuclear power stations also store spent fuel elements prior to transport to Windscale. The Health and Safety Executive (19) reported 'that the amount of spent fuel stored at Magnox stations in cooling ponds continues to remain at a high level and has increased by as much as 60% in some cases in the year 1977-78'. Some 2 x 10^4 m^3 of such wastes were in store at 1979 (18).

The high level liquid waste stored in cooled tanks at Windscale contains both fission products and actinides. The precise composition of this waste is determined by the isotopic composition of the fuel, the neutron spectrum of the reactor, the burn up achieved before discharge and the storage time prior to processing. Whilst most of the fission products have half-lives of less than one year, a few have half-lives in the range 30 to 10^5 years.

The actinides are mainly α emitters with half-lives up to 10^7 years. It is desirable to immobilise these wastes at the earliest opportunity and current indications are that they will be vitrified by the Harvest process or some similar technique, beginning in the mid 1980's. The volume of waste will be reduced during processing to about 0.01 to 0.05 m^3 per tonne of fuel reprocessed. The vitrified waste will be incorporated into a stainless steel vessel and artificially cooled for about 30 years in a supervised and monitored store. Internal temperatures within the containers will reach about 275°C. Ultimately, the waste package will be stored in a repository which would not require artificial cooling or excessive monitoring. The state of development of the available glassification processes has been described by Heimerl (20) and Sousselier (21) and alternative technologies using cement and ceramics are being pursued (22, 23, 24).

5.6 Decommissioning Wastes

The decommissioning of irradiated equipment at the end of its useful life presents special problems. The ultimate objective is to remove all redundant plant so that no further surveillance is necessary. The decommissioning of a Magnox reactor, for example, is considered to be a three-stage operation.

Stage 1 is to shut down and make safe,
depressurize the coolant and
dispatch the fuel.

Stage 2 is the dismantling of non-
active plant and the sealing
of active plant including
cooling ponds, effluent
treatment plants and solid
waste storage vessels.

Stage 3 is the complete clearance
of the site (including the
reactor moderator, its support
structure, the pressure vessel
and the biological shield) and
its release for unrestricted
use.

The reactor structure represents the biggest problem in terms of volume and radioactivity. Table 3 shows the wastes produced by a 250 MW (e) Magnox station. After 40 years operating life and a decay period of one year a radioactive inventory of 1.5 x 10^{17} Bq (4.5 x 10^{6} Ci) would be expected but the situation is very complex and the presence of trace metals will have a very significant impact on the inventory. Initially ^{60}Co is the most important radionuclide but it decays rapidly. Consequently, cooling and monitoring for a period of 100 years or so is likely to be implemented. Ultimately packaging of the dismantled pressure vessel and irradiated parts of the biological shield for disposal in the deep Atlantic appears to be the only available option.

Table 3 Decommissioning Waste from a 250 MW (e) Magnox Station

	Weight (Tonnes)		
	Steel	Graphite	Concrete
Pressure vessel and internals	2400	2500	0
Biological shield	700	0	15000

Source: Reference 11

By the year 2000 most of the nuclear power stations currently operating will be near the end of their operating life and facing de-commissioning. Since practical experience of de-commissioning nuclear facilities is so very limited it is doubtful whether the total extent or magnitude of the problems to be faced are generally recognised at this time.

6.0 COMMENTS

Public concern and governmental research in Britain is centred on the problem of treatment and safe disposal of high level liquid radioactive wastes but there is less awareness of other waste management aspects of the nuclear power industry.

Other large areas which warrant detailed attention are:

Disposal aspects of uranium mill tailings.

The substantial volume of intermediate level wastes which have no established treatment and disposal technology.

The accumulation of high level solid wastes from fuel element de-cladding.

The substantial volumes of active waste which will be produced during the next few decades as a result of plant de-commissioning.

The research described in this thesis is focused on the development of immobilisation techniques applicable to low and intermediate level wastes and the study of their key characteristics.

SECTION 2

CHEMICAL AND ENVIRONMENTAL ASPECTS

1.0 THE CHOICE OF IMMOBILISATION SYSTEM

Cement is the prime candidate material for the immobilisaton of waste materials. It is capable of solidifying aqueous residues, it is abundant, has a low cost and its stability and resistance to irradiation has been accepted for a long time. The ability of cements to react with aqueous residues at ordinary temperatures and pressures to produce a solid monolith is particularly attractive since it simplifies process engineering requirements and minimises costs. In contrast, the need to use elevated temperatures in vitrification and bituminisation techniques, both elevated temperatures and pressures in ceramic processes, and both vacuum and elevated temperatures in polymer impregnation techniques, must be regarded as serious disadvantages particularly where radiation protection considerations demand remote handling.

The attractive characteristics of cement products have also been recognised by the U.S. National Research Council (25). In a report published in 1978 it states:

> 'In the interests of relative processing simplicity (and probable low hazard and cost) cement based composites and low temperature ceramics should be researched vigorously as the prime candidates for solidification of nuclear wastes'.

> 'Research and development are also needed on special additives for cement/concrete waste solidification technology to fix each radio nuclide in a low solubility crystalline phase'.

2.0 THE NATURE OF CEMENT

Cement has been used for thousands of years in building applications. However, it is not a simple substance with fixed properties but rather a complex mixture whose composition can be varied slightly to produce desirable characteristics. Cement is produced by intimately mixing calcareous and argillaceous, or other silica, alumina and iron oxide materials, burning them at clinkering temperature and grinding the resulting clinker.

Cements need to conform to accepted standards. In Britain for example Portland Cement needs to conform to BS 12: 1958 which defines the fineness, strength, setting time, soundness and chemical composition. Typical chemical compositions of various cements are shown in Table 4.

Table 4. Percentage Composition of Cements

	Portland	High Alumina	Portland Blast-furnace
CaO	64.1	37.7	59.0
Al_2O_3	5.5	38.5	8.1
Fe_2O_3	3.0	12.7	1.0
FeO	-	3.9	0.5
SiO_2	22.0	5.3	22.8
MgO	1.4	0.1	3.5
SO_3	2.1	0.1	1.7
S	-	-	0.5

Source: Reference 15.

A diagram showing the area of Portland cement compositions is shown in Fig. 3.

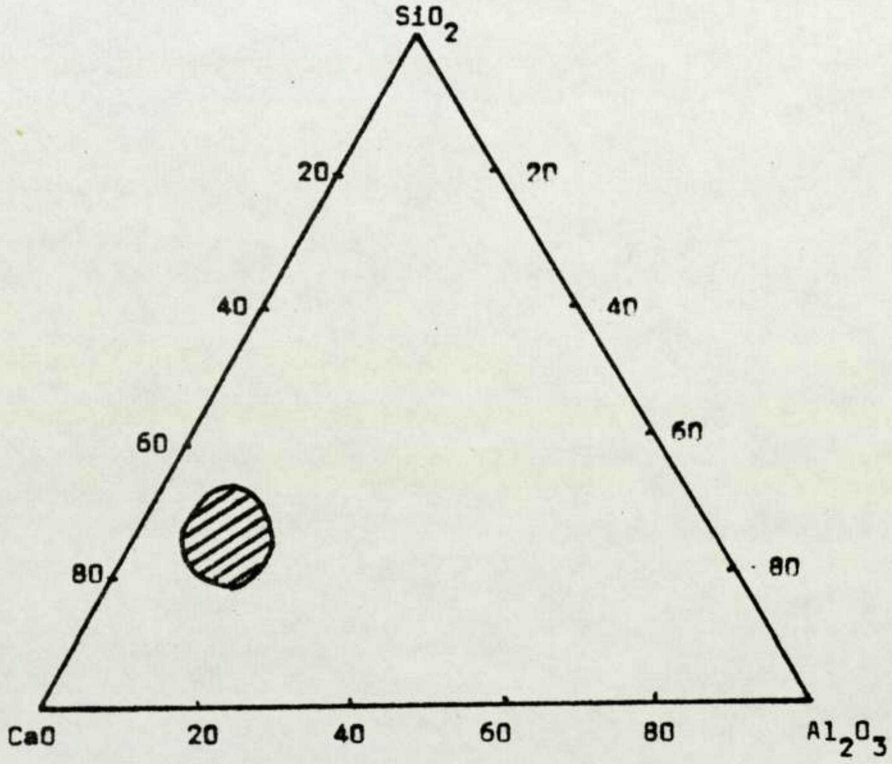


FIG. 3 DIAGRAM SHOWING AREA OF PORTLAND CEMENT COMPOSITION

It is recognised that this represents a simplified view of the complex structure of cement and that the influence of minor ingredients such as Fe_2O_3, MgO, $CaSO_4$ and TiO_2 in terms of the characteristics of the cement obtained is considerable.

Ordinary Portland Cement conforming to BS12:1958 was chosen as a base material for the purpose of these studies.

3.0 HYDRATED CEMENT

It is important to appreciate the structure of hydrated cement pastes and it is convenient to consider this at several levels.

3.1 Molecular Structure

Considering the molecular structure of cement pastes it is clear that they are primarily assemblages of calcium, silicon and oxygen. Aluminium, iron, sulphur and hydrogen (from water) form a second group of constituent elements and small amounts of magnesium, potassium, sodium and trace elements from clinker form the minor constituents. In cement chemistry abbreviated compound formulae have become conventionally used in which

$C = CaO$ $S = SiO_2$

$H = H_2O$ $A = Al_2O_3$

$T = TiO_2$ $F = Fe_2O_3$

Typical examples of these formulae are:

$C_3S = 3CaO.\ SiO_2$

$C_2S = 2CaO.\ SiO_2$

$C_3A = 3CaO.\ Al_2O_3$

$C_2F = 2CaO.\ Fe_2O_3$

$C_4AF = 4CaO.\ Al_2O_3.\ Fe_2O_3.$

The atomic constituents in cement paste are assembled into a variety of crystalline, quasi-amorphous and amorphous phases. Properly crystalline components include calcium hydroxide, ettringite

$3CaO.\ Al_2O_3.\ 3Ca\ SO_4.\ 31H_2O$,

calcium aluminate monosulphate hydrate

$CaO.\ 3Al_2O_3.\ SO_3.H_2O$ and C_4AH_{13}, C_3S, C_2S and C_4AF.

Other phases of lesser crystallinity involve primarily calcium silicate hydrate gel (C-S-H gel) but may also include small amounts of residual glassy material from the clinker and amorphous calcium hydroxide.

Caution is needed when endeavouring to indicate the relative amounts of different phases present in a hardened cement paste but reasonable estimates suggest that a fully hydrated cement paste consists approximately of:

	% by weight
C-S-H gel	70
calcium hydroxide	20
ettringite and calcium aluminate monosulphate hydrate	7
unhydrated residue and minor constituents	3

3.2 Crystalline Structure

The crystalline structure of cement has been studied by Pressler et al (26). They found that fully hydrated ordinary portland cement paste dried by desiccant contained approximately 22% of $Ca(OH)_2$. Crystals of $Ca(OH)_2$ are trigonal and the structure contains layers of $Ca(OH)_2$ octahedra. There is no evidence of hydrogen bonding between the OH groups but the mechanical incorporation of other components of the cement paste within the layers is common (27). Ettringite and calcium aluminate monosulphate 12 hydrate are quite well crystallised in cement pastes though substitution of iron for aluminium and carbonate or chloride for sulphate can occur.

C-S-H gel which forms the bulk of hydrated cement paste has a chemical composition often expressed as $C_{1.5}SH_{1.5}$ but this must not be regarded as a fixed value. The ratios are strongly influenced by the water:silica ratio and the maturity of the paste. Foreign ions such as Al^{+++}, Fe^{+++}, K^{+}, Na^{+}, and Cl^{-} can also be incorporated into the C-S-H gel in cement paste. The X-ray diffraction pattern of the C-S-H gel is so nearly amorphous that no detectable changes seem to accompany the incorporation of foreign ions (27). This leaves the true nature of the atomic arrangement of the C-S-H gel very much open to question.

The surface area of hydrated cement paste is extremely high and it is believed that it includes internal surfaces within the particles on a scale that makes internal surface a prominent feature of the molecular arrangement of the material. Typically the surface area of desiccant dried hydrated cement paste is approximately 600 m^2g^{-1} and this increases to 700 m^2g^{-1} for ignited samples (27, 28). Using a reasonable estimate of the gel content, the internal surface of the C-S-H gel has been calculated to be approximately

950 m^2g^{-1}. Hence two thirds of this surface is lost on desiccant drying but is recoverable on re-saturation.

Consequently it would appear that the C-S-H gel is not only complex compositionally but structurally as well. The atomic arrangement is such that it provides a very extensive internal surface most of which can be reversibly removed on drying.

3.3. Particle Structure

Scanning electron microscopy (SEM) provides a technique for the study of the particle structure of hydrated cement paste (29,30). The most prominent component is seen to be the elongated material usually found radiating outwards from the cement grains. These particles have been called 'spines', 'needles', 'fibrous crystals' and various other names. There is also a 'reticular network' or 'interlocking structure' in hardened cement pastes which forms a 3 dimensional network. A third type of particle is also distinguishable consisting of irregular flattened particles or 'equant grains'.

In general fibrous crystals dominate in immature cement pastes with reticular network occurring only occasionally. Equant grains appear as hydration proceeds.

The calcium hydroxide component of hardened cement paste appears in the early stages as thin hexagonal plates which grow massive and lose their hexagonal outline as they invade and encapsulate other regions of the paste. Mature pastes are marked by extensive deposits of such material recognised by parallel planes and smooth featureless surfaces. Where the calcium hydroxide encapsulates the C-S-H gel, it takes the form of the equant grains described above.

Ettringite occurs as long narrow rods with no branching and the calcium aluminate monosulphate hydrate particles occur as hexagonal plate-like crystals.

4.0 THE DISADVANTAGES OF CEMENT

This review has indicated that although man has been using cement for thousands of years, the study of its nature and properties is not yet complete. It is only since the 1950's that insight into its particle structure has been gained and continued development of SEM may possibly reveal more detail. It is now known that its structure is much more complex than was first realised. It consists of a variety of components with a high surface area and contains pores of various sizes which run between the components. Though it would appear from history to be a highly stable product its structure changes very slowly through hydration, dehydration and carbonation.

The porous nature of cement products is greatly influenced by the water content of the paste. At high water contents, porosity increases and compressive strength falls. In these studies consideration is given to the incorporation of radioactive wastes into cement compounds. The wastes are considered to be in the form of aqueous solutions and the expression 'water (or waste)' is used to refer to such solutions. Products with high porosity would be expected to permit the permeation of water into the block. Yet high water (or waste) contents are desirable for the immobilisation of aqueous wastes since they correspond to lower chemical treatment costs.

As a result any attempt to develop and optimise the use of cement for the immobilisation of radioactive wastes must necessarily involve attempts to overcome the porosity (and permeability) characteristics of cement pastes. This study reports the results of studies of various 'additives' selected for this purpose.

5.0 POZZOLANIC CEMENTS

A pozzolan is a cementitious material capable of reacting with lime and setting into a solid in the presence of water. Weeren (31) has described the use of fly ash as a pozzolan in the process of hydrofracturing of radioactive wastes at Oak Ridge National Laboratory. Fly ash (Pfa) is a waste product produced at pulverised coal fired power stations in the form of minute spherical particles. It is collected in the electrostatic precipitators as a fine dry spherical powder. It is an aluminosilicate with a variable composition which changes according to the type of coal being burned. Certain power stations are equipped to collect this product and package it in bags. One of these was the source of the material used in these experiments. Table 5 lists characteristics of pulverized fly ash.

Table 5. Characteristics of Pulverized Fly Ash (Pfa)

Typical Analysis

	Typical % by weight
Silica (as SiO_2)	48
Aluminium (as Al_2O_3)	27
Iron (as Fe_2O_3)	9
Calcium (as CaO)	3.3
Magnesium (as MgO)	2.0
Potassium (as K_2O)	3.8
Sodium (as Na_2O)	1.2
Carbon	trace
Specific gravity	1.9 to 2.3
Specific surface area	1500 - 5000 $cm^2\ g^{-1}$

The use of pozzolans in cement has been known since Roman times. Stratling (32) concluded that the reaction of fly ash in the hydration of cement is best represented by:

$$2Al_2O_3 \cdot 2SiO_2 + 7\ Ca(OH)_2 \longrightarrow 3CaO \cdot 2SiO_2\ aq. + 2(2CaO \cdot Al_2O_3 \cdot SiO_2)$$

It will be noted that calcium hydroxide, formed by the hydrolysis of lime present in cement, is effectively removed from the product which accounts for the high chemical resistance of pozzolanic cements when compared to ordinary portland cement (OPC). These products when compared to OPC also possess other desirable properties including:

1. The ability to react with much greater quantities of water.
2. The fine particle size produces a product with a smaller pore size (lower water permeability).
3. Improved 'workability' and reduced 'permeability'.

6.0 ORGANIC POLYMERS

The purpose of this phase is to reduce (or eliminate) the diffusion of water into and out of the product thereby protecting the environment from the effects of the leaching products. For this purpose the idea of including synthetic organic polymers in the product seemed attractive.

The choice of organic polymer system poses some difficulties. The composite produced must be resistant to radiation damage and compatible with the alkaline conditions which exist in cement processing. Charlesby (33) has shown that many organic polymers degrade when exposed to high energy gamma rays producing gaseous degradation products. Styrene is the most radiation resistant of the commonly available products. Consequently, styrene and some of its polymers were included in this study.

7.0 THE COPOLYMERISATION OF ORGANIC MONOMERS

7.1 Brookhaven Research

Brookhaven National Laboratory (34, 35) has developed a polymer impregnation technique to restrain the migration of radionuclides from solidified wastes. The concrete paste is prepared from cement, sand, gravel and aqueous radioactive waste and is cast into a block. After setting the free water is removed by drying and the block is immersed in an organic monomer in an evacuated vessel; a process known as vacuum impregnation. An extensive range of organic monomers of both the thermoplastic and thermosetting types have been tested. The composite produced contains 6.5 to 7.0% by weight of organic monomer. The monomer is then polymerised in situ either by external irradiation from a ^{60}Co source or by a thermal catalytic method using a peroxide catalyst at an elevated temperature. Products made in this way using styrene have shown a radiation stability up to 10^{10} rads (which is the totally integrated dose expected from exposure for 1000 years) and compressive strengths of up to 90MN m^{-2}. However, in terms of radioactive waste management the processing complications of pre-casting, drying, vacuum impregnation, draining and irradiation represent a severe limitation and naturally increase treatment cost.

Consequently Brookhaven researchers (36) experimented with the addition of monomers to the wet concrete mix prior to curing. Radiation was then used to polymerise the monomer after curing for one day. In many of the tests the concrete did not harden and for those specimens that did, the compressive strength was no higher than that of the control specimen without monomer. The researchers believed that the organic monomers interfered with the hydration process of the cement and resulted in loss of physical strength.

7.2 Washington State University Research

Subramanian at Washington State University has studied the use of some polyester resins for the encapsulation of both hazardous chemical waste and low level radioactive waste (39, 40, 41, 42). Both laboratory and small scale pilot studies are reported and the products have been examined by scanning electron microscopy. The wastes were confined in the organic matrix in the form of microdrops with diameters ranging from 1 to 10 µm. The polyesters examined contained functional groups of maleic and fumaric types only and no studies were made of composites containing cement products and polyester. Leaching rates were determined by a static leach test and it was reported that the leach rate of strontium from these products was much lower than its leach rate from cement products. Under particular conditions Subramanian reported that all of the strontium would be lost from a cement product in 172 years whereas only 0.03 to 3% of the strontium would be lost from the polyester matrix in 1000 years. Increasing the water content of the product from 50 to 60% showed no change in leaching rate but water contents of 70% showed sharp increases in the leachability. The effect of changing the waste content of the water (i.e. increasing the concentration of pollutant in the aqueous phase) was not reported. Exposure to external gamma radiation was studied. A dose of 10^8 rads increased leaching rate by 10%. These authors compared their products with modified cement products and urea formaldehyde which are used in the USA for the disposal of chemical and nuclear waste. Superior leach resistance, absence of bleeding (release of water during curing) and impressive compressive and tensile strengths are claimed for the polyesters. However, they reported that treatment costs using polyester are about twice those of existing commercial processes using modified cements and urea formaldehyde.

7.3 French Research

Since the start of the work described in this thesis a report has been published (44) in May 1980 describing the work of Aubouin on thermosetting polyester and epoxy resins. These authors stress the importance of 'being able to handle wet waste material'. The research, however, concentrated on immobilisation of solid wastes such as evaporator concentrates, ion exchange resins in pellet and powder form, filtration sludges and solid wastes from decommissioning operations. Drying, using four thin film or horizontal dryers and chemical pretreatment (addition of precipitants) was undertaken prior to treatment with the thermosetting resin. Solid wastes were either placed in a mesh basket which is immersed in the resin or the waste is placed in a prefabricated container made of thermosetting resin and coated with more resin.

An inert mineral charge (not identified) is added to reduce contraction as the resin sets.
The physical strength of the products as reported by these authors is shown in Table 6. Studies of the leaching characteristics were also undertaken by immersing specimens in water and renewing the water at intervals, the leaching rate being expressed as a diffusion coefficient, D. It was found that caesium diffused from the specimens quite readily unless the waste was pretreated with nickel ferrocyanide. The authors developed a model to show leaching of caesium from a 200 litre drum and showed that in the absence of pretreatment about half of the caesium would be expected to escape in a 100 year period. They developed a double layer thermosetting resin to envelope the waste package in order to reduce caesium leaching rates. It is reported that these techniques are in industrial use at Grenoble Nuclear Research Centre and Chooz Nuclear Power Station (a PWR station).

Table 6. Physical Characteristics of Thermosetting Resins used in France.

Compression Strengths kg cm^{-2}

(figures in brackets show compression strength in MNm^{-2})

	Polyester Resin	Epoxy Resin
Pure Resin		
Before exposure	1000 (98)	1000 (98)
After 3 x 10^9 rads exposure	900 (94)	1000 (98)
Resin containing Ion Exchange Resin Waste		
Before exposure	175 (17.1)	280 (27.4)
After 5 x 10^9 rads exposure	50 (4.9)	250 (24.5)
Resin containing Filtration Sludge Waste		
Before exposure	-	290 (28.4)
After 5 x 10^9 rads exposure		190 (18.6)

Source: Reference 44.

7.4 This Author

The work of this author (37) has the same objectives as the studies described above. Section 3 describes the experimental studies.

8.0 THE LEACHING CHARACTERISTICS OF MATERIALS

It is instructive to consider mechanisms of leaching as applied to our natural environment.

A molecule of water has the structure of an isosceles triangle but since the oxygen atom is more electro negative than hydrogen, the bonding electrons are drawn towards it creating a dipole in which the hydrogen atoms have a slight positive charge and the oxygen atom a slight negative one. This polar nature of water explains its outstanding properties as a solvent since the force between the dipole and the ions of a crystal are responsible for the destruction of crystals in solution; a process called solution. In organic compounds where covalent bonds link the components there is no charge separation which explains why non-polar solvents are much less effective in dissolving inorganic compounds.

Water also plays an important role in the transport of components. When an ion is released from a crystal it is immediately surrounded by an envelope of water molecules because of the water dipole. The subsequent behaviour of the dissolved ion is determined by whether or not the water molecules are attracted more strongly to other water molecules than to the ion (i.e. whether the ion will be hydrated or whether it will be precipitated). The strength of ion-water attractive forces for ions of like charge varies according to the inverse square of the ionic radius. Larger ions are less hydrated simply because the same electronic charge is distributed over a greater surface area.

The relative degree of hydration of ions is expressed by Z/r where Z is the electronic charge and r is the radius. This quantity is called the ionic potential and is shown in Fig. 4.

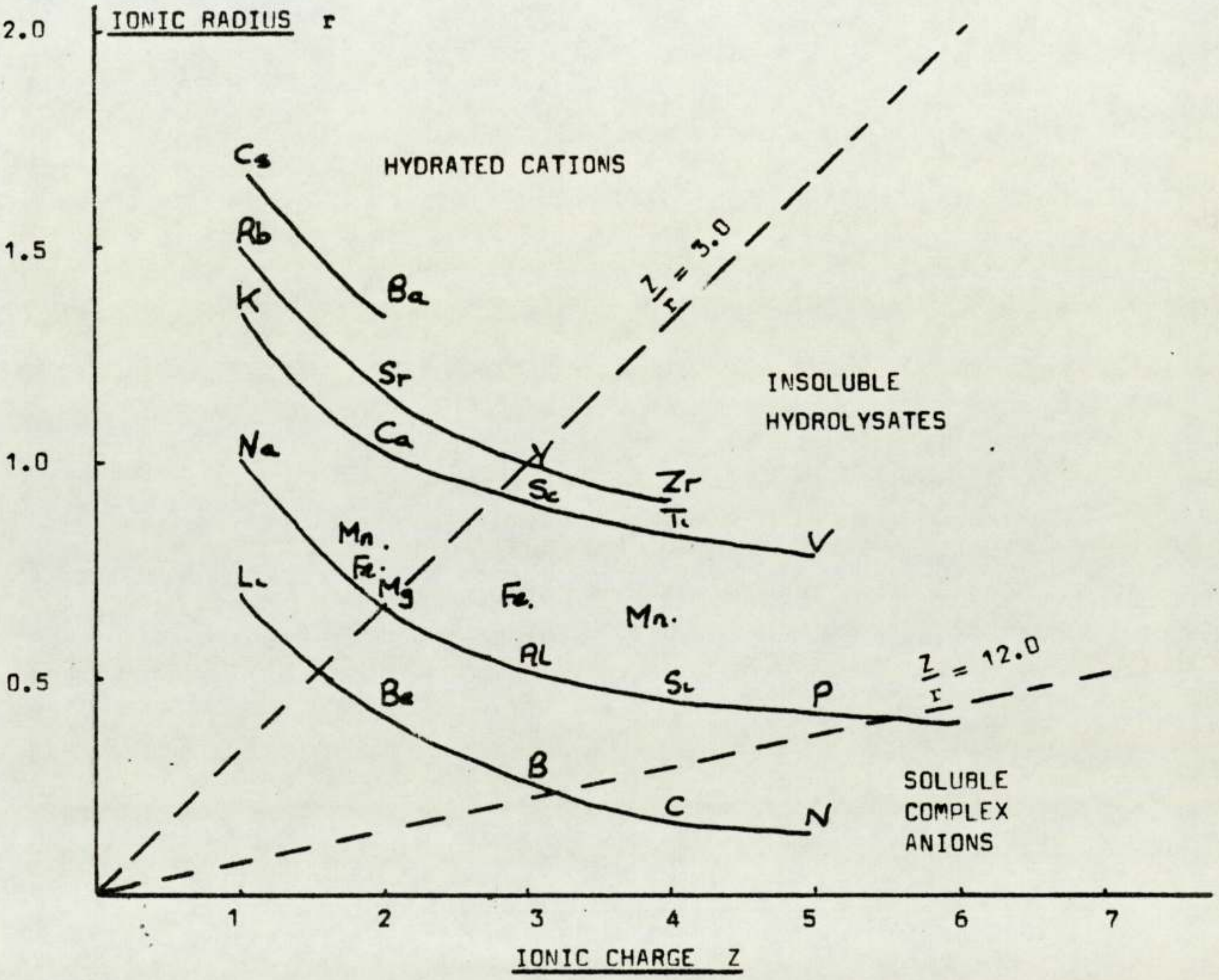


Fig. 4. RELATIONSHIP BETWEEN IONIC CHARGE AND IONIC RADIUS.

Source: Reference 43.

Fig. 4 has been divided into three areas according to the known behaviour of ions with respect to water. Water acts as an important medium for ions with an ionic potential of less than 3 (strongly cationic) and greater than 12 (strong complex anions). When the ionic potential lies between 3 and 12 the ions are precipitated as hydroxides and their mobility is reduced in aqueous environments. This data explains why ions such as Cs^+, K^+, Na^+ and Sr^{++} would be expected to leach readily from solid materials.

9.0 THE SELECTION OF RADIONUCLIDES

The fission of uranium in a nuclear reactor produces about 300 different nuclei of which about 180 are radio active. A large number of these fission products have very short half-lives and decay to stable elements in seconds, minutes or hours. Other fission products have half-lives of days or weeks and these are permitted to decay during the spent fuel cooling period. Table 7 shows the half-life and specific activity of the principal fission products. This table illustrates the very rapid fall in activity in the first months or years after removal from a reactor, the importance of caesium and strontium over the mid term and the small residual activity of the weak long lived fission products.

The physical form and source of these fission products has been identified in Section 1.

Table 7. Typical Fission Product Activities in 1 kg of Total Fission Products

Isotope	Half Life	Activity (Ci) after years			
		1	10	100	1000
Barium 143	12 s	–	–	–	–
Iodine 131	8 d	–	–	–	–
Ruthenium 103	40 d	20	–	–	–
Cerium 144	284 d	$2.5x10^4$	9	–	–
Ruthenium 106	1 y	$1.9x10^3$	2	–	–
Krypton 85	11 y	$3x10^2$	$2x10^2$	0.6	–
Strontium 90	29 y	$3x10^3$	$2.5x10^3$	$2.9x10^2$	–
Caesium 137	30 y	$3.2x10^3$	$2.6x10^3$	$3.2x10^2$	–
Samarium 151	90 y	4	4	2	0.002
Technetium 99	2.0×10^5 y	0.5	0.5	0.5	0.5
Iodine 129	1.7×10^7 y	0.001	0.001	0.001	0.001

s = seconds d = days y = years

Further evidence of the importance of caesium and strontium radionuclides has been provided by Dlouhy (45). He has studied the likely activity of low and intermediate level radioactive waste stored in a repository serving several nuclear power plants for a 20 to 25 year period. His data are shown in Table 8 and his figures are maximum activities since the addition of extra waste is compensated for by radioactive decay.

Table 8 The Activity of LLW and ILW in a Repository serving several Nuclear Power Plants

Isotope	Activity (Bq)
Caesium 137	7.7×10^{14}
Strontium 90	6.3×10^{13}
Cobalt 60	1.5×10^{14}
All others	2.7×10^{13}

Source: Adapted from Reference 45.

It is important to recognise that naturally occurring minerals possess the ability to attenuate radionuclides which might migrate away from a nuclear waste repository. The attenuation mechanisms are complex but adsorption on to the mineral surface is the principal attenuating force. Seitz et al (46) have conducted studies on the adsorption on to minerals of solutions containing ^{134}Cs, ^{237}Pu, ^{239}Np and ^{241}Am. Shale, chalk, limestone, sandstone and tuft were studied. To simulate groundwater in contact with the minerals distilled water was conditioned by stirring it with rock samples for one week and filtered through a 0.45 μm Millipore filter. The selected radionuclides were added to this conditioned water and column infiltration experiments conducted in which the water was passed down columns containing the mineral species. The radionuclides eluted from the columns were determined and after the experiments were concluded the concentration of radionuclides in various sections of the rocks was determined. The results showed that the radionuclides migrated more slowly than the infiltrating fluid. In all cases concentration gradients of the radionuclides in the column were detected. At low velocities the caesium migrated through the columns whereas plutonium and americium were largely retained. Movement of the concentration peak of radionuclides down the columns confirms that desorption does occur and that this is dependent on fluid velocity as well as other parameters.

Similar studies have been conducted by Essington et al (47) in column experiments using leachate actually collected from a nuclear waste repository and four types of soil. Caesium and strontium migration was again more rapid than hafnium, americium and yttrium. This work is quoted to illustrate the fact that attenuation and adsorption of radionuclides in minerals occurs and that the process is reversible.

A further proof of the importance of particular radionuclides is provided by a study of practical experience at a LLW repository at Oak Ridge National Laboratory USA. Webster (48) reports that radiocaesium and strontium have migrated beyond the perimeter of the waste repository.

Robertson (49) reports surveys of 11 low level waste burial grounds in the USA. Radionuclides such as ^{60}Co, ^{137}Cs and ^{90}Sr were found to have migrated short distances and tritium was shown to have migrated several hundred metres in some cases.

For these reasons radioactive isotopes of caesium and strontium were chosen for use in this study to simulate the behaviour of LLW and ILW.

10.0 LEACH TEST METHODS

For the purpose of comparison it is necessary to develop a standard leaching test in which specimens are subjected to leachants under controlled conditions and leaching rates determined. There have been several attempts to develop standard techniques of this type, and since they do not produce comparable data it is constructive to review them here.

The method suggested by Hespe (50) has become known as the IAEA method and is most widely used. It consists of allowing a specimen of known size to be immersed in demineralised water, the leachant, for periods of time up to one year. At intervals the leachant is decanted off, allowed to settle and analysed. This test procedure is open to criticism not only because it is very slow, but also because concentration gradients, or films, of leached material in the static leachant are likely to develop and retard the leaching rate in an uncontrolled way. Indeed, Moore (51) found that the frequency of leachant renewal had a considerable bearing on the cumulative fraction leached and went on to develop an elaborate automatic mechanism for replacing leachant daily to overcome this deficiency (52).

Hatta (53) used a similar technique and studied the leaching rate of ^{60}Co and ^{137}Cs into distilled water and sea water. He established that while ^{60}Co was leached only from the surface of the specimen, ^{137}Cs was leached from the interior and concluded that the important kinetic processes were;

1. solubilisation at the surface of the solid,
2. diffusion of the leachant through the solid, and
3. diffusion of the solubilised species within the leachant.

Terashima (54) also stressed the importance of the diffusion rate within the solid. Matsuzuru (55) studied the leaching of ^{137}Cs from crushed samples of cement composites using the IAEA leach test and concluded;

1. that the leach rate depends on the flow rate of the external solution, the specimen radius and the composition of the cement product,
2. that the rate determining step in the

dynamic condition is the internal diffusion through the matrix of cement, and

3. that the rate determining step in the static condition is determined by the external diffusion through the interface layers between solid and liquid.

Amarantos (56) used the IAEA method to study the leaching of caesium from cementitious products. He considered that the first stage of the transfer was the dissolution of the ion within the solid and was a first order kinetic process. His observations were complicated by the heterogeniety of the solid and he interpreted his data as showing the accumulation of caesium ions near the surface i.e. a film.

Stanley (57) criticised the IAEA method and from experimental observations deduced that a concentration gradient developed under static conditions which retarded leaching. He developed a standard leaching test method to overcome this failing. It consisted of a distillation unit which boiled, condensed and cooled the leachant and allowed it to circulate at a fixed rate through a vessel containing the specimen. Leachant was automatically returned to the boiler. This technique produced leaching data in a few days compared to the IAEA one year test and avoided film formation by maintaining turbulent flow conditions around the specimen.

Mention must also be made of a draft British Standards Institution (BSI) method details of which were circulated in March 1980 for public comment. This draft technique resembled the Hespe method (49) in many respects. It proposed that laboratory scale specimens be immersed in leachants for a minimum period of 1 year. The leachants are conditioned deionised water with pH = 7, 2.3, 5.7 and 9.5 and simulated sea water and the studies are made at temperatures of 23, 45, 70 and 100°C. The leachant is renewed daily during the first five days, twice per week during the second week, once per week during third, fourth, fifth and sixth weeks and monthly thereafter. If the pH varies by more than ± 0.2 units during the test the results are rejected. Caesium and strontium are recommended for low level waste leaching studies but the method for determining the caesium and strontium content of the leachant is not specified. The criticisms described above relating to the Hespe method apply also to the draft BSI method but the difficulties are magnified by the requirement to study each specimen over a one year period with two different leachants at three different pH's and four different temperatures! The impracticalities of this technique are enormous particularly when it must be recognised that the results in no way simulate the leaching behaviour of materials placed in a nuclear waste repository. It is understood that BSI has withdrawn its draft and no longer intends to pursue the development of a British Standard Method.

The International Standards Organisation (ISO) has also produced a draft Standard Leach Test using a Soxhlet unit. In this test distilled leachant is condensed and collected in a cup containing the specimen of known dimensions. The Soxhlet cup is arranged to empty itself by syphoning every fifteen minutes and the leachant is returned to the boiler. In this way turbulent flow of freshly distilled leachant in the Soxhlet cup inhibits the formation of concentration gradients and films. Since the test operates at 100 ± 2°C accelerated leach rates are to be expected. Since the data were to be used for the purposes of comparing one specimen with another, this technique was selected for this project. The analytical procedure is described in Appendix 2.

Several factors are worthy of special note. Firstly, no leaching test method can claim to simulate the conditions which might occur in a nuclear waste repository. The quantity of a specific radionuclide migrating from such a repository will be influenced by factors such as;

1. the velocity and hence contact time of leachant with the waste,
2. the pH and dissolved solids content of the leachant,
3. the presence or absence of micro-organisms or organic components such as chelants,
4. the free oxygen concentration of the environment (anaerobic conditions tend to

develop an acidic nature),

5. the competition from other leachable radio nuclides, and
6. the temperature and pressure.

Clearly these parameters can not be standardised in a simple laboratory technique. Consequently the purpose of all standard leaching tests is simply to permit comparisons between one waste immobilisation medium and another. In this respect the ISO method is no better or worse than other techniques. However it does produce meaningful comparisons in a relatively short period of time though its use is limited to the study of pure leachants at elevated temperatures.

Twelve Soxhlet leaching tests were constructed in a B grade laboratory at Birmingham Radiation Centre and these are shown in Fig. 5 and the Automatic Beta Gamma Counter employed for analysing leachate is shown in Fig. 6.

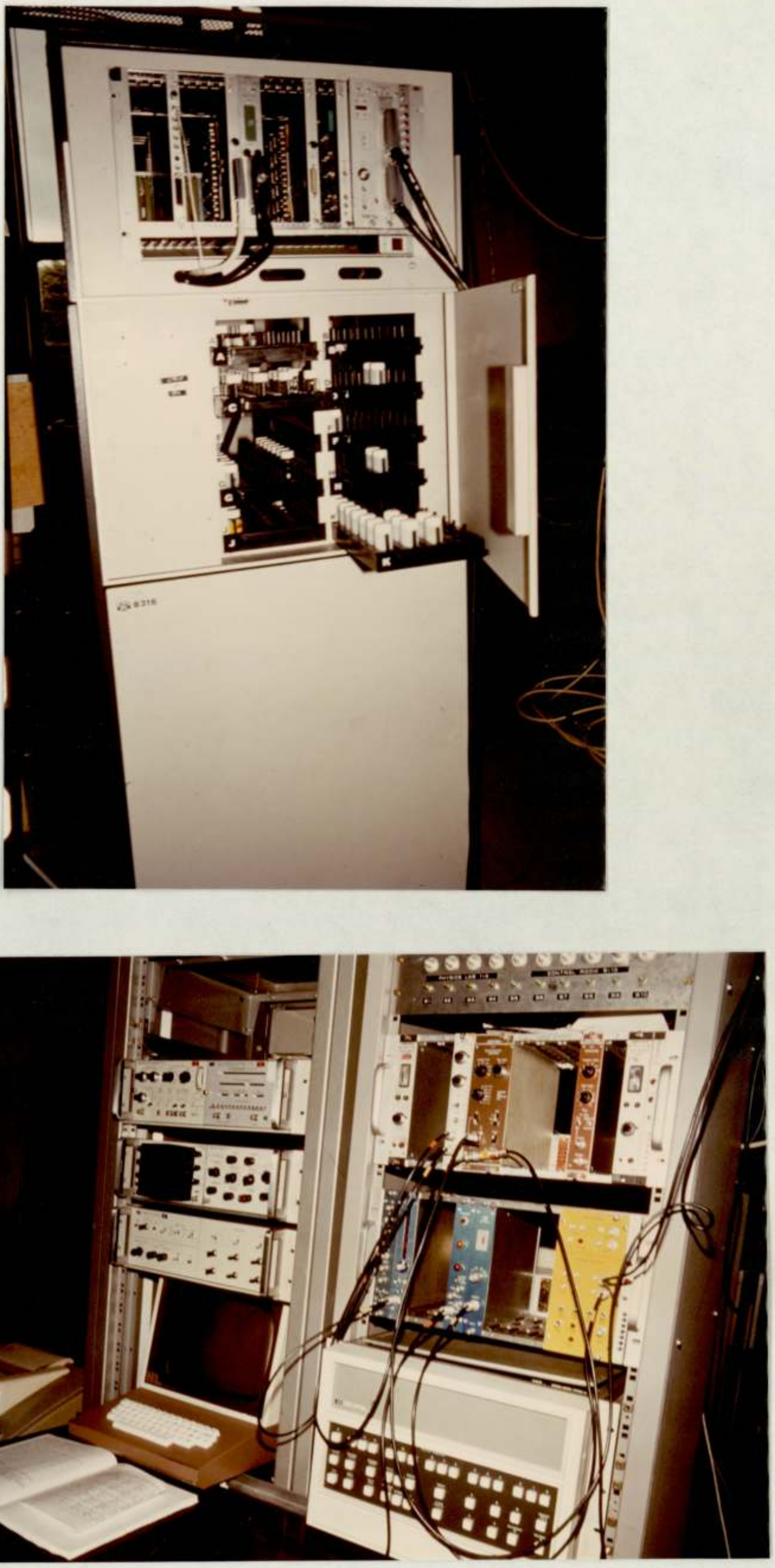


Fig. 6. AUTOMATIC BETA GAMMA COUNTER AND SAMPLE CHANGER.

SECTION 3

EXPERIMENTAL STUDIES

1.0 THE INCORPORATION OF POLYMERS

Styrene copolymers are used in the cement trade to improve the water resistance of cement grouts and concretes. From a review of the styrene copolymers available a styrene-butadiene copolymer was selected. The product was an aqueous emulsion of polymerised styrene-butadiene with a solids concentration of 47± 1% and a pH = 9. It is thought to be a mixture of a randomly crosslinked copolymer

S - S - S - B - S - B - B - S - S
|
S - B - S - S - B - S - S - B - B random

and a random straight chain copolymer

\- B - B - S - S - S - B - S - B - B - random

where S = styrene and B = butadiene. Light scattering measurements have indicated that the mean particle size of the copolymer is 0.2 µm.

During the setting of cement the water is removed from the copolymer emulsion by hydration leaving particles of copolymer dispersed within the capillaries of the composite. This forms a barrier preventing the penetration of liquid water into the composite. For the purpose of this work the product was identified as 'COPOLYMER 3'. When COPOLYMER 3 is left in a dish exposed to the atmosphere water is lost by evaporation and a continuous opaque flexible film is formed.

The technique adopted for the preparation of specimens was to weigh the required ingredients, mix them by manual stirring and to pour the mixture into a prepared paraffin wax mould being 2.4 cm in height x 3.4 cm diameter. Only those formulations which could be poured from the mix vessel and which set in 1 to 3 days into a hard solid were regarded as satisfactory. Once the specimens had solidified they were removed from the mould by cutting it away. Specimens were allowed to stand at room temperature in a 'weticcator' (a sealed vessel containing water) for a 28 day period before any testing began.

For the reasons specified in Section 2, paragraph 9.0 caesium was selected as the first indicator of radionuclide behaviour. The isotope ^{134}Cs was chosen since it has a convenient half life of two years, is a gamma emitter and has a distinctive spectrum recorded by a NaI(Tl) scintillation detector. Caesium chloride solutions were prepared of known molarity with a specific activity of 1 - 2 $mCi l^{-1}$. These synthetic solutions were used to simulate aqueous wastes in these tests.

The procedure adopted for leaching studies is described in the Appendix 2. Although the tests usually extended over a three to six day period, a few experiments were continued for periods of twenty-one days and more, to ensure that the leaching had reached an equilibrium situation.

Duplicate samples of specimens prepared from the same mix at the same time were subjected to leaching studies to ensure that the leaching characteristics were reproducible. Excellent reproducibility was demonstrated.

In comparing the leaching rates of nuclides from cementitious products it is necessary to consider the influence of the waste to cement ratio $\frac{Wa}{C}$

$$\frac{Wa}{C} = \frac{\text{weight of AS used in preparing the specimen}}{\text{total weight of cementitious components}}$$

AS = aqueous solution

The expression C refers to the weight of OPC or, in the case of pozzolanic cements, the total weight of OPC and Pfa. The experimental results are shown in Table 11 in Appendix 3 and graphically in Fig. 7.

Fig. 7 shows the leaching characteristics from Ordinary Portland Cement (OPC) containing 1 M CsCl at various $\frac{Wa}{C}$ ratios. It is seen that the higher the $\frac{Wa}{C}$ ratio, the greater is the quantity leached at any particular time. The incorporation of flyash into cement produces a 'pozzolanic cement' which is capable of reacting with greater quantities of waste (when compared to OPC alone). Table 12 in Appendix 3 and Fig. 8 show the leaching characteristics for pozzolanic cements produced from 84% Pfa and 16% OPC at various $\frac{Wa}{C}$ ratios. The ratio of 84% Pfa and 16% OPC is frequently used in civil engineering applications for the preparation of an inexpensive grout which solidifies into a low strength solid suitable for use in voidfilling.

Fig. 7. THE EFFECT OF $\frac{Wa}{C}$ RATIOS ON LEACHING CHARACTERISTICS OF OPC CONTAINING 1 M CsCl

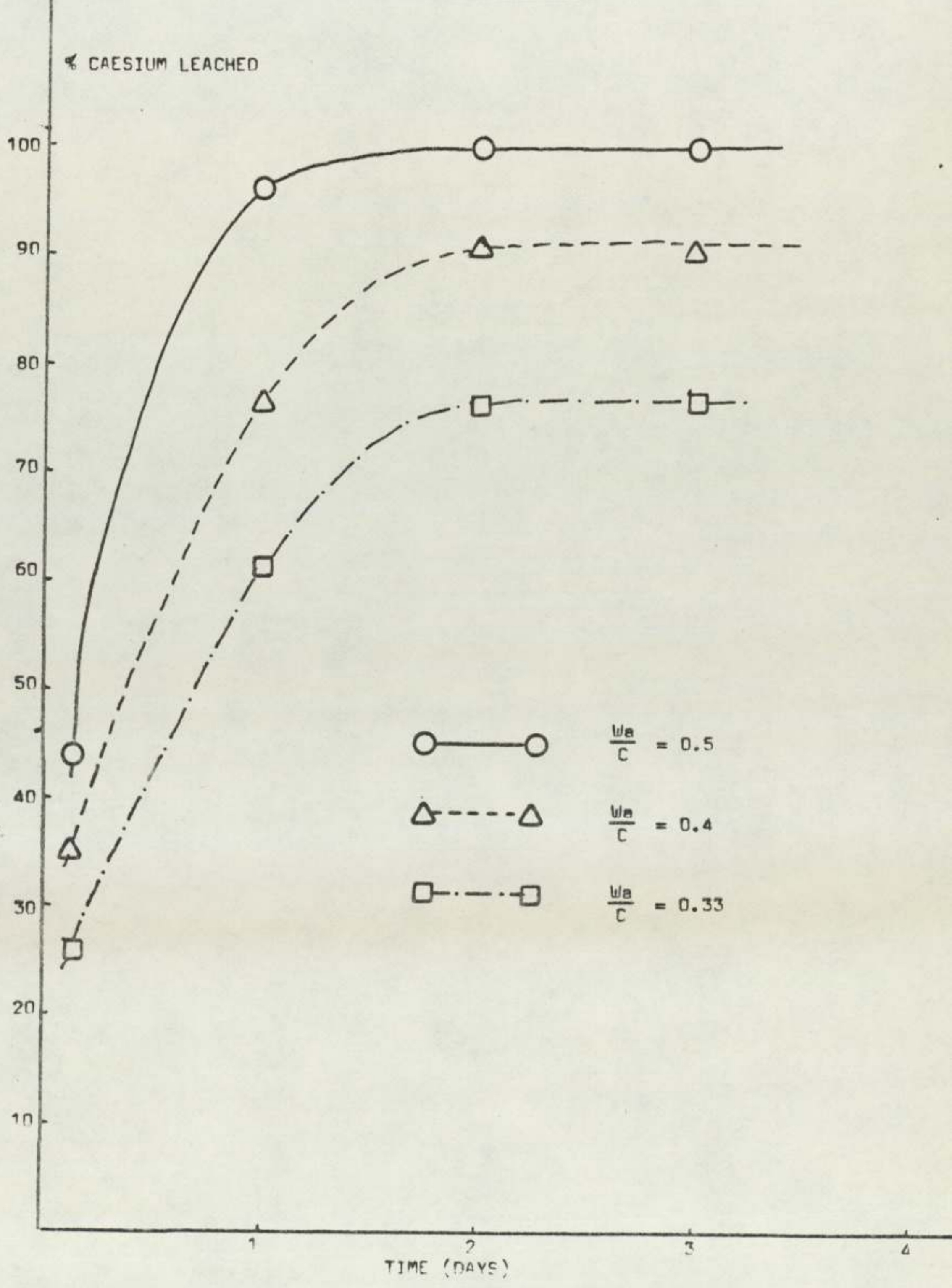
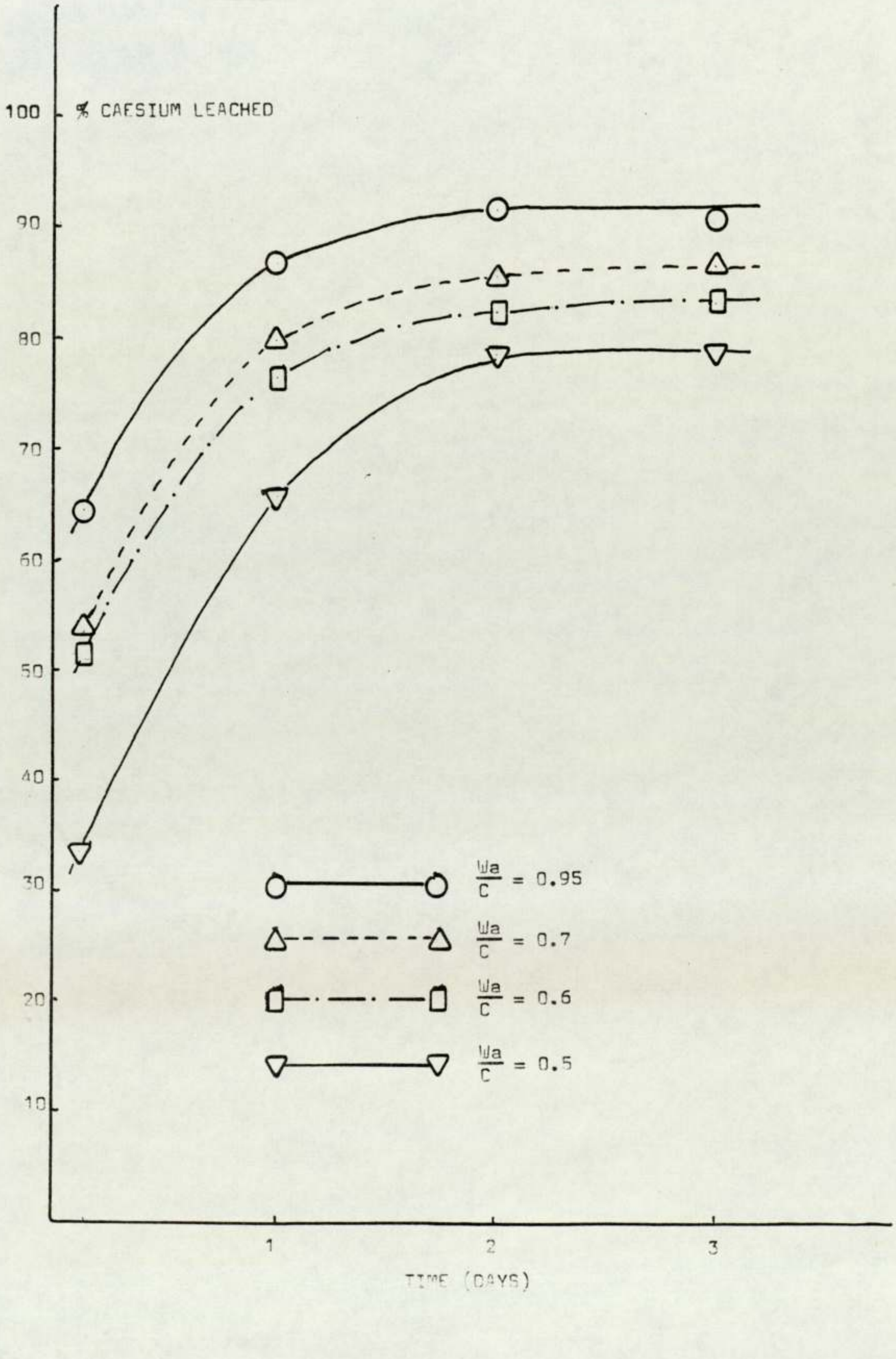


Fig. 8 THE EFFECT OF $\frac{Wa}{C}$ RATIOS ON LEACHING CHARACTERISTICS OF POZZOLANIC CEMENTS CONTAINING 1M CsCl



Throughout this work the term 'the pozzolanic cement' refers to this ratio of Pfa and OPC.

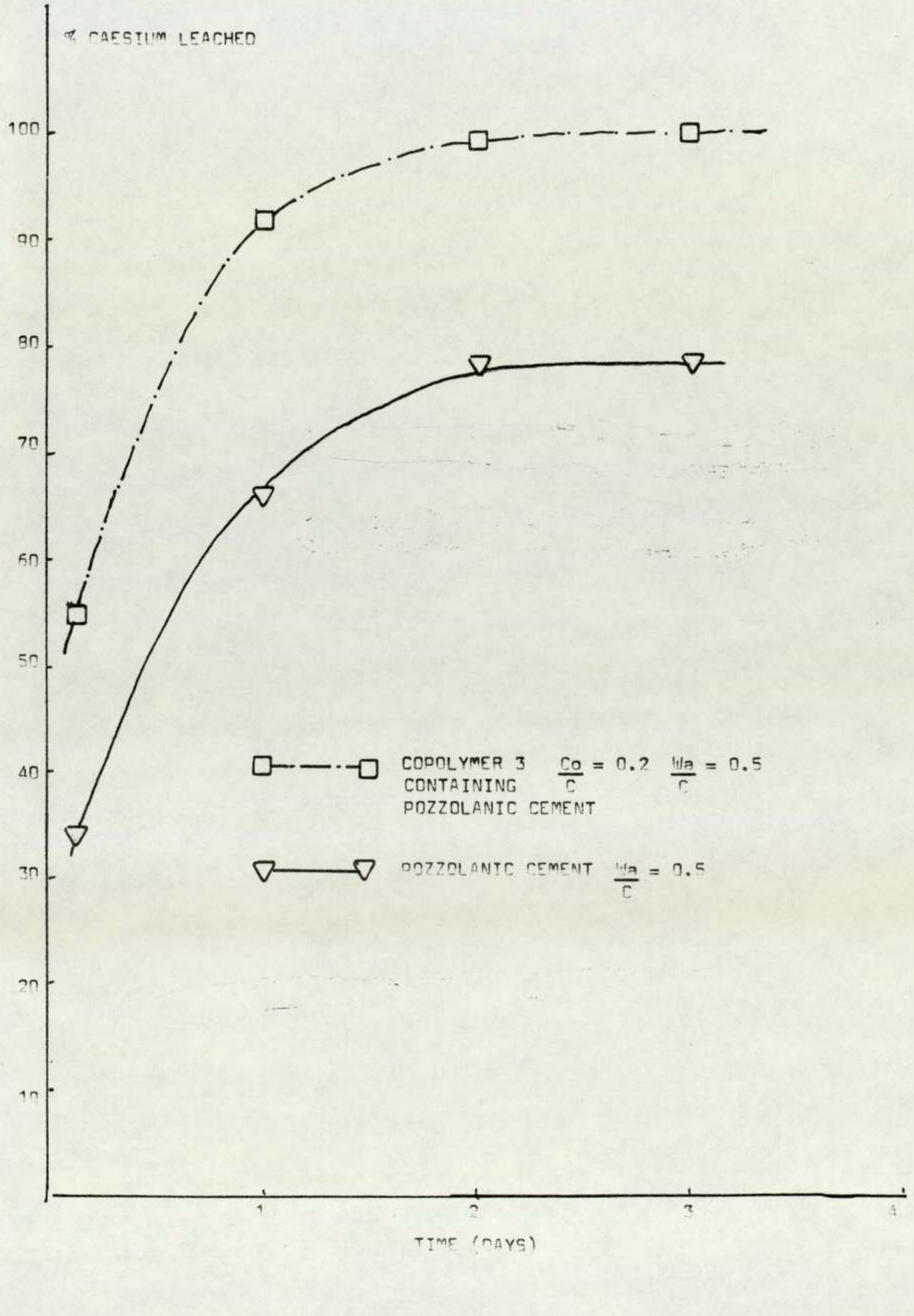
Comparing Figs. 7 and 8 clearly shows the considerable benefits to be gained by incorporating Pfa in the composite. For example, suppose that 75% leach rate after 3 days is an acceptable limit from the point of view of environmental protection, it can be seen that using OPC alone it would be possible to incorporate about 33% waste into the product whereas with the pozzolanic cement 50% of waste can be incorporated whilst achieving the same degree of environmental protection. Considering also the relatively low cost of Pfa compared to OPC another advantage is generated.

The incorporation of COPOLYMER 3 into the composite and its effect on the leaching rate of caesium has been studied. Specimens were prepared by dry mixing the weighed quantities of OPC and Pfa and adding a weighed quantity of the aqueous emulsion of polymerised styrene-butadiene and the aqueous waste. The components were mixed by manual stirring until homogeneous and poured into moulds for solidification.

Table 13 of Appendix 3 shows the leaching characteristics of COPOLYMER 3 containing pozzolanic cement ($\frac{Co}{C} = 0.2$, $\frac{Wa}{C} = 0.5$) and Fig. 9 compares this data with pozzolanic cement alone ($\frac{Wa}{C} = 0.5$).

COPOLYMER 3 had no beneficial effect on the leach rate. Although this was contrary to early expectations it may be explained by the following reasoning.

Fig. 9. THE EFFECT OF COPOLYMER 3 ON THE LEACHING CHARACTERISTICS OF POZZOLANIC CEMENT CONTAINING 1M CsCl



It has been seen from Fig. 7 that increasing the $\frac{Wa}{C}$ ratio causes a marked increase in the leaching of caesium. It will be remembered that COPOLYMER 3 is an aqueous dispersion of copolymerised styrene and butadiene.

Consequently adding COPOLYMER 3 to any particular cementitious mixture actually increases the $\frac{Wa}{C}$ ratio due to its inherent water content. In this case the actual $\frac{Wa}{C}$ ratio was increased from 0.5 to 0.6 thereby increasing the leaching rate.

There is also visual evidence which tends to support this explanation. During the preparation of these specimens, it was noticed that the greater the concentration of COPOLYMER 3 the longer was the time to set. Long set times provide a greater opportunity for phase separation to occur within the composite matrix. Inspection of specimens revealed that a layer of organic material (presumed to be COPOLYMER 3) tends to form on the uppermost surface of the specimen during setting. The higher the COPOLYMER 3 concentration the greater is the thickness of the layer.

It was concluded from this evidence that the incorporation of COPOLYMER 3 into OPC or the pozzolanic cement had no beneficial effects in reducing the leaching rate of caesium. The mixtures tend to form a two phase product with the organic component separating near to the uppermost surface rather than forming a continuous organic phase distributed uniformly between the inorganic crystals. As a result interest in this approach declined and experiments were discontinued.

2.0 THE COPOLYMERISATION OF MONOMERS

An alternative approach to the incorporation of polymers into a cement composite is the polymerisation of monomers in situ within the cement matrix as the cementitious material sets. However, polymerisation reactions are generally incompatible with the alkaline conditions which occur during the hydration of cement, and this is why researchers at Brookhaven National Laboratory (36) concluded that work within this area would be unproductive. This author (37) has succeeded in copolymerising monomers within the hydrating cement.

3.0 COPOLYMER 6

3.1 Organic Synthesis

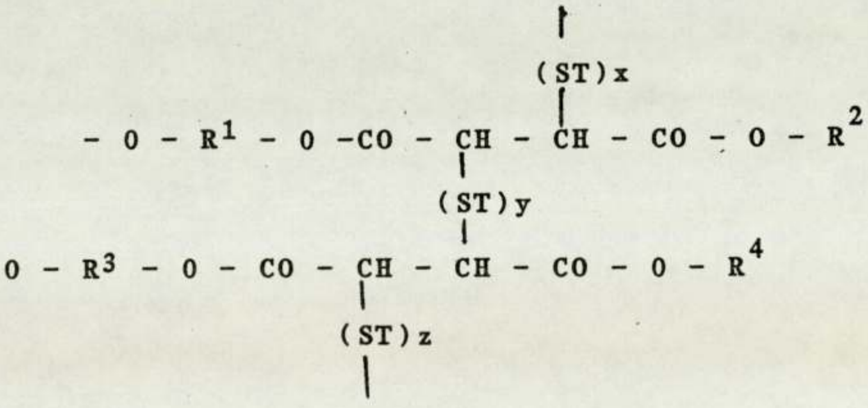
It is known that styrene (38) can be polymerised with unsaturated alkyds by means of free radical initiators such as peroxides. The alkyd (a product derived from an alcohol and an acid) is first prepared by reacting an unsaturated dibasic acid or anhydride with a dihydric alcohol or glycol. The synthesis of the organic monomer used was undertaken for the author by Mr. F. Bassford and Dr. J. Goulding. The alkyd was synthesised (see Fig. 12) by reacting 2 moles of phthallic anhydride, 1 mole maleic anhydride, 2.15 moles propylene glycol and 1.15 moles diethylene glycol under reflux in a stirred flask and in an inert atmosphere until its condensation product had an acid number (the number of milligrams of KOH equivalent to the acid present in 1 gram of resin) of 28 - 30 mg KOH per gram.

The water produced in the condensation reaction was removed by azeotropic distillation with xylene. The product was a viscous amber coloured liquid and was diluted with half its weight of styrene. This mixture is easily pourable and can be safely stored and transported. The addition of 100 ppm of hydroquinone is beneficial in preventing oxidation, product deterioration and darkening colour.

3.2 Polymerisation

The resin produced above is capable of polymerisation when mixed with a free radical initiator. Ammonium persulphate is a commonly used free radical initiator and was used for this experiment at a concentration of 2% of the weight of resin. The polymerisation process itself is exothermic.

The copolymer produced has the general structure



$$-O-R^1-O-CO-\underset{|}{CH}-\overset{\overset{|}{(ST)_x}}{\overset{|}{CH}}-CO-O-R^2$$
$$(ST)_y$$
$$O-R^3-O-CO-\underset{\underset{|}{(ST)_z}}{\underset{|}{CH}}-\overset{|}{CH}-CO-O-R^4$$

where ST = styrene

and R^1, R^2, R^3, R^4 may be phthallic, maleic, propylenic or diethylinic.

During this work it became clear that mixing was an important variable (see section 3.3), hence a variable speed stirrer complete with speed indicator and programme timer as shown in Fig. 10 was constructed to permit reproduction of mixing conditions.

For the sake of completeness details of the stirrer design are given in Appendix 1 but there is no suggestion that the design has been optimised. However, the design does permit (where necessary) the rapid dispersion of one material in another whilst avoiding the inclusion of air. In operation, mixing occurs without the formation of a vortex and consequently the risk of air inclusion is much reduced. The inclusion of air tends to retard certain organic polymerisations and also creates voids which increase the permeability of the product and is therefore best avoided. The speed indicator coupled to the mixer shaft was not a revolution counter but was simply used to permit reproduction of speed from one test to another. A standard mixing vessel was used for all preparations. The programme timer was arranged to illuminate warning lights at pre-set intervals.

To demonstrate the polymerisation of this resin and its capability to solidify aqueous waste solutions a series of experiments was conducted in which aqueous solutions of 1M CsCl and 0.2M CsCl were prepared labelled with 1 mCi of ^{134}Cs. A weighed quantity of the resin described in 3.1 above was added to the mixer. Care was taken in all cases to ensure that the mixer impellor was totally submerged in the resin to prevent

FIG. 10 MIXING EQUIPMENT

air inclusion. The mixer was operated at high speed and ammonium persulphate (2% of resin) was added. After two minutes of mixing the aqueous solution of caesium chloride was slowly added over a further two minute period. During this time the mix developed a pale straw colouration but remained as a single phase. The mixing was stopped and the contents transferred to paraffin wax moulds. Details of the quantities of materials employed are given in section 3.3.

The viscosity of the mix steadily increased and within a period of three hours the material had set into a hard solid monolith. After the standard twenty-eight day storage period in a weticcator, the leaching characteristics were determined by the method described in Appendix 2. Table 14 in Appendix 3 and Fig. 11 show the leaching characteristics of these products with $\frac{Wa}{Co} = 0.5$ and demonstrate the influence of the caesium chloride concentration within the waste on the leaching characteristics. As might be expected the higher the caesium chloride concentration the greater the amount of caesium leached at any one time.

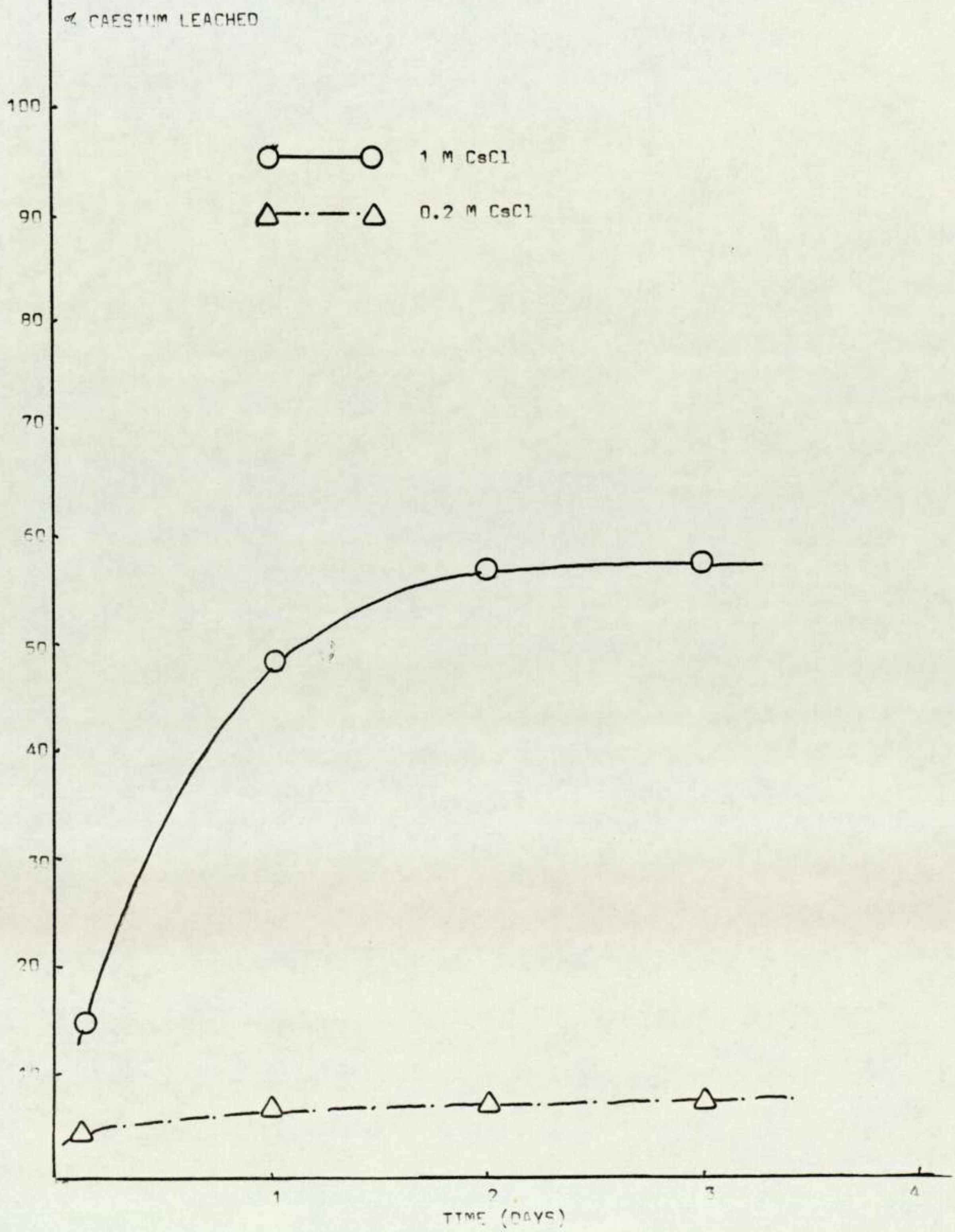
3.3 Composites of COPOLYMER 6

Control of the copolymerisation technique described in Section 3.2 has been developed so that it takes place at the same time as the hydration of cement compounds and produces a viscous mix which can be poured (or pumped) from the mixing vessel into a disposable container. The copolymerisation reaction and the hydration reaction take place at the same time in the

Fig. 11 LEACHING CHARACTERISTICS OF COPOLYMER 6

EFFECT OF MOLARITY OF CsCl

$\frac{Na}{Co} = 0.5$



mixing vessel at ordinary temperatures and pressures and produce a composite of high mechanical integrity. The technique can also be used to incorporate solid waste in an active or inactive form but this has not been studied as part of this thesis.

Before proceeding to describe the preparation and properties of such composites it is valuable to identify the variables which could affect the characteristics of the composites under consideration. These include:

1. The nature of the R groups in the monomer. Four groups (R^1, R^2, R^3 and R^4) have been identified in section 3.1 but others are also possible.
2. The relative proportions of R^1, R^2, R^3 and R^4.
3. The proportion of styrene added to the alkyd.
4. The choice of emulsifier (when necessary) and its concentration.
5. The choice of initiator (catalyst) and its concentration.
6. The choice of promoter (when necessary) and its concentration.
7. The ratio of organic monomer to inorganic cement products $\frac{Co}{C}$ used in the composite.
8. The choice of type of cement.
9. The choice of pozzolan and its concentration.
10. The ratio of aqueous waste to organic polymer $\frac{Wa}{Co}$.

11. The ratio of aqueous waste to cement product $\frac{Wa}{C}$. (In this ratio C includes both cements and pozzolans).
12. The sequence of ingredient additions.
13. The choice of mixer design.
14. The choice of pollutant (radionuclide) or mixtures of pollutants (radionuclides) to simulate waste behaviour.
15. The concentration of pollutant (radionuclide) in the waste.
16. The time permitted for hydration, curing and copolymerisation prior to submitting the specimen to testing.

Clearly with all these variables the researcher has no option but to standardise certain parameters and study the effects of a few of what may be considered the critical ones.

In this work the parameters which have been standardised include;

(a) The proportion of styrene added to the alkyd (see 3 above).

(b) The choice of emulsifier (when used) (see 4 above).

(c) The choice of type of cement (see 8 above).

(d) The choice of pozzolan and its concentration (see 9 above).

(e) The sequence of ingredient addition (see 12 above.

(f) The choice of mixer design (see 13 above).

(g) The time permitted for hydration, curing and copolymerisation prior to submitting specimens to test (see 16 above).

Fig. 12 summarises the technology employed for the preparation of COPOLYMER 6 composites.

Specimens of COPOLYMER 6 were prepared using the formulation;

142.8 g of pozzolanic cement (22.8g OPC and 120g Pfa)
85.7 g of resin
1.7 g of initiator (ammonium persulphate)
71.4 g of aqueous solution (simulated waste)

$\frac{Wa}{C} = 0.5$ $\frac{Co}{C} = 0.6$ $\frac{Wa}{Co} = 0.83$

The mixing technique employed was to add the free radical initiator to the resin in the mixer shown in Fig. 10 and stir at high speed for two minutes. The aqueous solution was added to the cementitious ingredients in a separate vessel and mixed. This mixture was then slowly added to the resin prepared as above with very slow speed mixing. High speed (high shear) mixing during this operation needed to be avoided since it produced separation into two distinct phases. The products obtained were pourable single phase mixtures which were cast into paraffin wax moulds and stored in a weticcator as before. After twenty-eight days the leaching characteristics were determined by the method described in Appendix 2. Results are shown in Table 15 of Appendix 3 and Fig. 13 compares

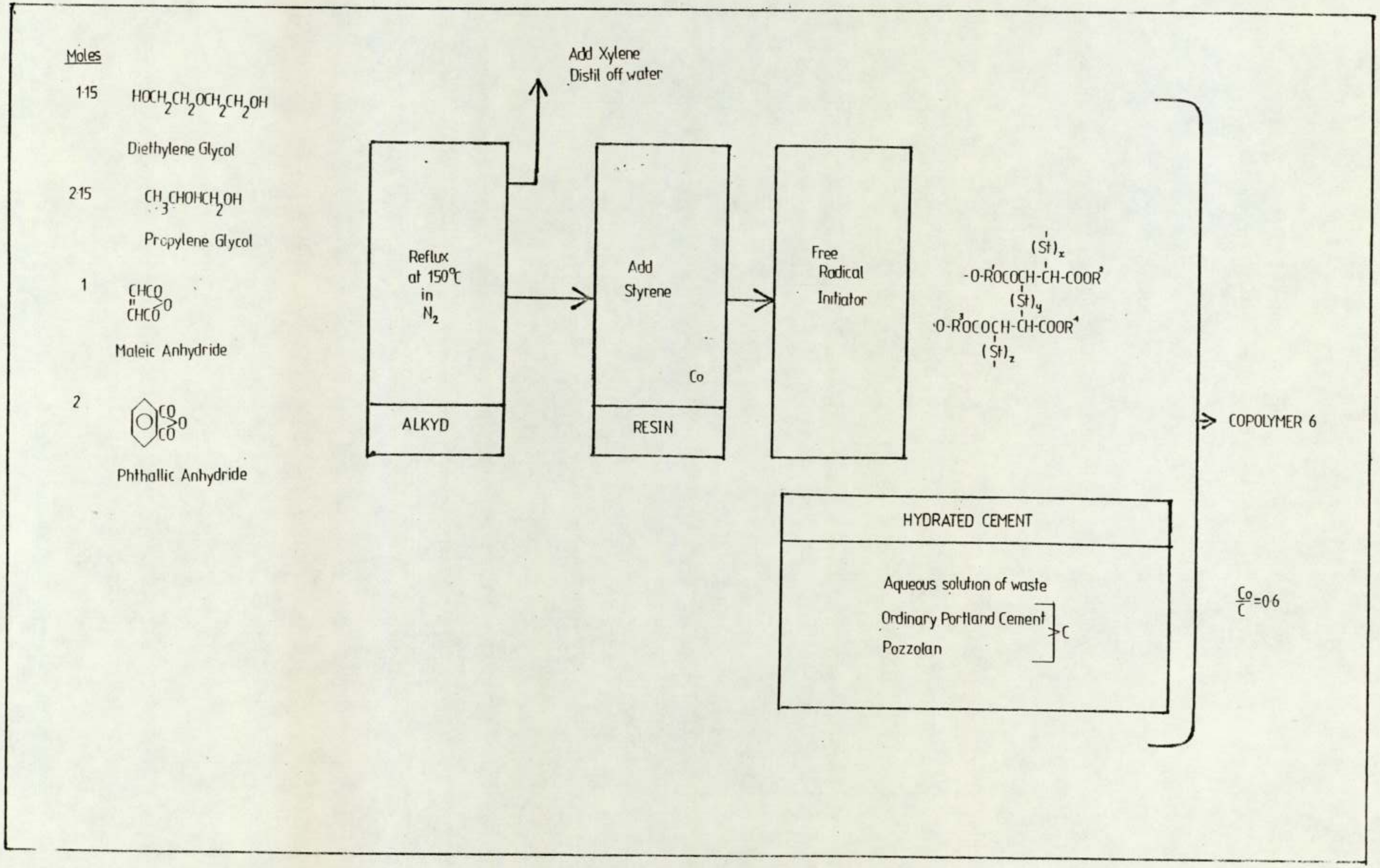
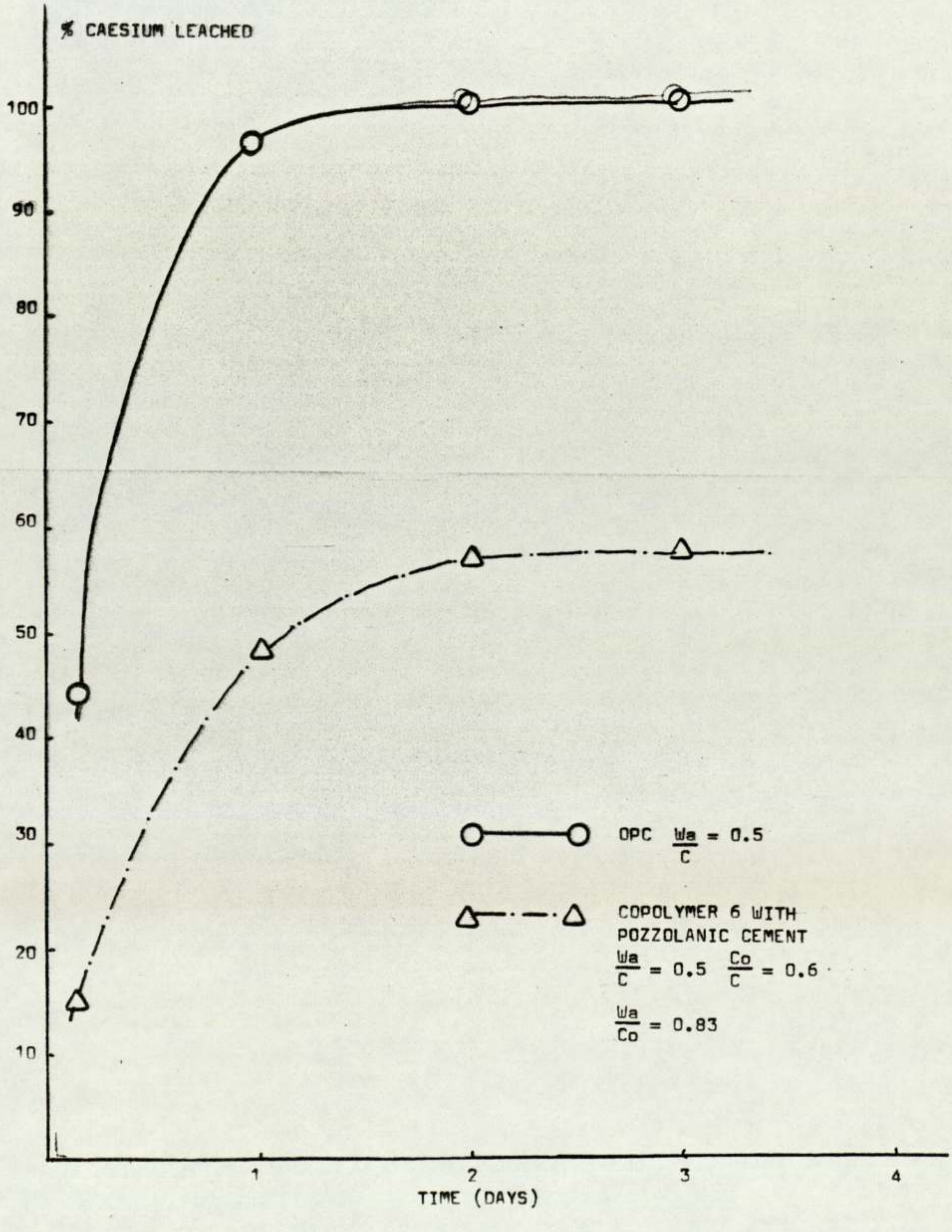


FIG. 12 THE PREPARATION OF COPOLYMER 6 COMPOSITES

Fig. 13. LEACHING CHARACTERISTICS OF COPOLYMER 6 COMPARED TO O.P.C. BOTH CONTAINING 1M CsCl



the leaching characteristics of OPC ($\frac{Wa}{C}$ = 0.5) with COPOLYMER 6 containing pozzolanic cement ($\frac{Wa}{Co}$ = 0.5). It will be seen that COPOLYMER 6 has about half the leaching rate of OPC when tested under identical conditions. Fig. 14 is another expression of these results and shows that COPOLYMER 6 is superior to the pozzolanic cement.

The physical strength of such composites is an important characteristic in terms of resistance to damage during transport or disposal.

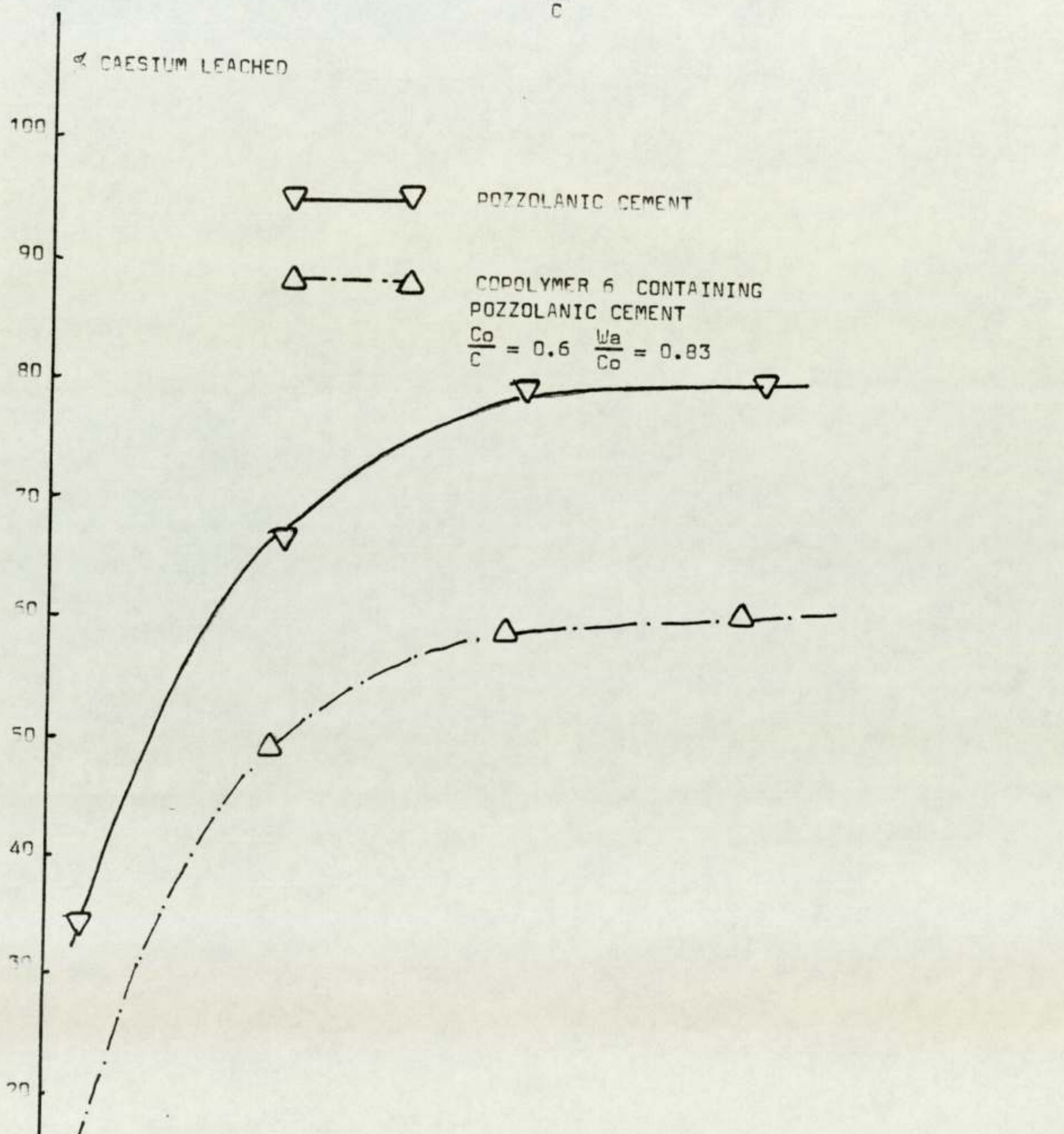
To measure the compressive strength of COPOLYMER 6, specimens were cast into two-inch cube moulds and allowed to set. After 3 to 5 days the specimens were removed from their moulds and allowed to cure for a duration of twenty-eight days in a weticcator. They were then compressed in a Mohr and Federhoff compression Testing Machine under a constant load (see Fig. 15). Fig. 16 shows the compressive strength of COPOLYMER 6 at various $\frac{Wa}{C}$ ratios. It was noted that fracture of the specimen was not entirely brittle and that there was evidence of plastic deformation before failure occurred. No particular inference has been made at this stage from Fig. 16 due to the limited number of determinations made.

4.0 COPOLYMER 7

This alkyd was prepared by the technique described in paragraph 3.1 except that 3.3 moles of polyethylene glycol were used instead of propylene and diethylene glycols. The aim was to increase the aqueous solution

Fig. 14. LEACHING CHARACTERISTICS OF COPOLYMER 6 COMPARED TO POZZOLANIC CEMENT CONTAINING 1 MCsCl

$\frac{Wa}{C} = 0.5$



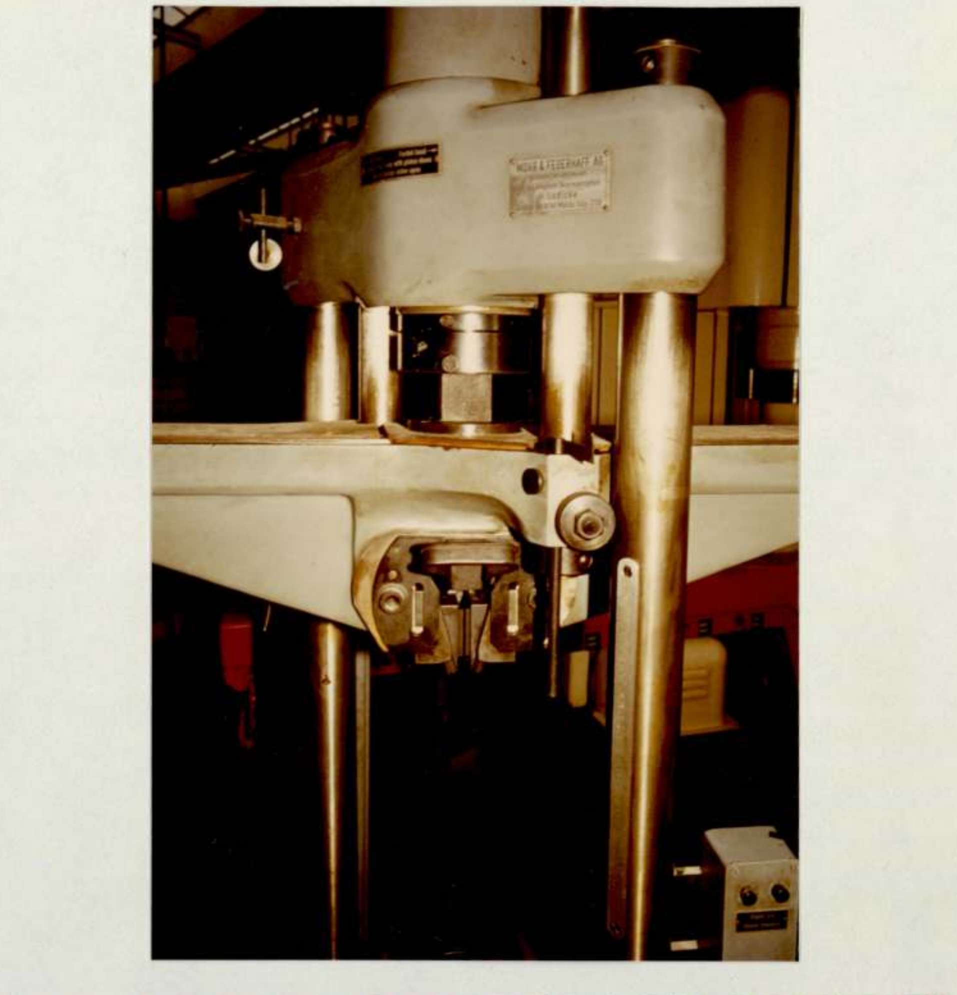
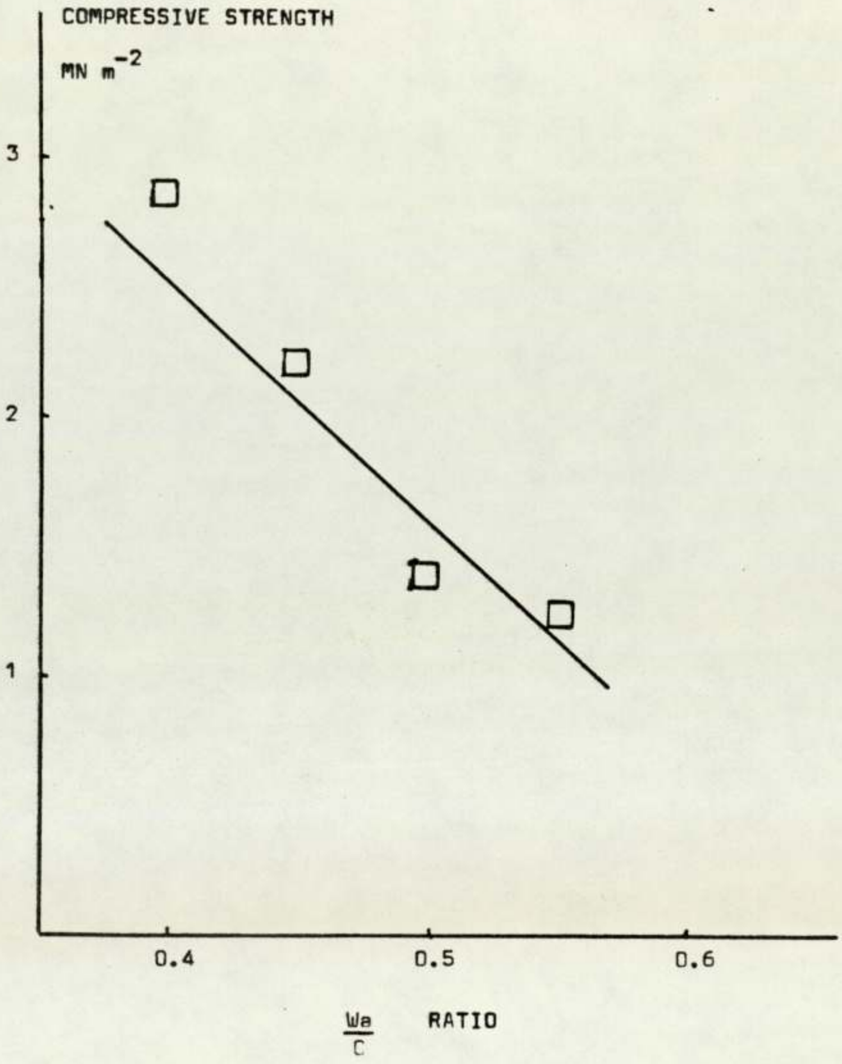


Fig. 15. A MOHR AND FEDERHOFF COMPRESSION TESTING MACHINE.

Fig. 16. COMPRESSIVE STRENGTH OF COPOLYMER 6



uptake ($\frac{Wa}{Co}$ ratio). Solid monoliths were formed with $\frac{Wa}{Co}$ ratio = 1 with composites which included OPC or the pozzolanic cement. Fig. 17 summarises the technology employed for the preparation of COPOLYMER 7. However the external surfaces of the monoliths remained moist as water was readily lost from the interior of the composites. This phenomenon, known as sweating, indicated that the composite had a more open lattice structure which would be unlikely to restrict movement of leachants into and out of the product and consequently would be expected to have poor leaching characteristics. Studies of COPOLYMER 7 were therefore discontinued.

5.0 COPOLYMER 8

5.1 Organic Synthesis

This alkyd was prepared by the technique described in paragraph 3.1 except that 1 mole of phthallic anhydride, 4 moles of maleic anhydride and 5 moles of propylene glycol were used. High maleic to phthallic anhydride ratios would be expected to produce greater frequency of crosslinking in the polymer and a more brittle product. Propylene glycol incorporation would be expected to increase the uptake of aqueous solution.

5.2 Polymerisation

The free radical initiator, ammonium persulphate, was not found to be effective with this monomer. An alternative initiator combination of methyl ethyl ketone peroxide and cobalt octoate was therefore used.

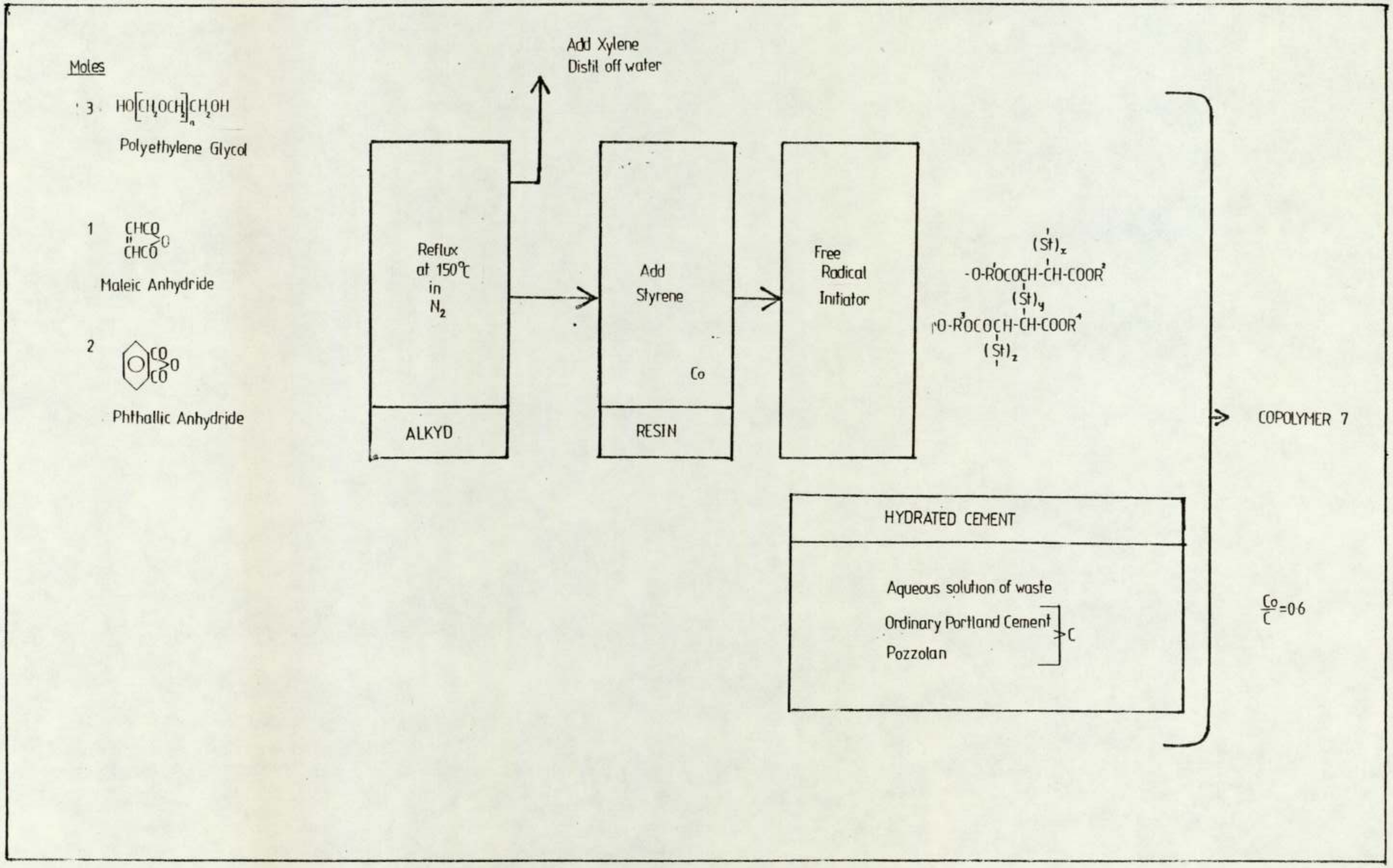


FIG. 17 THE PREPARATION OF COPOLYMER 7 COMPOSITES

0.5g of cobalt octoate (a solution in white spirit containing 10% cobalt) and 2.0g of methyl ethyl ketone peroxide (a 50% solution in dioctyl phthallate) were used for each 100g of resin. Additionally the incorporation of a non-ionic emulsifying agent (a highly oxylated castor oil) at a concentration of 10g per 100g of resin was found to assist in stabilising the mixture during the polymerisation stage.

The polymerisation process began at ambient temperatures but the process is strongly exothermic. A battery of electronic thermometers was arranged to measure the exotherms from products prepared in this way. In some extreme cases the product temperature exceeded 100°C which not only constituted a danger but evaporated off the aqueous waste leaving an unsatisfactory solid. These extremes were only attained with very low aqueous solution contents (eg $\frac{Wa}{Co}$ = 0.1). At normal $\frac{Wa}{Co}$ ratios in the range 0.5 to 1.0 the reaction was non-hazardous and the exotherm barely detectable. Attempts were made to use exotherm measurements to aid the selection of the best formulations. Except for very general observations this was not found to be helpful since changes in composition (for example changes in $\frac{Wa}{Co}$ ratio) significantly affected the temperature rise. Higher aqueous solution contents simply acted as a heat sink.

It is desirable to know the leaching characteristics of COPOLYMER 8 in the absence of cementitious ingredients. Specimens were prepared using 1M CsCl solution as simulated waste and, after curing for twenty-eight days in a weticcator, the leaching characteristics were determined. Table 16 in Appendix 3 and Fig. 18 show this data at high $\frac{Wa}{Co}$ ratios. Caesium immobilisation is very poor indicating that the organic polymer alone could not be used at high $\frac{Wa}{Co}$ ratios for radioactive waste treatment. Specimens of these products were dried in an oven at 60°C and weight loss determinations made at intervals. After 4 days it was found that more than 75% of the aqueous solution added had been lost by drying. These indicators are interpreted as showing that the aqueous solution in COPOLYMER 8 in the absence of cementitious ingredients is trapped by an encapsulation process and that it is able to move readily as a result of changes in its environment (i.e. a temperature increase or exposure to leachant). Under these conditions the aqueous solution is seen to be held by weak physical forces rather than chemical bonding.

5.3 Composites of COPOLYMER 8

Fig. 19 summarises the technology employed for the preparation of COPOLYMER 8 composites and a typical formulation is shown below

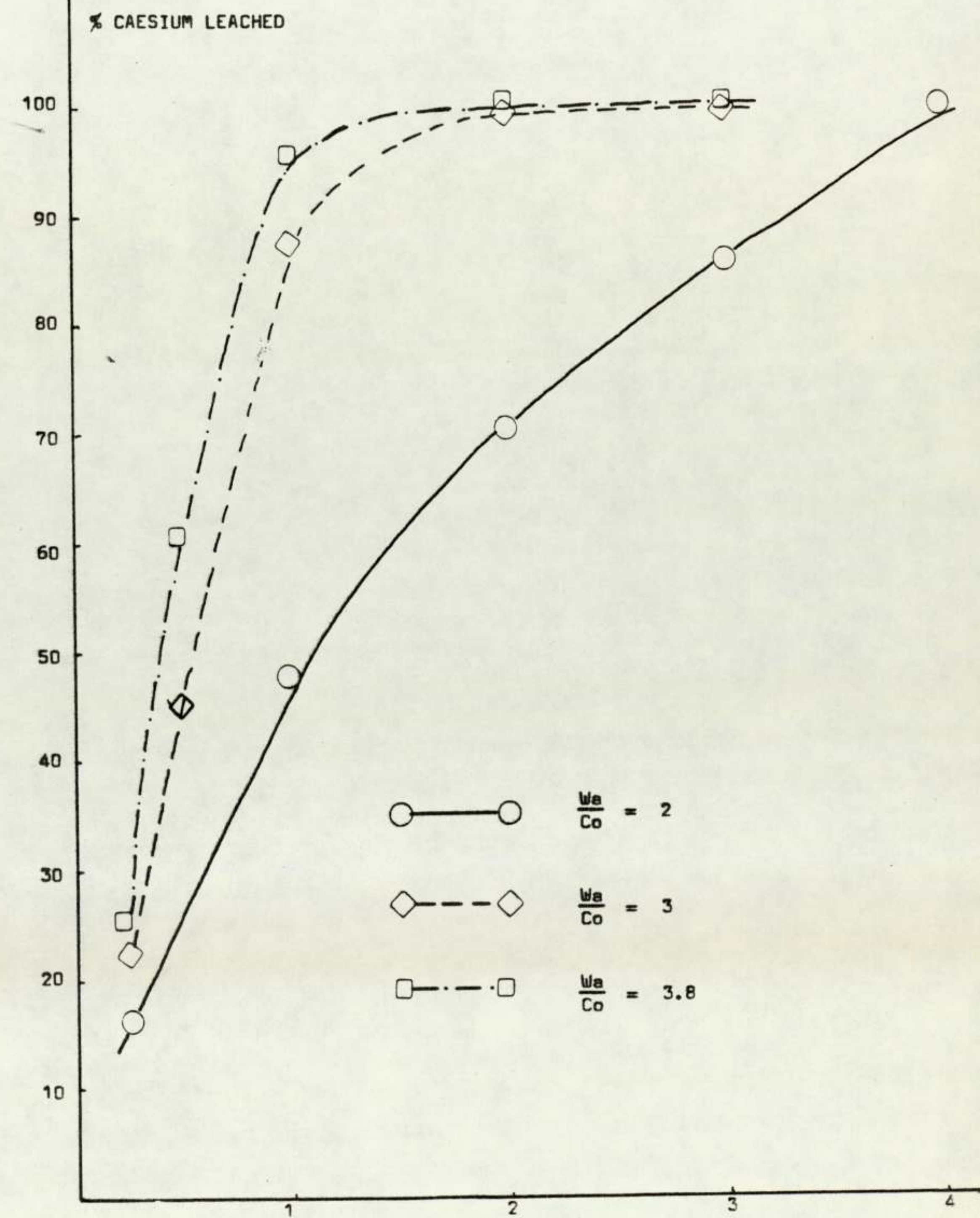
100 g of cement (or 16g OPC and 84g Pfa)
60 g of resin
6.0 g of emulsifying agent
0.3 g of promoter (cobalt octoate)
1.2 g of initiator (methyl ethyl ketone peroxide)
50 g of aqueous solution (simulated waste)

$$\frac{Wa}{C} = 0.5 \qquad \frac{Co}{C} = 0.6 \qquad \frac{Wa}{Co} = 0.83$$

FIG.18 LEACHING CHARACTERISTICS OF COPOLYMER 8

ORGANIC POLYMER ALONE

1 M CsCl



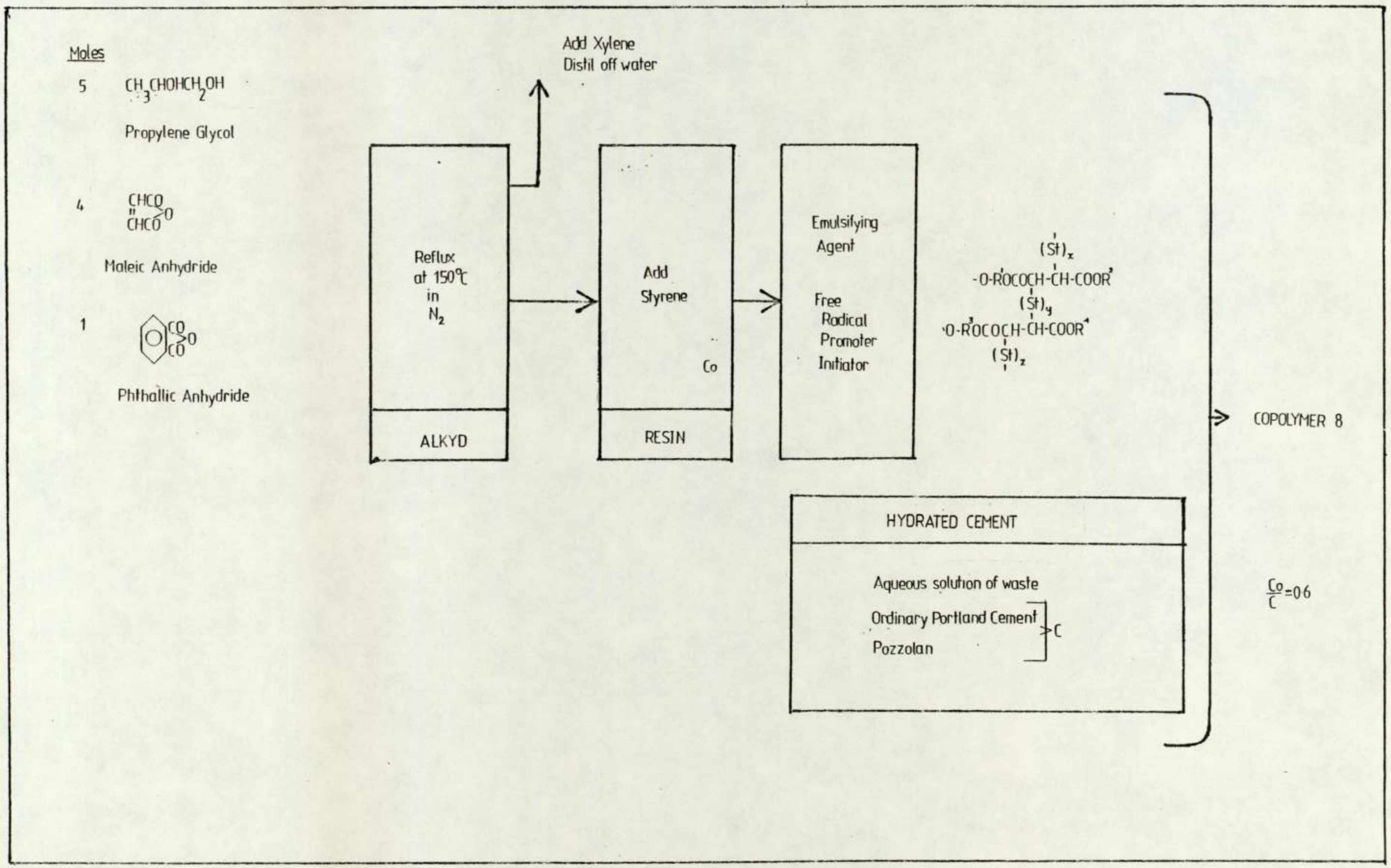


FIG. 19 THE PREPARATION OF COPOLYMER 8 COMPOSITES

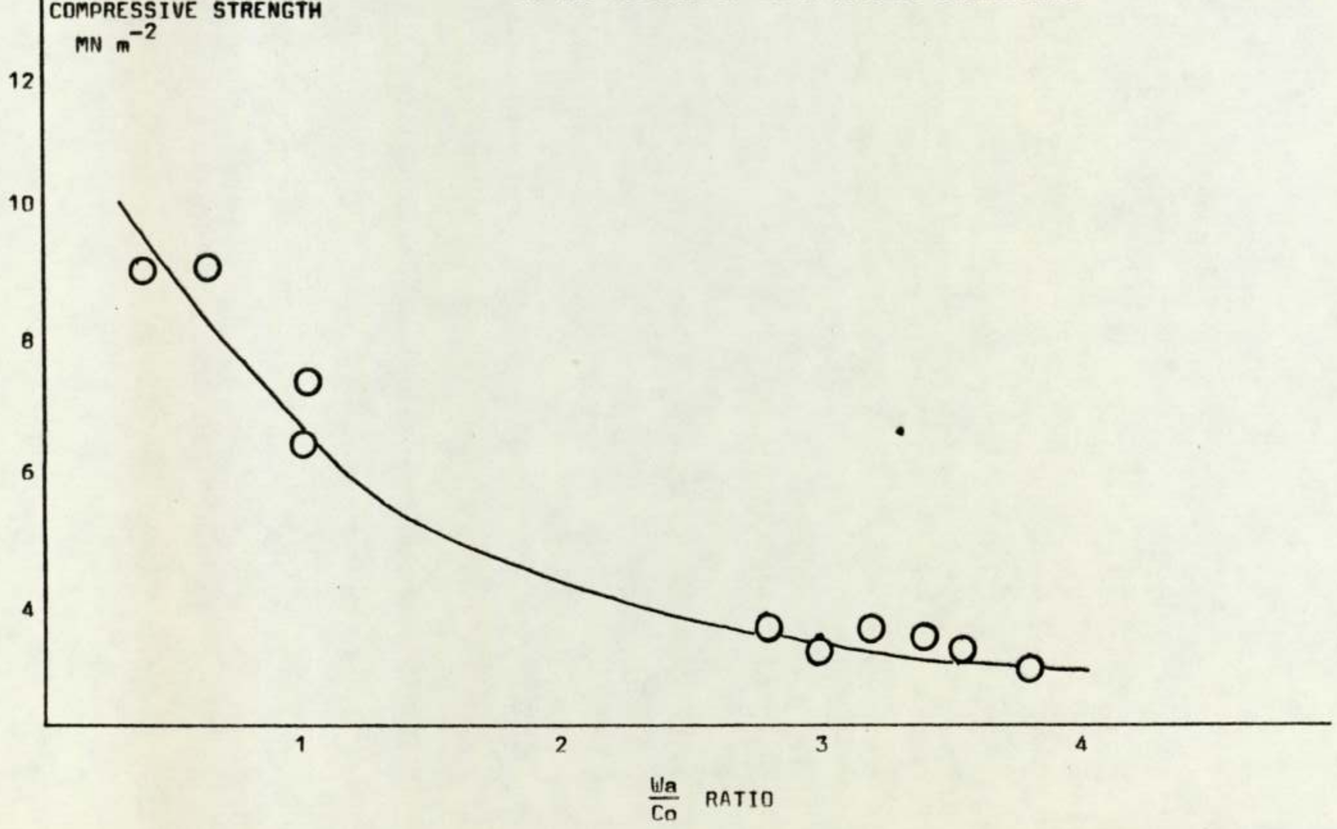
The mixing technique employed was to add the emulsifying agent and the cobalt octoate to the resin in the mixer shown in Fig. 10 and stir at high speed for two minutes. The mixture produced was amber in colour and quite stable. The free radical initiator was then added to this mix and high speed stirring continued for a further two minutes. The aqueous solution was added to the cementitious ingredients in a separate vessel and manually mixed. This mixture was then slowly added to the resin prepared above with very slow speed mixing. Again precautions were taken to minimise air inclusion and to avoid high speed stirring during the last mixing stage which tended to cause separation of the mix into two phases.

Composites produced from this alkyd were shown to have very high water uptake capacity as was expected. $\frac{Wa}{Co}$ ratios of 3.0 still produced a solid monolith within a few hours of preparation. However, at high $\frac{Wa}{Co}$ ratios the composites exhibited the same sweating characterics found in COPOLYMER 7.

Specimens of COPOLYMER 8 composites at various $\frac{Wa}{Co}$ ratios were prepared and cast into two inch cube moulds and allowed to set. After 3 to 5 days the specimens were removed from their moulds and allowed to cure in a weticcator for twenty-eight days. The compressive strength was then determined and the relationship between compressive strength and $\frac{Wa}{Co}$ ratio is shown in Fig. 20.

In order to study the leaching characteristics of

FIG. 20 COMPRESSIVE STRENGTH OF COPOLYMER 8 AS A FUNCTION OF $\frac{Wa}{Co}$ RATIO IN THE ABSENCE OF CEMENTITIOUS INGREDIENTS



COPOLYMER 8 composites a specimen with $\frac{Wa}{Co} = 0.83$ and $\frac{Co}{C} = 0.6$ was prepared using 1M CsCl solution as simulated waste. After the standard twenty-eight day curing duration, the leaching characteristics were determined as described in Appendix 2 and are shown in Table 17 of Appendix 3 and Fig. 21. Strict comparison with the organic polymer alone is not possible but extrapolation of results shown in Fig. 18 indicates that the leaching characteristics of COPOLYMER 8 composites containing cementitious ingredients are improved. Nevertheless, the leaching characteristics do not provide the degree of environmental protection which is desirable and consequently consideration was given to methods of further reducing the caesium leaching rate by pretreatment.

5.4 Pretreatment

Pretreatment techniques are used in other immobilisation technologies. For example Hild (16) used nickel ferrocyanide in bitumen for caesium retention. He showed that only very low concentrations of nickel ferrocyanide are necessary and reported the data shown in Table 8.

FIG. 21 LEACHING CHARACTERISTICS OF COPOLYMER 8 CONTAINING CEMENTITIOUS INGREDIENTS

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$ 1 M CsCl

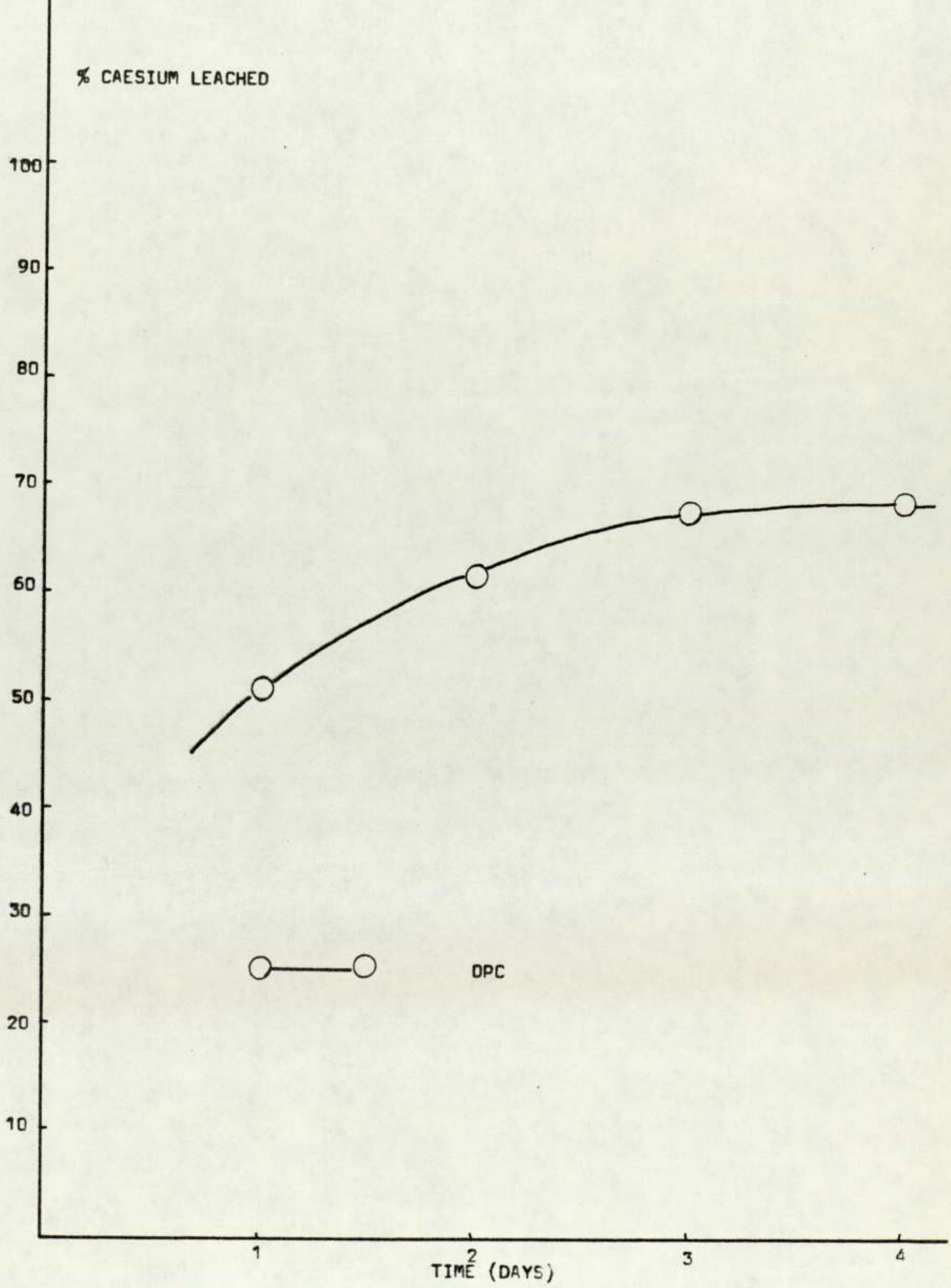


Table 8 Retention of Caesium in Bitumen using Nickel Ferrocyanide Pretreatment

Concentration of $K_4[Fe(CN)_6]$ Molarity	Decontamination Factor
4.88×10^{-2}	$> 10^5$
2.44×10^{-2}	$> 10^5$
1.22×10^{-2}	5×10^3
6.1×10^{-3}	2.5×10^3
2.44×10^{-3}	0.5×10^3

Source: Reference 16

However Hild did not report the caesium content of the waste in question. The precipitation of caesium salts by the addition of ferrocyanides is well known but the reaction is not stoichiometric. Consequently, this author found it necessary to conduct a simple experiment to determine an effective concentration which might be used in practice. A solution of 0.2 M CsCl containing 1 mCi of ^{134}Cs was used. Solutions of 0.2 M $NiSO_4$ and 0.2 M $K_4[Fe(CN)_6]$ were also prepared. To 10 cm^3 of 0.2 M CsCl 1 cm^3 of 0.2 M $NiSO_4$ and a measured volume of 0.2 M $K_4[Fe(CN)_6]$ added, mixed, centrifuged and the centrifugate sampled and counted. The concentration of caesium precipitated was expressed as a 'Decontamination Factor' and plotted against the quantity of $K_4[Fe(CN)_6]$. In a similar experiment the 10 cm^3 of 0.2 M CsCl were treated with 1 cm^3 of 0.2 M $K_4[Fe(CN)_6]$ and a measured volume of 0.2 M $NiSO_4$ added. Again the Decontamination Factor was determined. Results of these experiments are shown in

Table 18 of Appendix 3 and Fig. 22.

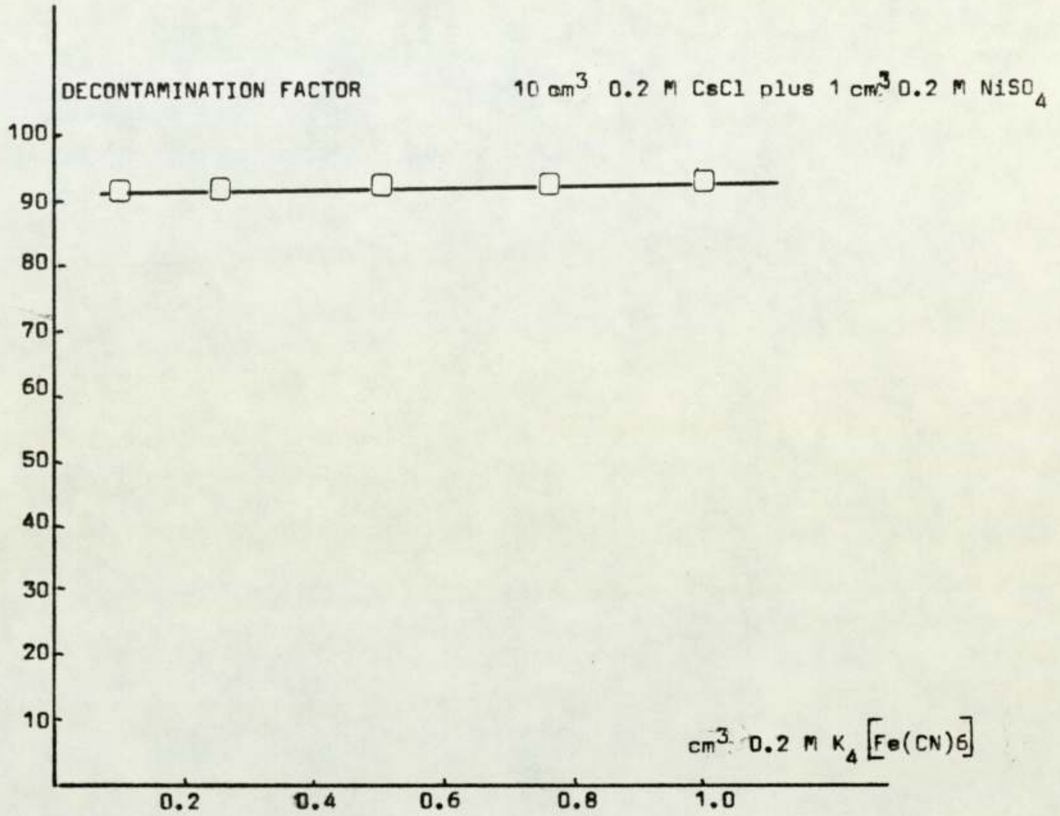
The high efficiency for decontamination is demonstrated and in each case the precipitate is dense and bulky. Removal efficiencies of around 92% were obtained no matter whether the nickel sulphate or the potassium ferrocyanide were in excess. Precipitation of 1 g of CsCl was shown to require 0.275g $Ni_2[Fe(CN)_6]$.

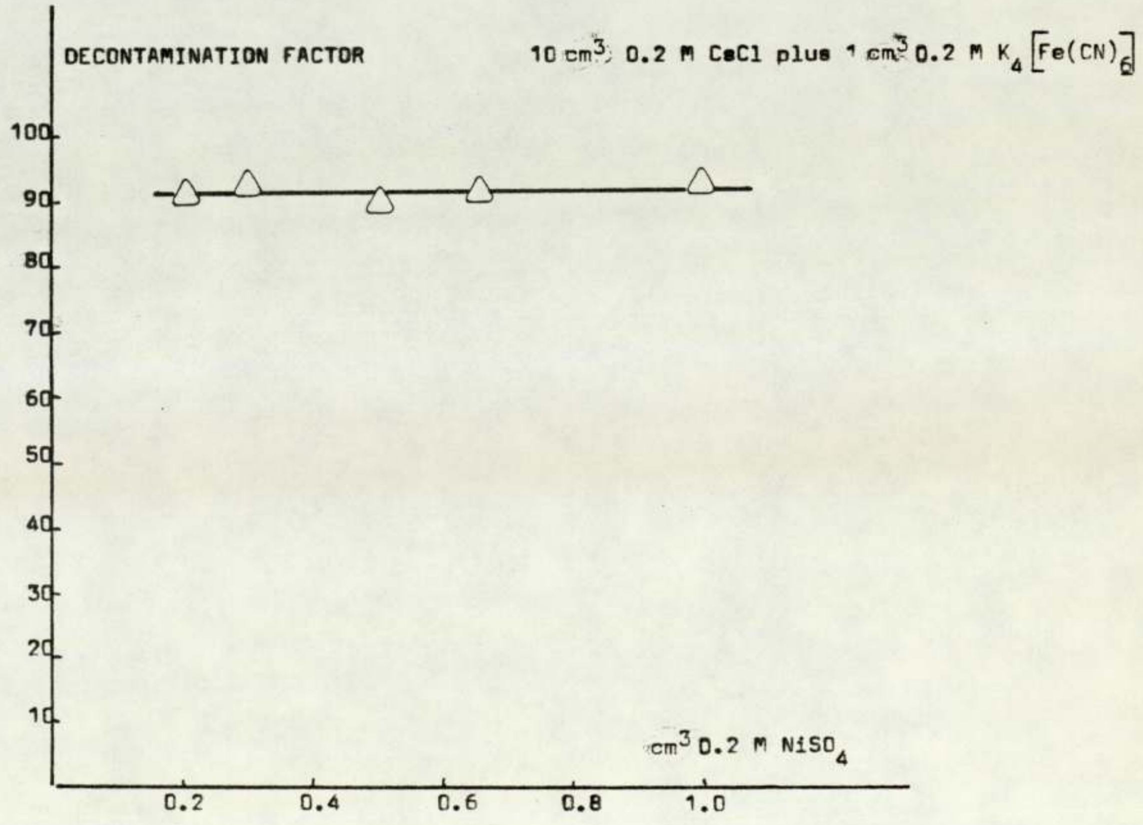
In practical waste treatment terms no attempt would be made to equate the caesium content of the waste with the exact amount of nickel ferrocyanide required. Instead an excess of nickel ferrocyanide would be used. Nevertheless these experiments were necessary to help estimate the quantities of ingredients required. It will be seen later than it is advantageous to add the nickel sulphate component first followed by the potassium ferrocyanide.

As a result of these experiments significant benefits were to be expected by pretreating waste solutions with nickel ferrocyanide and then incorporating all the components of this mix into the copolymers being studied. A study was therefore made of the leaching characteristics of COPOLYMER 8 incorporating nickel ferrocyanide pretreatment and employing 1 M CsCl as simulated waste.

Fig. 23 summarises the technology employed for the preparation of COPOLYMER 8 composites with pretreatment. The mixing sequence for the organic components was the same as that described in paragraph

FIG. 22 CAESIUM PRECIPITATION WITH NICKEL FERROCYANIDE





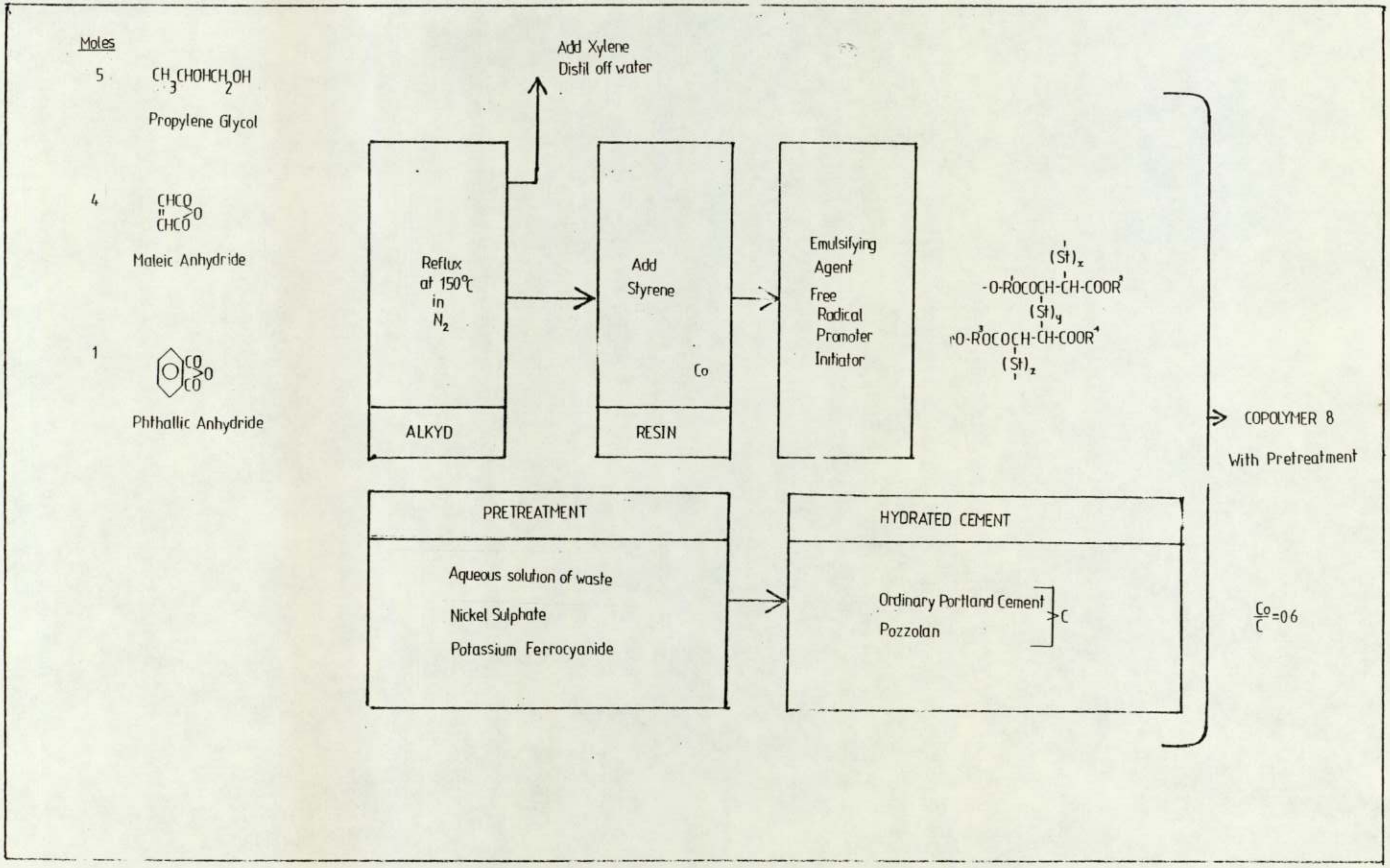


FIG. 23 THE PREPARATION OF COPOLYMER 8 COMPOSITES WITH PRETREATMENT

5.2 but the aqueous waste was pretreated by the addition of nickel sulphate which resulted in the production of a green solution. To this was added potassium ferrocyanide which produced a dense bulky precipitate. The concentration used was equivalent to 78.9g $NiSO_4.7H_2O$ and 59.3g $K_4[Fe(CN)_6]$ $3H_2O$ per litre of 1 M CsCl solution. No attempt was made to separate the precipitate. The cementitious components were simply manually stirred into the ferrocyanide mixture and the total mix slowly added to the organic resin containing the emulsifying agent, free radical promoter and initiator. Again slow speed stirring was employed at this stage.

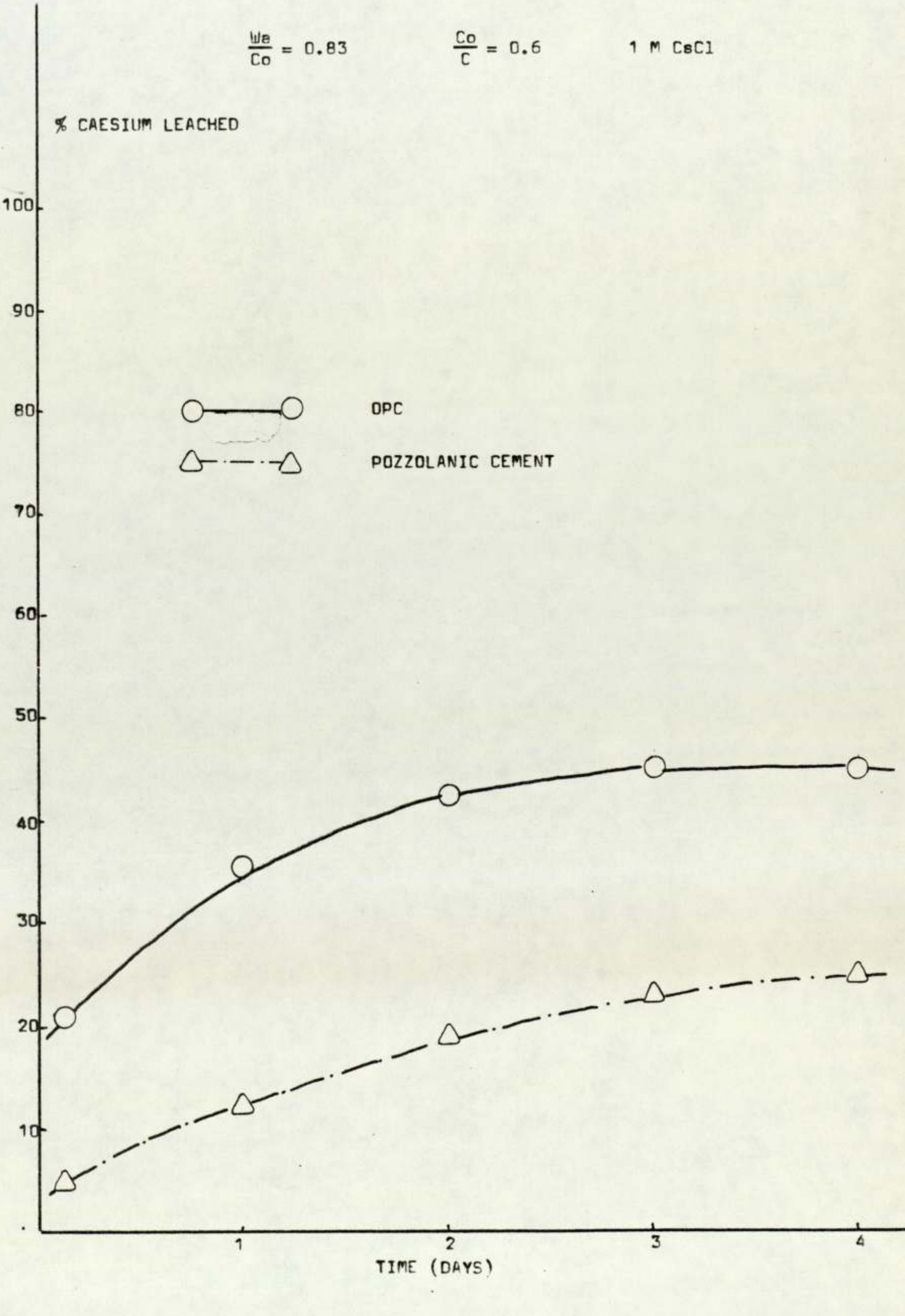
COPOLYMER 8 composites with pretreatment were produced containing 1 M CsCl solutions. Specimens of this kind with $\frac{Wa}{Co} = 0.83$, $\frac{Co}{C} = 0.6$ appeared to be uniform to the human eye and produced solid monoliths within a few hours of mixing. They did not exhibit any sign of sweating. After curing for twenty-eight days in a weticcator the leaching characteristics were determined as described in Appendix 2. The results shown in Table 19 of Appendix 3 and Fig. 24 demonstrate that the immobilisation of caesium has improved considerably compared with the products studied to date.

5.5 Strontium Studies

Studies have also been made of the leaching characteristics of strontium. COPOLYMER 8 composites were prepared as described in paragraph 5. 2 and Fig.19 except that a 1 M $SrCl_2$ solution containing

FIG. 24 LEACHING CHARACTERISTICS OF COPOLYMER 8

CONTAINING CEMENTITIOUS INGREDIENTS AND PRETREATMENT



1 mCi of ^{85}Sr was used as the aqueous solution representing simulated waste. The mixing and curing techniques were unchanged and leaching characteristics were again determined by the method described in Appendix 2. Results are tabulated in Table 20 of Appendix 3 and shown in Fig. 25.

In other experiments, the aqueous solution was first subjected to pretreatment as described in paragraph 5.4 and summarised in Fig. 23. The addition of nickel sulphate crystals to the aqueous waste produced a precipitate of strontium sulphate. Otherwise the preparation of the COPOLYMER 8 composite was identical to the procedure described in paragraph 5.4. The mixing and curing and leach test techniques were unchanged. Results are tabulated in Table 21 of Appendix 3 and shown in Fig. 26. Fig. 27 shows a comparison of leaching characteristics of both caesium and strontium from COPOLYMER 8 composites which incorporate pretreatment.

Some useful comments can be made on these results. The higher mobility of caesium when compared to strontium has been clearly demonstrated. Whereas composites containing pozzolanic cements retain caesium better than those containing ordinary portland cement, the reverse is true in relation to strontium. One possible explanation of this feature is that the higher alkalinity of products containing OPC tends to precipitate strontium as the hydroxide, whereas caesium

FIG.25 LEACHING CHARACTERISTICS OF COPOLYMER 8 CONTAINING CEMENTITIOUS INGREDIENTS

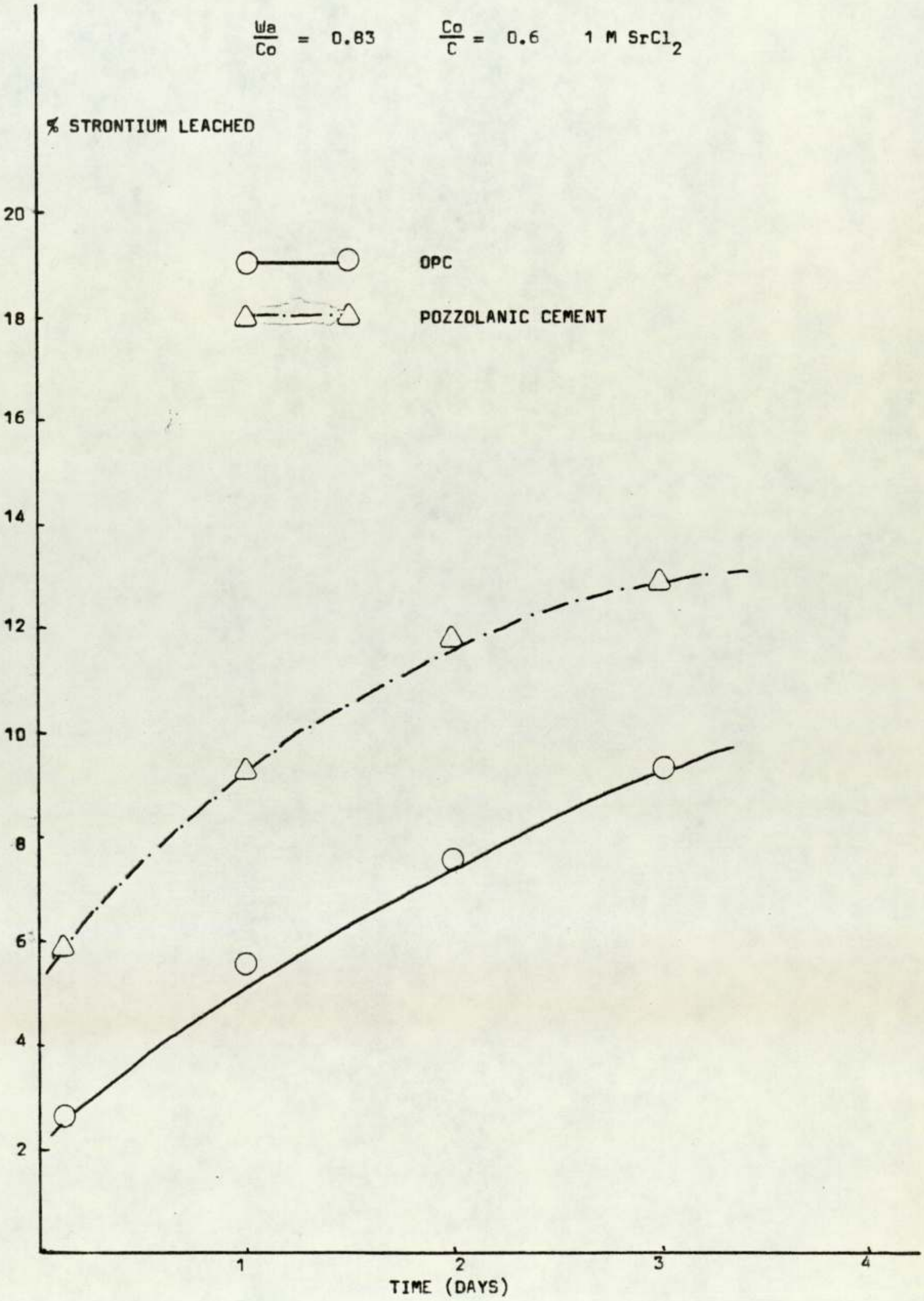


FIG. 26 LEACHING CHARACTERISTICS OF COPOLYMER 8

CONTAINING CEMENTITIOUS INGREDIENTS AND PRETREATMENT

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$ 1 M $SrCl_2$

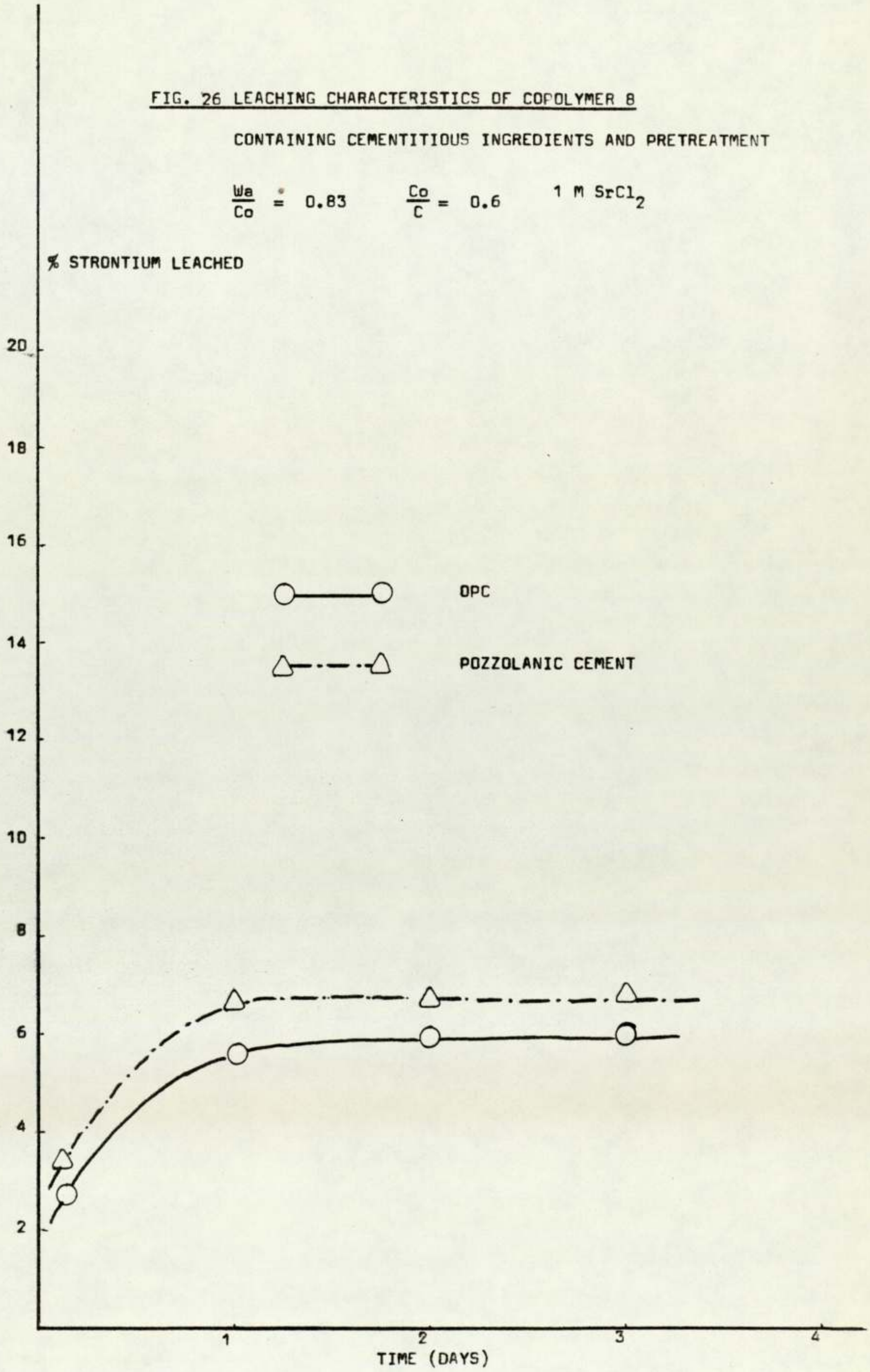
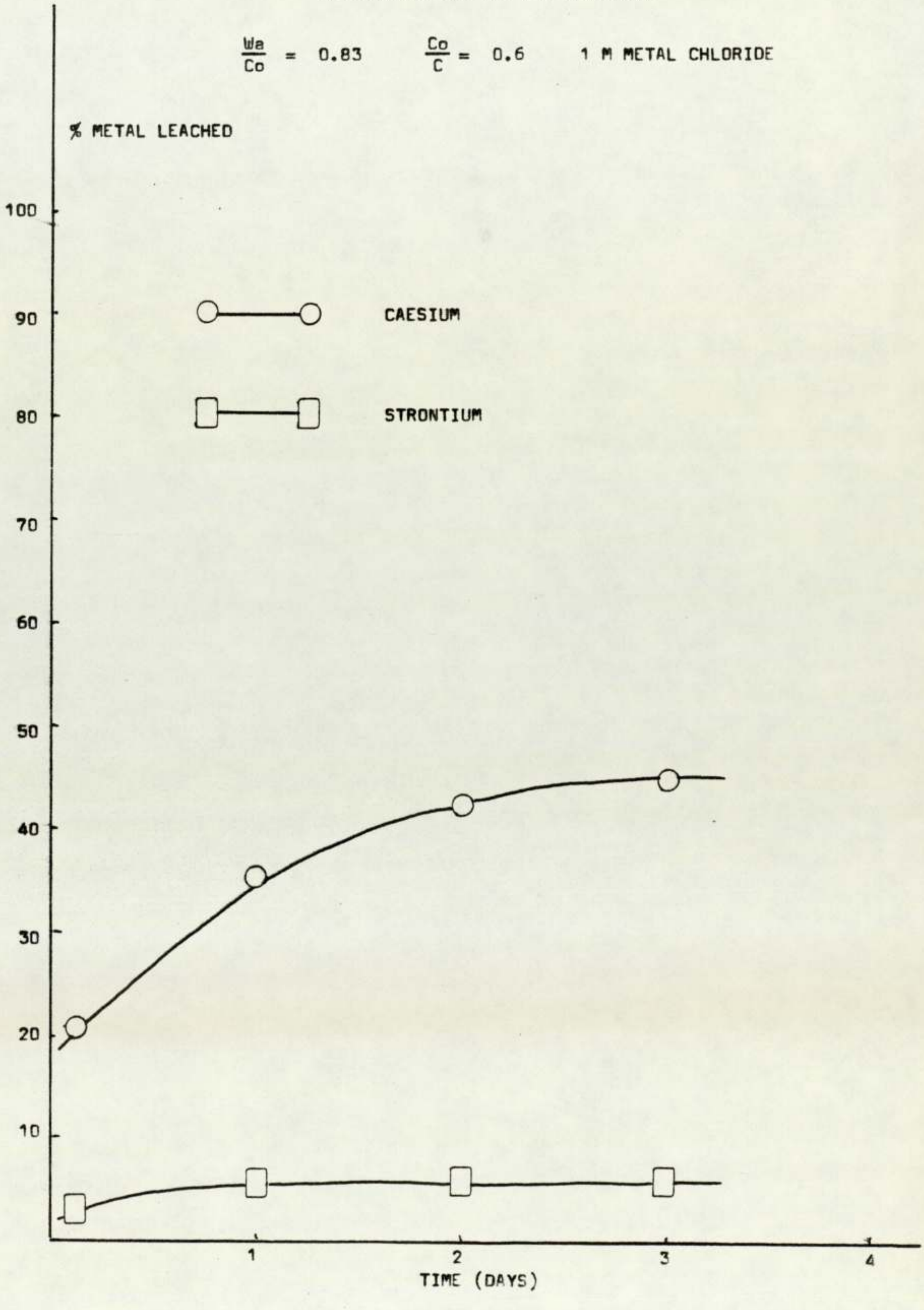


FIG. 27 COMPARISON OF LEACHING CHARACTERISTICS OF COPOLYMER 8

CONTAINING OPC AND PRETREATMENT

$\frac{Wa}{Co} = 0.83 \qquad \frac{Co}{C} = 0.6$ 1 M METAL CHLORIDE



hydroxide is highly soluble and no effect is noticed. A similar explanation applies to the difference observed in the leaching of strontium between COPOLYMER 8 with and without pretreatment. (Figs. 25 and 26). The addition of nickel sulphate to solutions of strontium salts produces a precipitate of strontium sulphate which is then incorporated into the product. Since this represents a further immobilisation technique it is to be regarded as welcome and this explains why the preferred pretreatment technique is the sequence described on page 86.

5.6 Thermal Stability

Intermediate level wastes are sufficiently radioactive to require radiation shielding to protect personnel concerned with their treatment and disposal. However, unlike high level wastes they do not normally require artificial cooling since they are not heat emitters. However, it is conceivable that plant decommissioning wastes (for example) might contain traces of high level waste which could result in some thermal output. For this reason it is useful to determine the thermal stability of the immobilisation products themselves. A Stanton Thermo Gravimetric Balance was used for this purpose in these studies. It is shown in Fig 28 and consists of a classical chemical balance with an extended non-heat conducting arm which supports the specimen within an electrical furnace. The furnace is heated at a controlled rate and a thermocouple records the temperature. The balance automatically

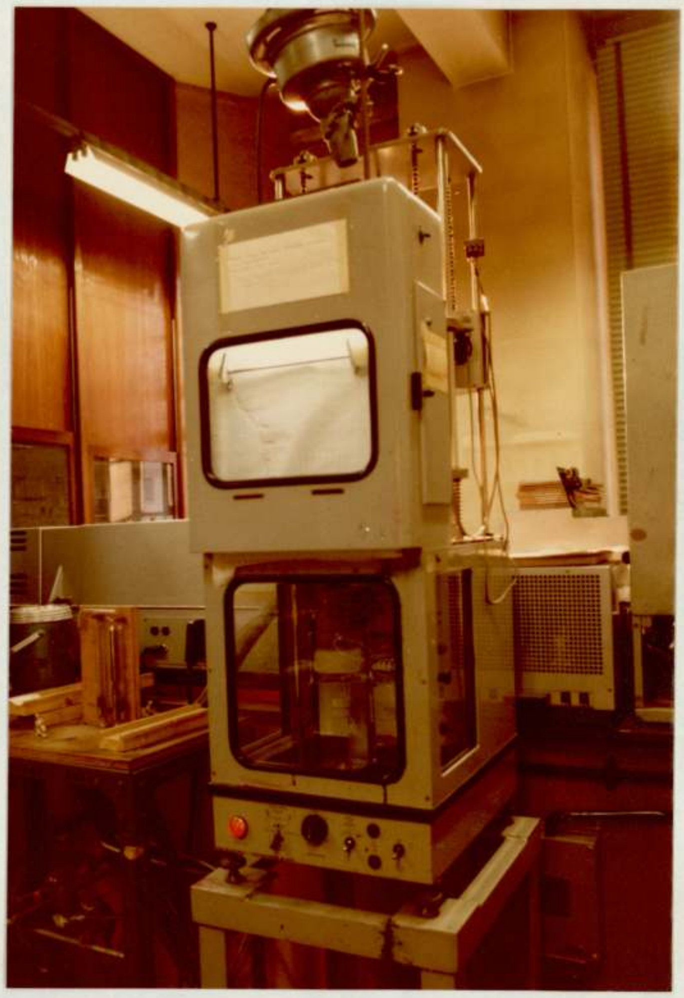


FIG. 28 A THERMOGRAVIMETRIC BALANCE

weighs the sample and plots out the weight on a recorder.

Specimens submitted for testing were all stored in a weticcator for twenty-eight days prior to study so that their condition was stabilised. Fig. 29 shows data comparing COPOLYMER 8 containing OPC and the pozzolanic cement. As the temperature increases water vapour is lost though even at 200°C the weight change is less than 5%. Above about 250°C the organic polymer begins to break down and above 700°C only the stable inorganic oxides are left. These tests demonstrate that COPOLYMER 8 composites are sufficiently temperature stable to be considered as a candidate material for intermediate level waste isolation.

5.7 Radiation Stability

At high doses of gamma irradiation organic polymers break down giving rise to gaseous byproducts. In order to determine the radiation stability of COPOLYMER 8 samples were submitted to AERE Harwell Irradiation and Dosimetry Service where they were sealed in small individual aluminium cans and placed in an assembly similar to a nuclear fuel element and exposed to a total integrated dose of 500Mrads of gamma radiation. The incorporation of intermediate level waste with a specific activity of a maximum of 10,000 Ci m^{-3} within a composite would be expected to give an internal integrated dose of approximately 500 Mrads over the first 100 years of its life.

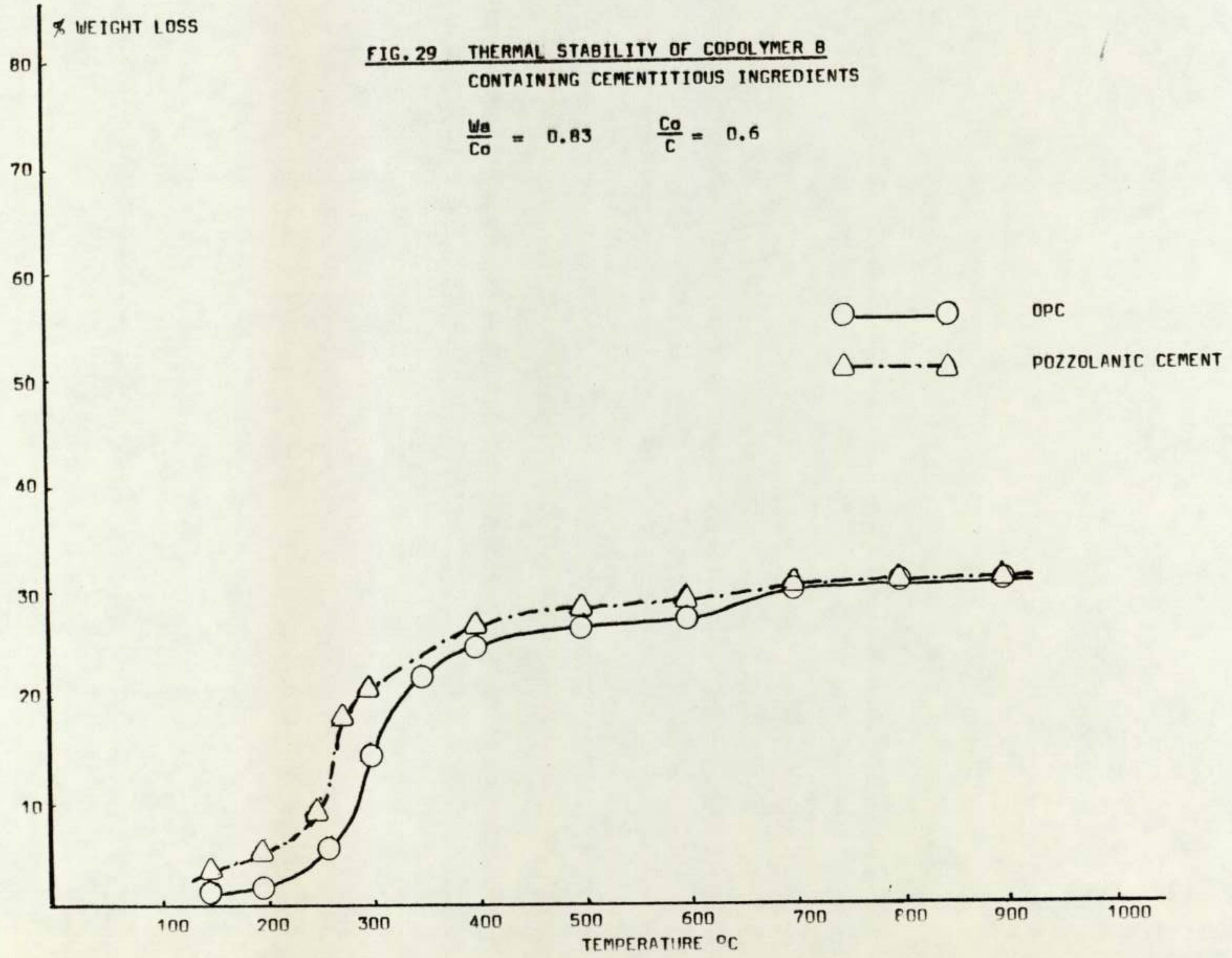


FIG. 29 THERMAL STABILITY OF COPOLYMER B CONTAINING CEMENTITIOUS INGREDIENTS

$\frac{Wa}{Co} = 0.83 \qquad \frac{Co}{C} = 0.6$

Results are tabulated in Table 22 of Appendix 3 and compared with non-irradiated specimens in Figs. 30 and 31. No significant changes were detected as a result of 500 Mrads radiation.

Table 9 shows the compressive strengths of these composites before and after irradiation. Since the method of measurement is a destructive test the study has been made on three specimens. An increase in compressive strength is observed as a result of irradiation which is believed to be due to the development of additional cross-linking within the polymer.

Table 9 Compressive Strength of COPOLYMER 8 Before and After Irradiation

in MN m^{-2}

	Before Irradiation	After 500 MRad Radiation
Copolymer 8 with OPC	10.30	14.75
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$	11.80	14.98
	9.20	12.06
Copolymer 8 with the pozzolanic cement	9.56	14.07
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$	10.06	12.80
	10.15	13.70

5.8 Porosimetry Studies

The improved leaching resistance of COPOLYMER 8 composites when compared to OPC or the pozzolanic cement products warranted further study. If the

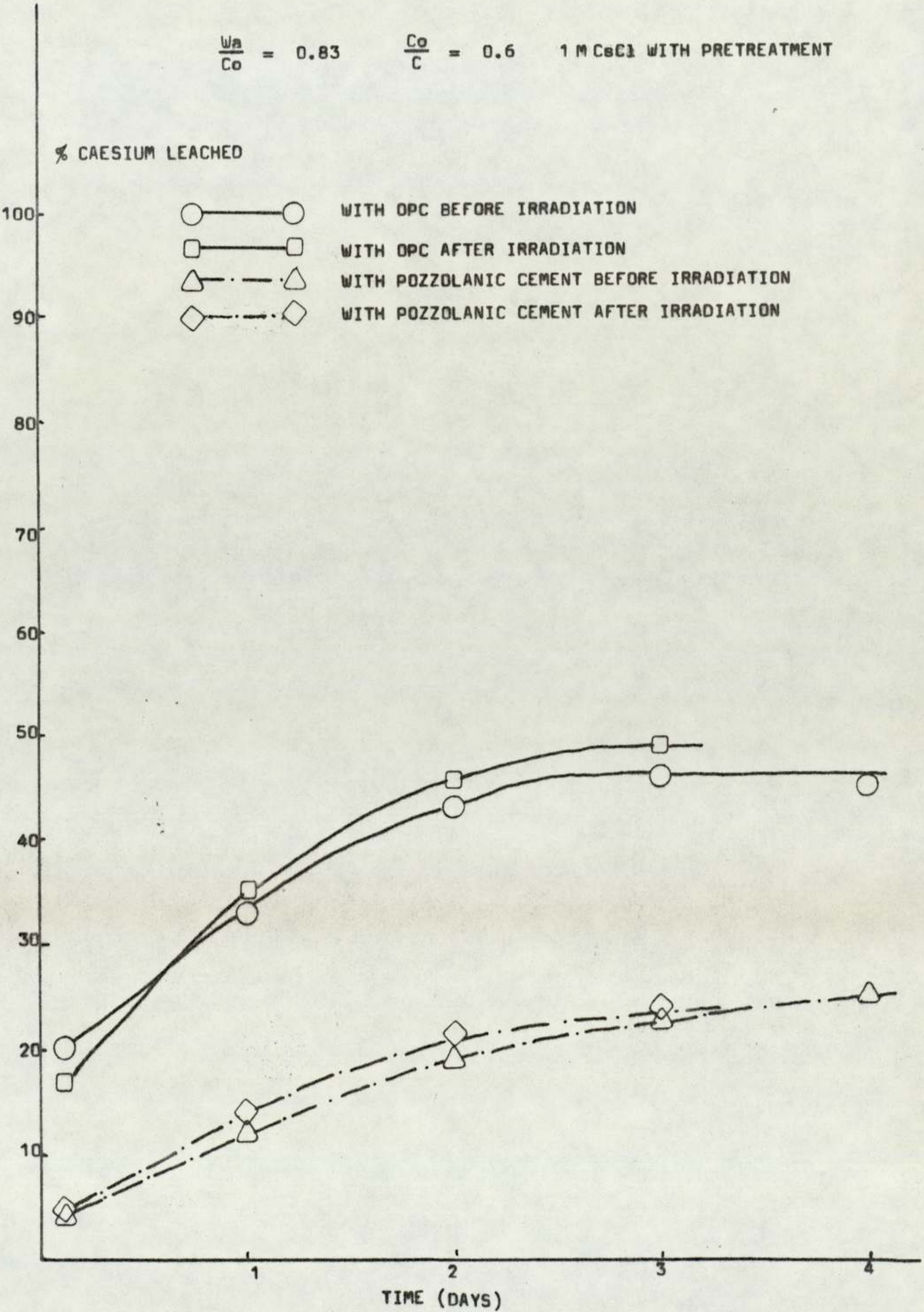


FIG. 30 LEACHING CHARACTERISTICS OF COPOLYMER 8

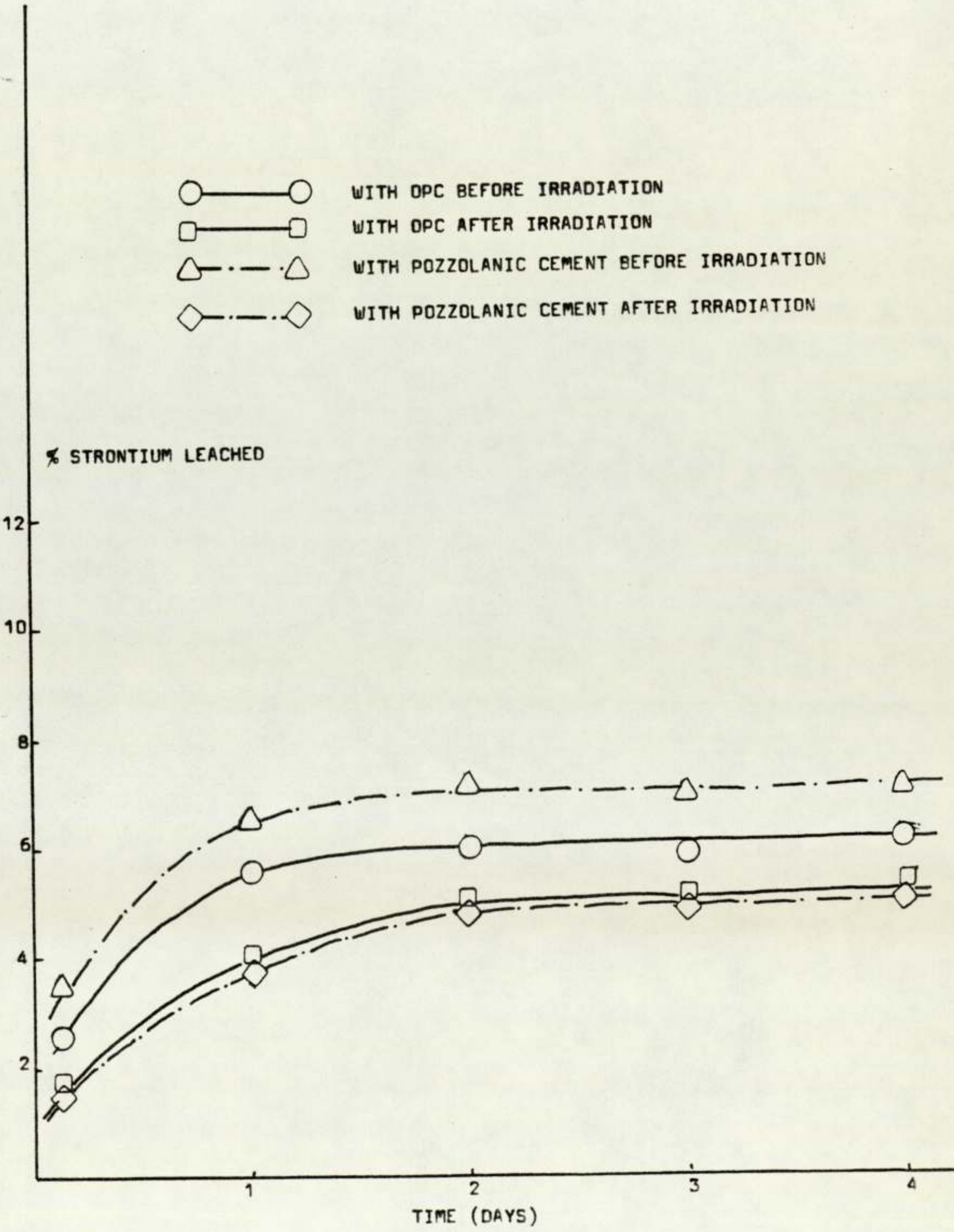
BEFORE AND AFTER IRRADIATION

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$ 1 M CsCl WITH PRETREATMENT

FIG. 31 LEACHING CHARACTERISTICS OF COPOLYMER 8

BEFORE AND AFTER IRRADIATION

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$ 1 M $SrCl_2$ WITH PRETREATMENT



capture mechanism of caesium and strontium were a physical entrapment caused by the reduction in pore size of the composite then pore size differences would be expected to be detected. For this study, a Micromeritics Instrument Corporation Mercury Porosimeter (see Fig. 32) was used. In this test 2 to 3g of product is first carefully dried by evacuation to 10^{-3} mm mercury and then introduced into a small glass cell which is housed in a stainless steel vessel. The vessel and contents are then evacuated and pure dry mercury is introduced. As mercury penetrates the pores of the product the level of mercury in the cell is monitored by means of a motorised contact. These measurements are made as the pressure in the cell is allowed to increase to atmospheric pressure. Thereafter the pressure is increased stepwise to 50,000 psi by means of an external pump. The mean pore radius can then be determined from;

$$r = -\frac{2\delta\cos\theta}{p}$$

where r = mean pore radius

δ = surface tension of mercury

θ = contact angle of mercury (130°)

p = applied pressure

Fig. 33 compares the pore size distribution of COPOLYMER 8 containing the pozzolanic cement with the pozzolanic cement alone. It can be seen that incorporation of the organic polymer has significantly reduced the pore size which correlates well with the

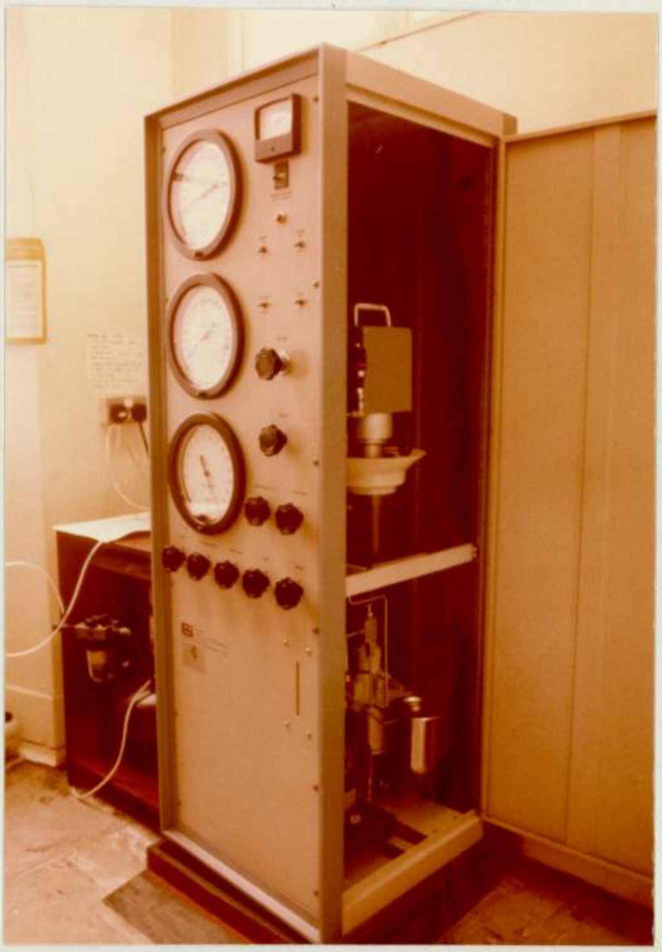
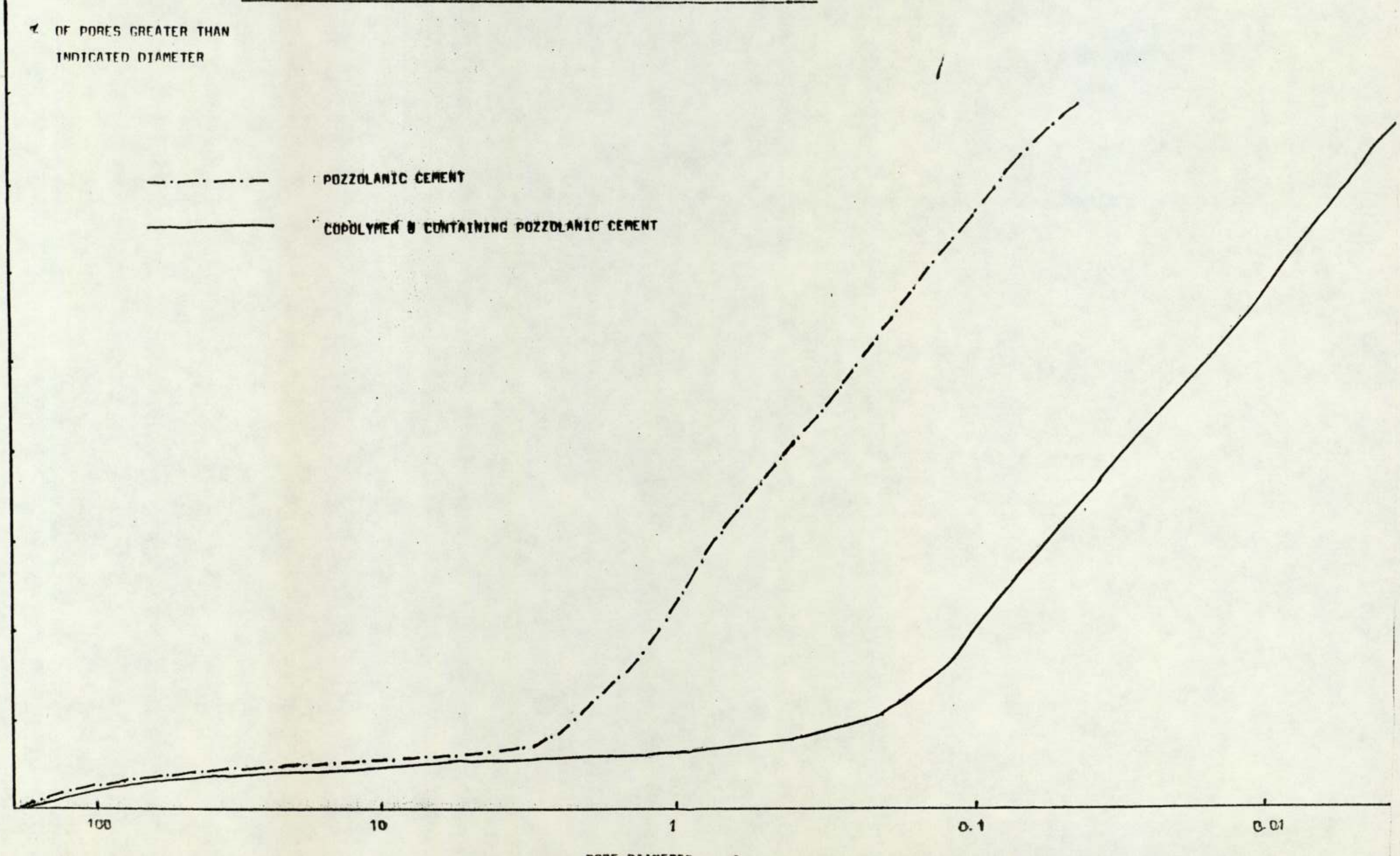


FIG. 32 A MERCURY POROSIMETER

Fig. 33 PORE SIZE DISTRIBUTION OF POZZOLANIC CEMENT AND COPOLYMER 8



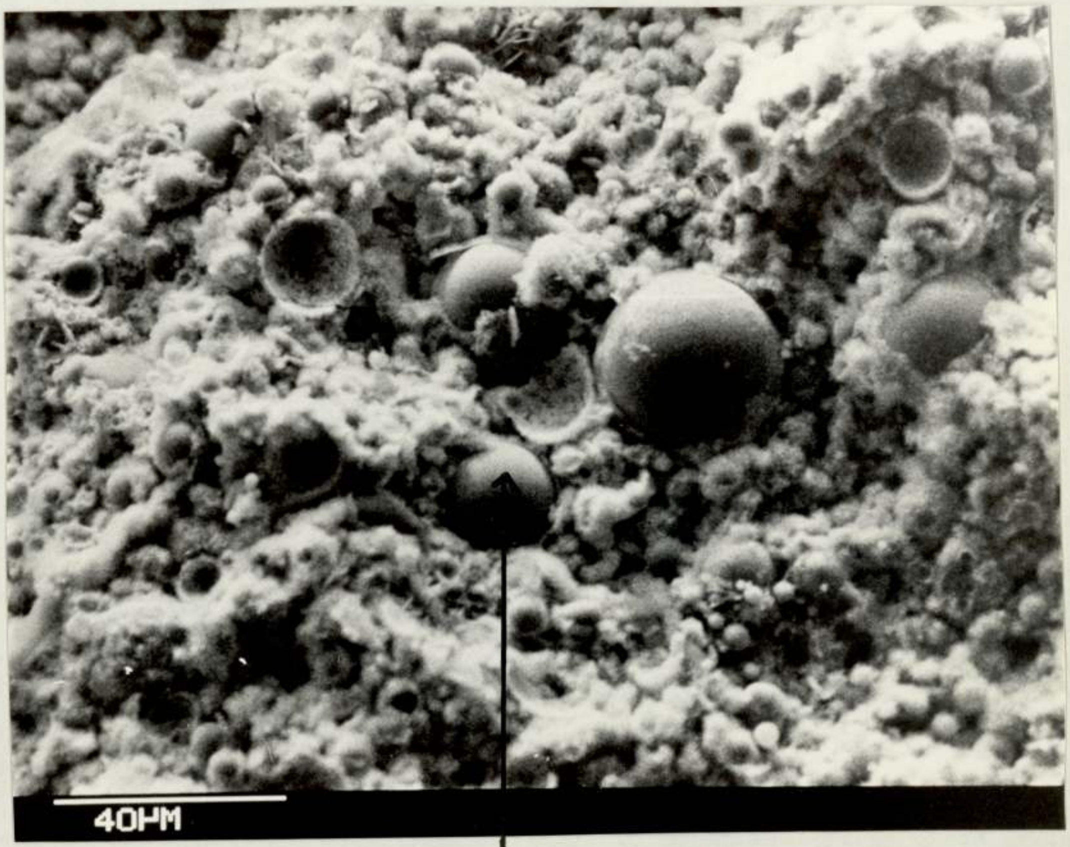
reduced leaching characteristics observed.

5.9 Scanning Electron Microscopy

A Cambridge 150 Scanning Electron Microscope (SEM) fitted with a Kevex Energy Dispersive Detector was used to examine COPOLYMER 8 composites. SEM consists of a device for focusing a beam of electrons at approximately 20 kV and scanning backwards and forwards across a prepared specimen. The mode of operation chosen for this study was to analyse the X-rays generated from electron bombardment of the specimens. The continuous energy spectrum produced contains sharp peaks which are characteristic of the elements present in the sample. By identifying the characteristic energies and measuring the number of X-ray quanta it is possible to obtain qualitative analysis of the specimen surface and images can be produced showing the distribution of particular elements within the specimen. The X-ray detector is connected to a multichannel analyser and the whole spectrum is displayed or printed out. Identification of the chemical components across the entire surface of a specimen can be obtained or alternatively the electron beam can be focused on a particle of interest and its components characterised. Despite this ability to focus the electron beam on a small area, the data obtained is not quantitative and can not be represented as the quantitative analysis of small particles. The electron beam can not be focused to a small enough point to eliminate ambiguities due to the irregular surface of the specimens and the penetration of electrons to subsurface layers. Furthermore, the SEM technique will not identify light elements such as boron, carbon, nitrogen, oxygen and fluorine because the X-rays generated by these elements do not penetrate the beryllium window of the detector. Consequently information concerning the nature and structure of the organic polymer components of the composites can not be obtained from this techique. Prior to use, the specimens were vacuum dried and coated with two layers of carbon which is necessary to provide a conductive route for the discharge of electrons to earth. All the specimens examined had been cured under saturated conditions in a weticcator for a period of at least twenty-eight days. Fig. 34 shows the SEM and the Kevex Energy Dispersive Detector.

The first specimen examined was the pozzolanic cement containing 1 M CsCl with $\frac{\underline{Wa}}{C}$ ratio = 0.5 shown in Fig. 35. The X-ray spectrum of the entire area of this photograph is shown in Fig. 36. Such a spectrum is typical of a pozzolanic cement in that it shows high silicon and aluminium content (in relation to the calcium content). The peaks attributable to caesium and chloride ions are also prominent. The electron beam was then focused on one of the spherical particles visible in Fig. 35 and the spectrum shown in Fig. 37 obtained. This shows high silicon and aluminium and low calcium which is a characteristic of

FIG. 34 THE SCANNING ELECTRON MICROSCOPE AND KEVEX ENERGY DISPERSIVE DETECTOR



see Fig. 37

FIG. 35 SEM PHOTOGRAPH OF POZZOLANIC CEMENT CONTAINING CAESIUM CHLORIDE

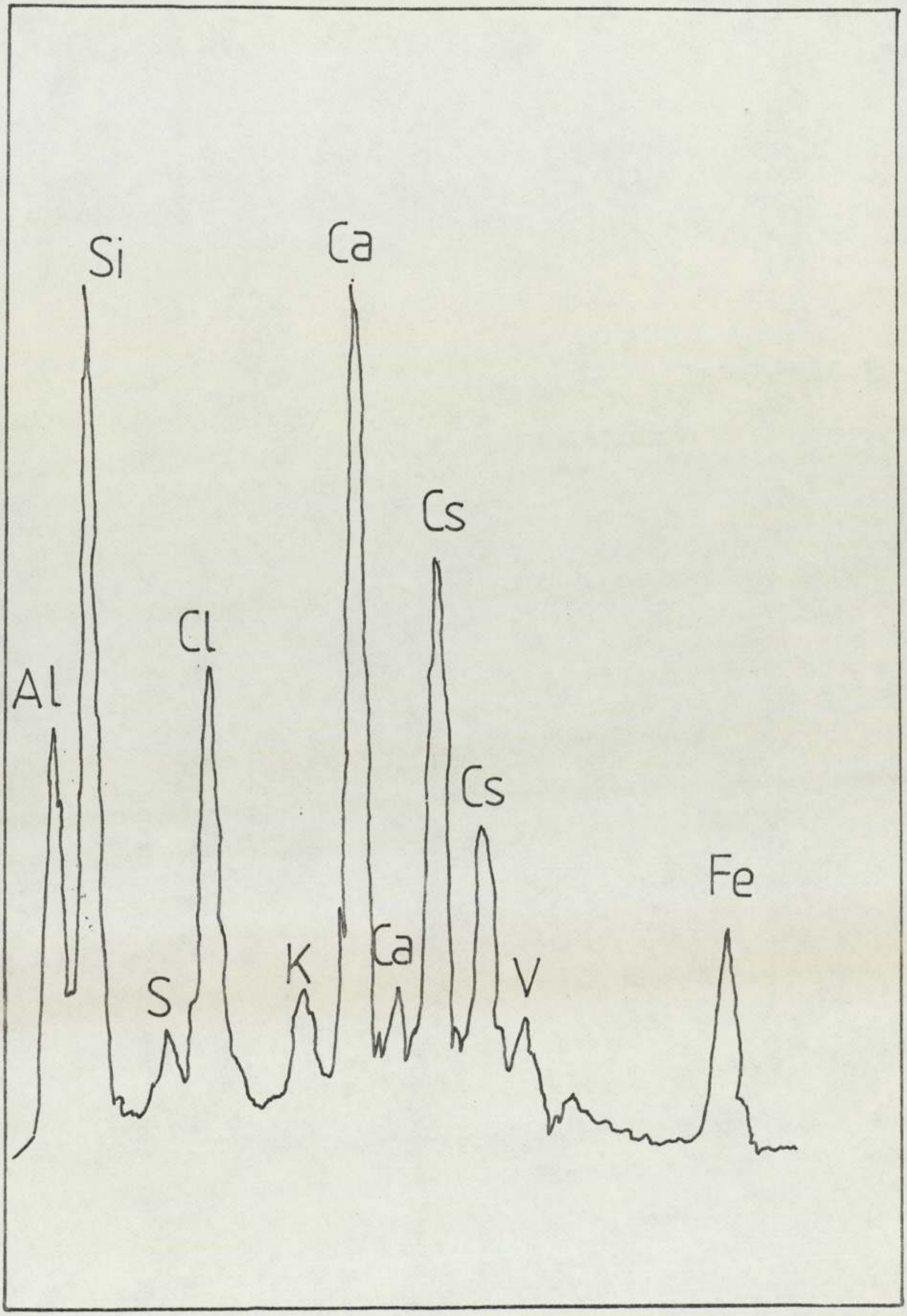


FIG. 36 X RAY SPECTRUM OF POZZOLANIC CEMENT CONTAINING CAESIUM CHLORIDE

GENERAL SCAN

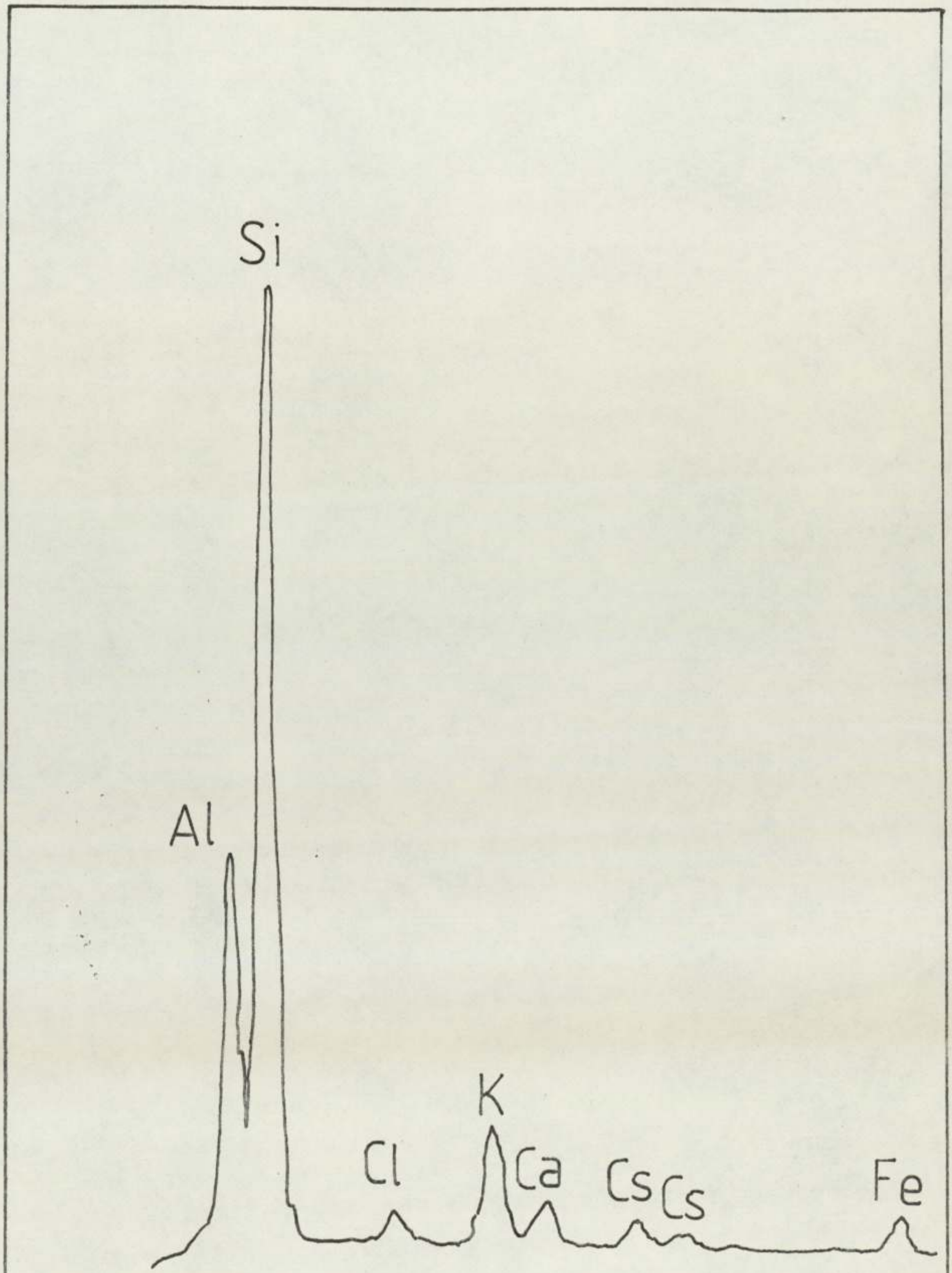


FIG. 37 X RAY SPECTRUM OF POZZOLANIC CEMENT CONTAINING CAESIUM CHLORIDE

SPHERICAL PARTICLE

the aluminium silicate spheres found in flyash. The hollow nature of these spheres (known as cenospheres) is evident from Fig. 35.

A composite of COPOLYMER 8 containing OPC and 1 M CsCl was next examined and the SEM photograph is shown in Fig. 38. The X-ray spectrum of the entire area shown on this photograph is shown in Fig. 39. The high calcium and relatively low aluminium and silicon contents contrast markedly with the pozzolanic cement constitution shown in Fig. 36. The electron beam was focused on the needle like trigonal particles visible in the SEM photograph, Fig. 38 and the X-ray spectrum is shown in Fig. 40. The high calcium content is indicative of $Ca(OH)_2$ crystals.

A COPOLYMER 8 composite containing the pozzolanic cement, 1 M CsCl and pretreatment chemicals was next examined and its SEM photograph is shown in Fig. 41. The X-ray spectrum of this entire area is shown in Fig. 42. The electron beam was focused on different particles in turn and the X-ray spectra recorded. Fig. 43 shows the spectrum from a spherical particle, a cenosphere, and the similarity with Fig. 37 is apparent. It is noticeable that neither caesium nor chloride is associated with this particle. Fig. 44 shows the X-ray spectrum of a grain like particle in this specimen and Fig. 45 corresponds to another grain like particle. The difference in aluminium and silicon components is noteworthy. Fig. 46 corresponds

see Fig. 40

FIG. 38 SEM PHOTOGRAPH OF COPOLYMER 8 COMPOSITE CONTAINING OPC AND CAESIUM CHLORIDE

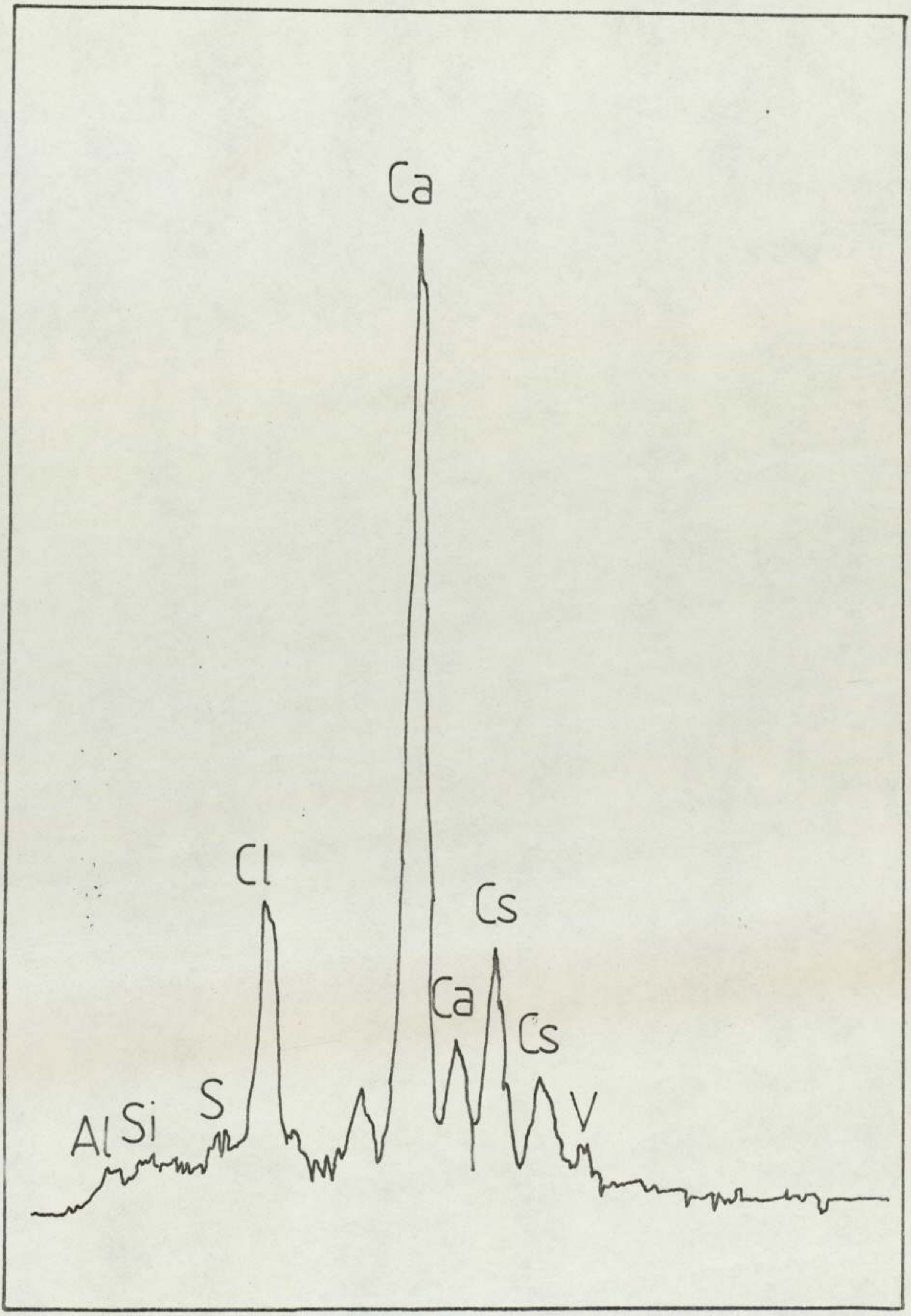


FIG. 39 X RAY SPECTRUM OF COPOLYMER 8 COMPOSITE CONTAINING OPC AND CAESIUM CHLORIDE

GENERAL SCAN

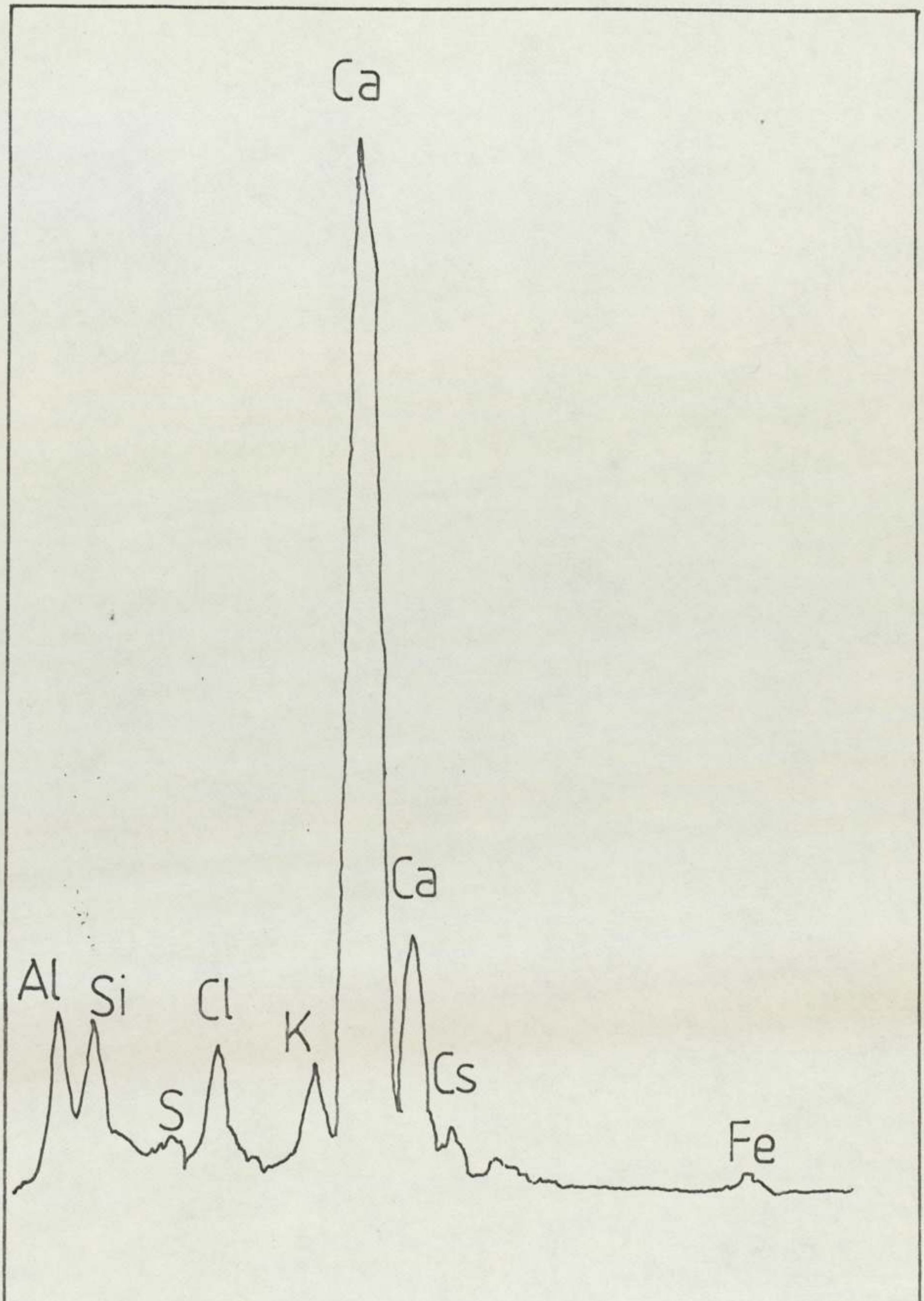
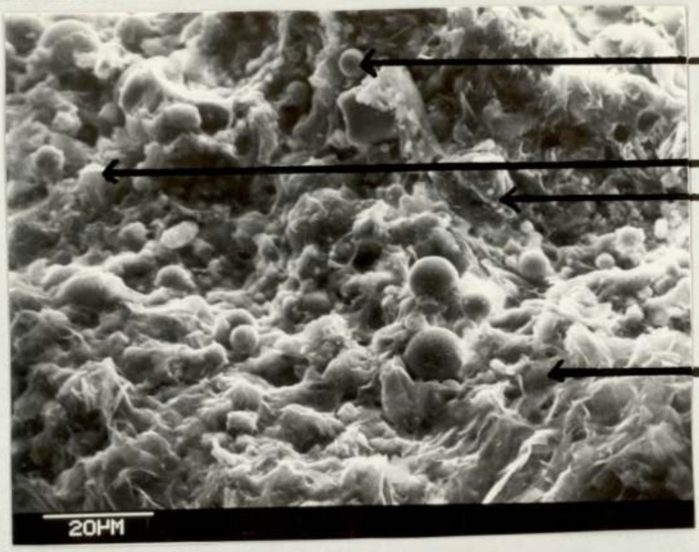


FIG. 40 X RAY SPECTRUM OF COPOLYMER 8 COMPOSITE CONTAINING OPC AND CAESIUM CHLORIDE

NEEDLE LIKE PARTICLE



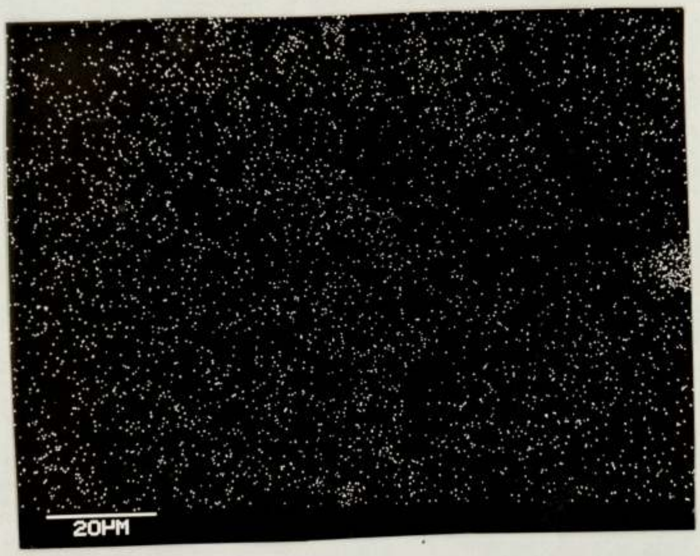
SPECIMEN SCAN

see Fig. 43

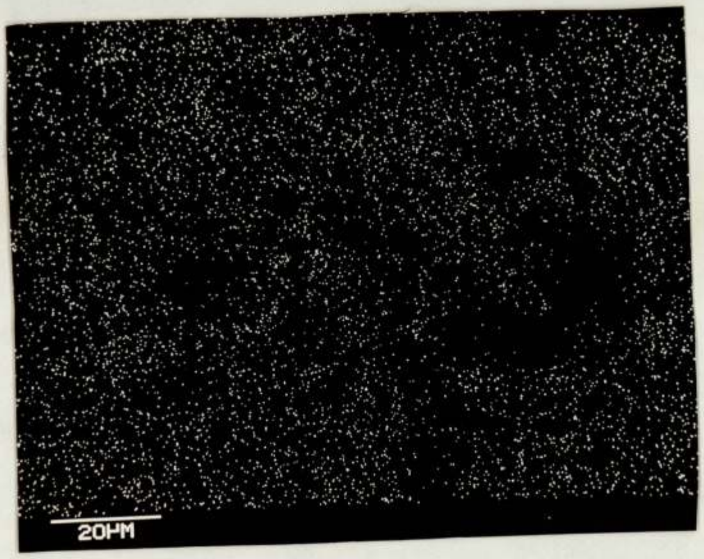
see Fig. 44

see Fig. 45

see Fig. 46



CAESIUM DISTRIBUTION



CHLORIDE DISTRIBUTION

FIG. 41 SEM PHOTOGRAPH OF COPOLYMER 8 COMPOSITE CONTAINING POZZOLANIC CEMENT, PRETREATMENT AND CAESIUM CHLORIDE

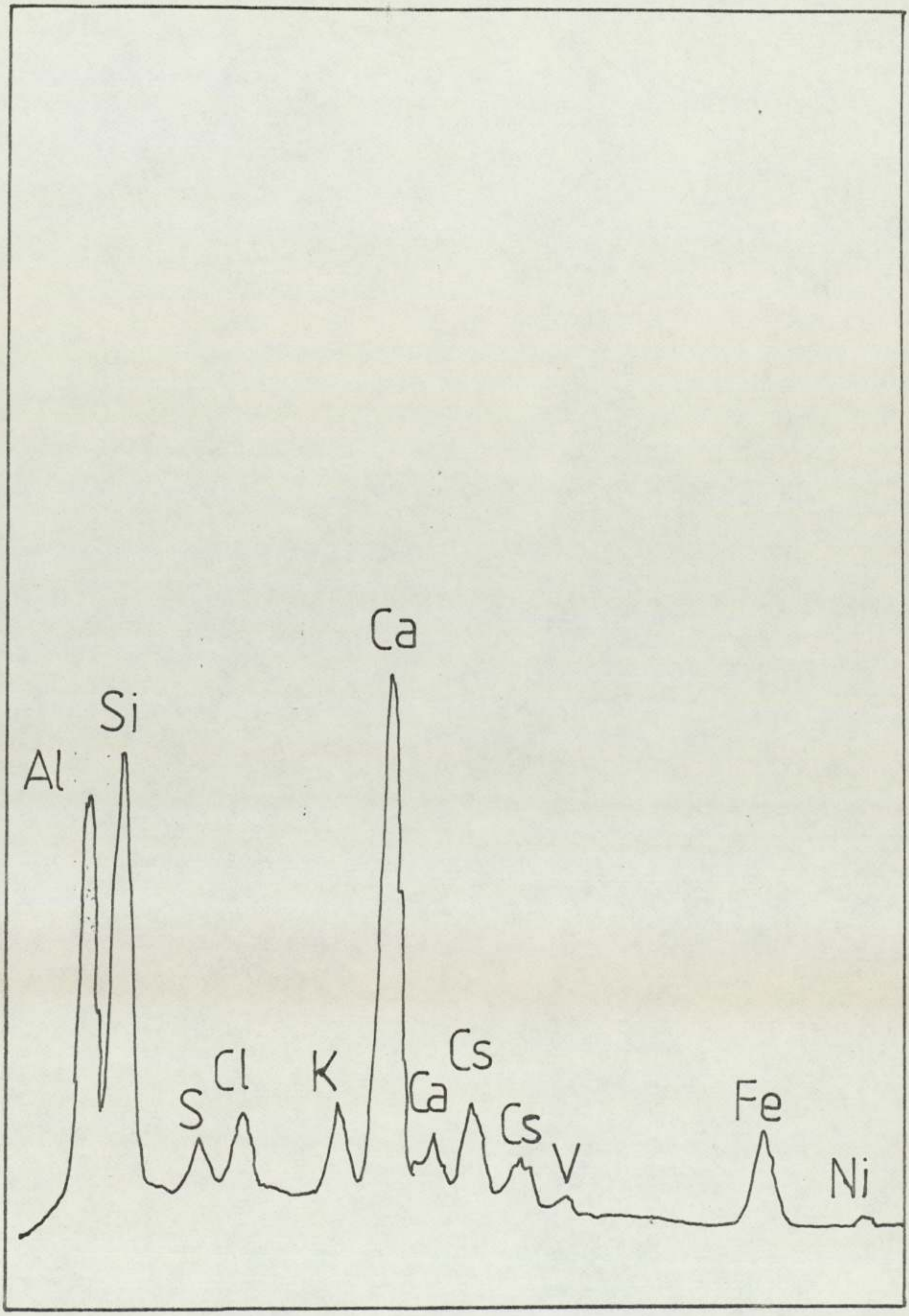


FIG. 42 X RAY SPECTRUM OF COPOLYMER 8 COMPOSITE CONTAINING POZZOLANIC CEMENT PRETREATMENT AND CAESIUM CHLORIDE

GENERAL SCAN

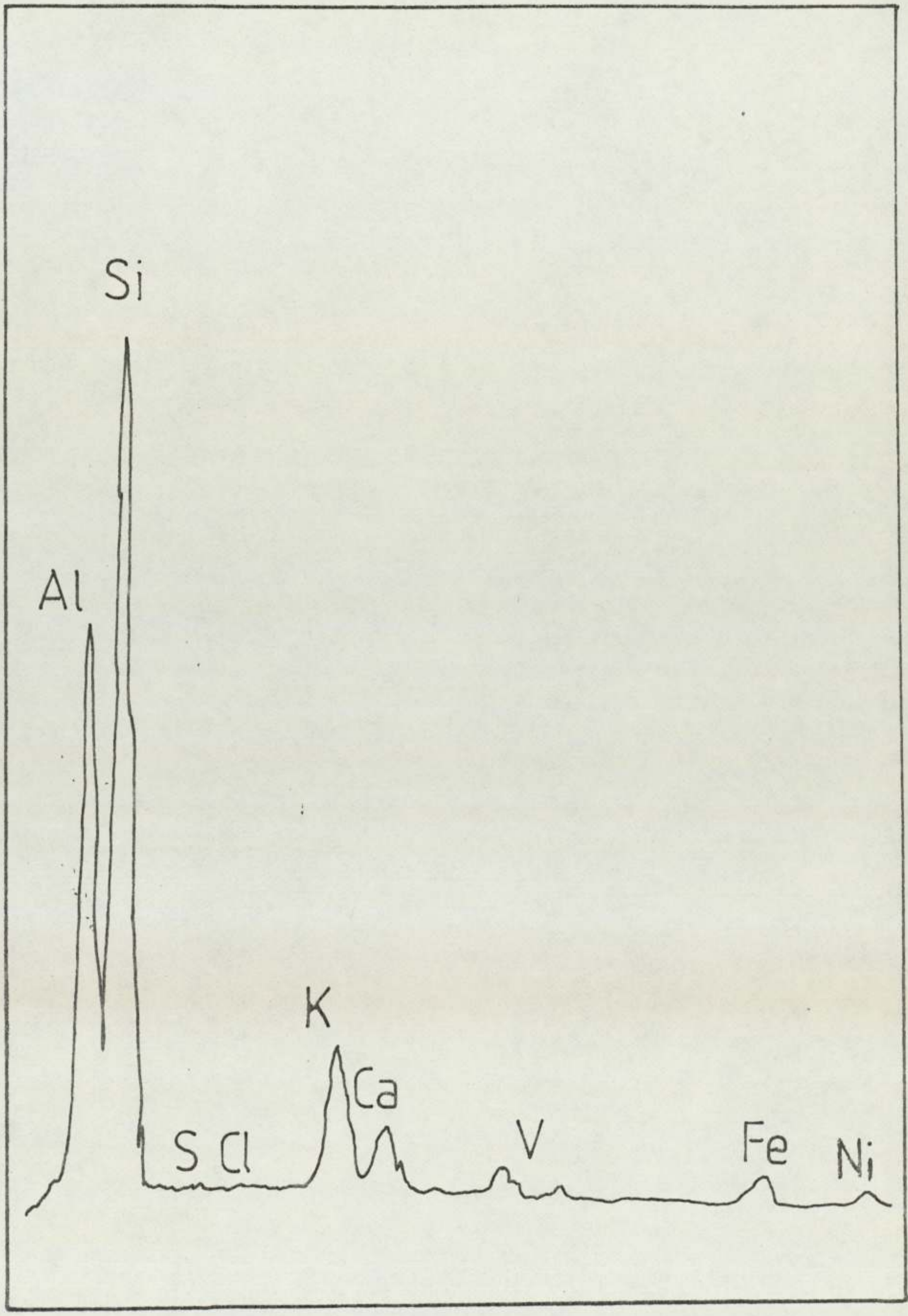


FIG. 43 X RAY SPECTRUM OF COPOLYMER 8 COMPOSITE CONTAINING POZZOLANIC CEMENT, PRETREATMENT AND CAESIUM CHLORIDE

SPHERICAL PARTICLE

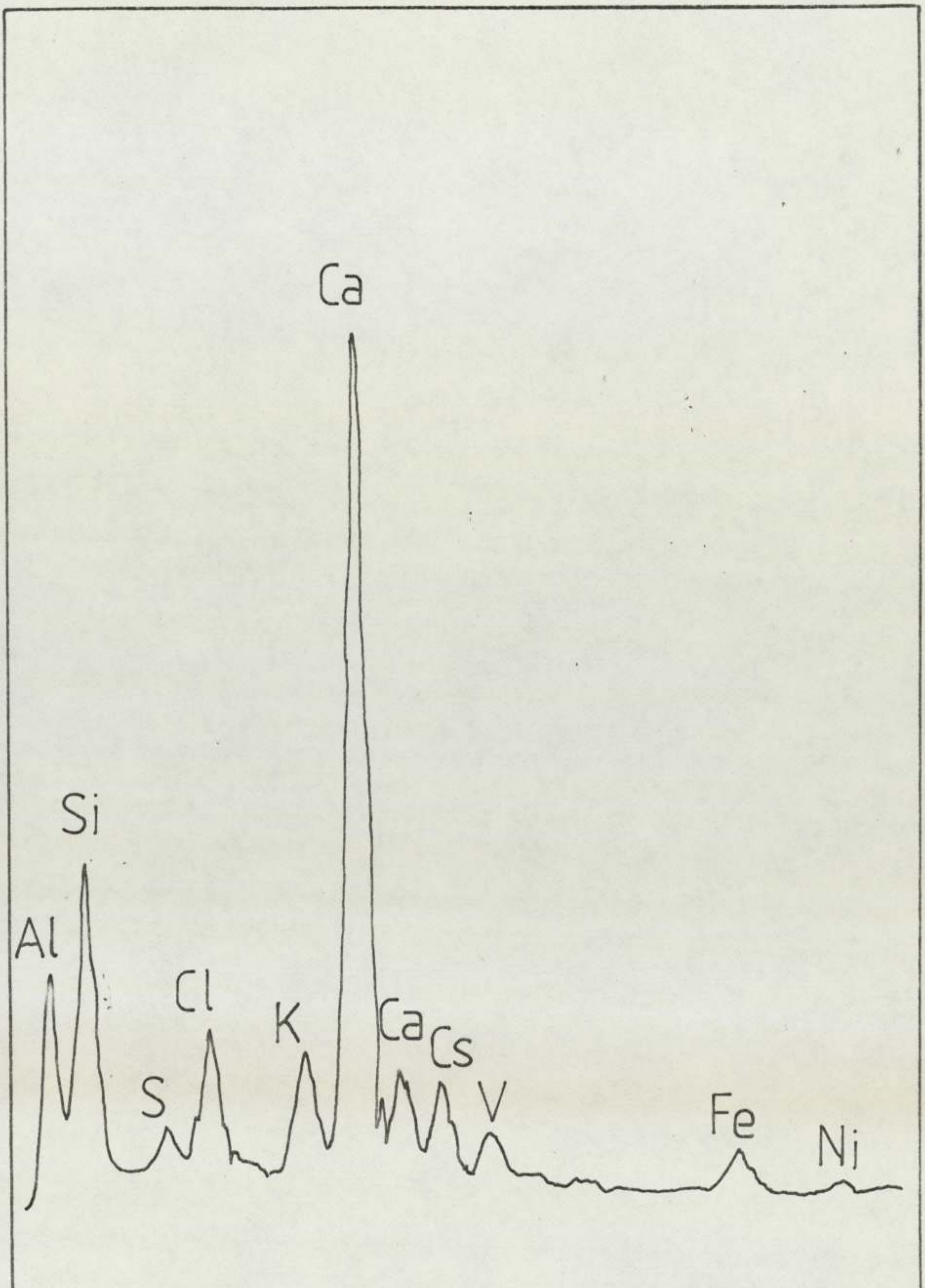


FIG. 44 X RAY SPECTRUM OF COPOLYMER 8 COMPOSITE CONTAINING POZZOLANIC CEMENT, PRETREATMENT AND CAESIUM CHLORIDE

GRAIN LIKE PARTICLE

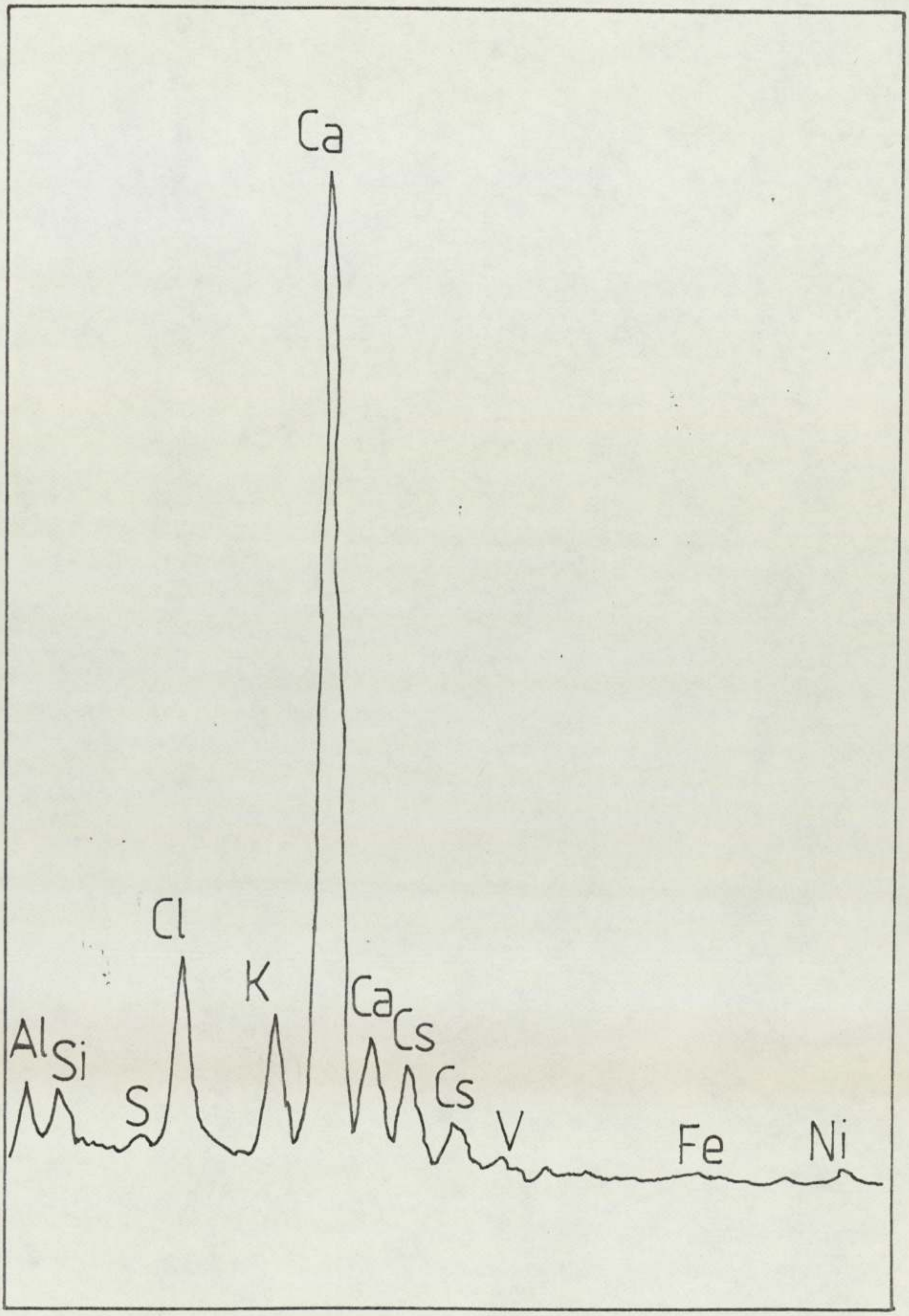


FIG. 45 X RAY SPECTRUM OF COPOLYMER 8 COMPOSITE CONTAINING POZZOLANIC CEMENT, PRETREATMENT AND CAESIUM CHLORIDE

GRAIN LIKE PARTICLE

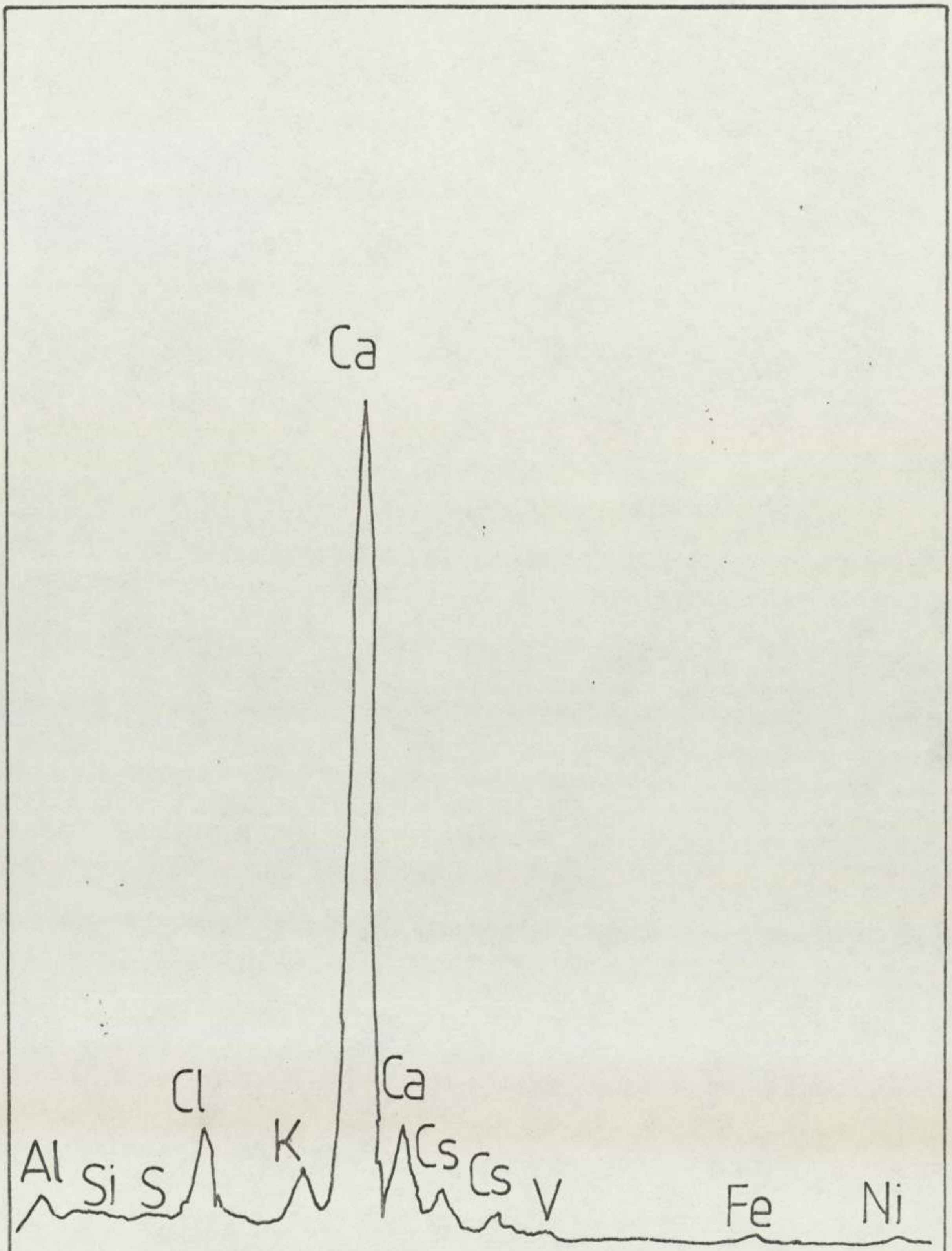


FIG. 46 X RAY SPECTRUM OF COPOLYMER 8 COMPOSITE CONTAINING POZZOLANIC CEMENT, PRETREATMENT AND CAESIUM CHLORIDE

AMORPHOUS AREA

to an amorphous area and is indicative of $Ca(OH)_2$

By selecting particular X-ray energies the location of specific elements within the specimen can be determined and photographed. Fig. 41 shows the distribution of caesium and chloride in the COPOLYMER 8 composite (which contains the pozzolanic cement, caesium chloride and pretreatment chemicals) shown in the top of this figure. In summary, this evidence suggests that the caesium and chloride ions are distributed randomly within the matrix. Caesium and chloride ions were shown to be associated with all the particles (except cenospheres) examined and is not combined with any one particular calcium alumino silicate compound.

SEM with Kevex Energy Dispersive Detector studies can not be interpreted on a more quantitative basis for the reasons given above.

Diamond (27) believes that foreign ions can be incorporated into mature calcium hydroxide crystals and into the C-S-H gel but no changes in the X-ray diffraction patterns are detectable. This does not mean that structural changes do not take place near the sites of incorporation; only that present techniques are unable to detect them.

6.0 COPOLYMER 9

6.1 Organic Synthesis

This alkyd was prepared by the technique described in paragraph 3.1 except that 1 mole of isophthallic acid, 2.5 moles of maleic anhydride, 3 moles of diethylene glycol and 1 mole of propylene glycol were used.

Alkyds based on isophthallic acid often exhibit better water and alkali resistance and have higher heat distortion temperatures than those based on phthallic acid (38, 58). Increasing the molecular weight of the glycol reduces the frequency of the double bond and reduces the mechanical strength but improves the hydrophillic character of the resin. The selection of diethylene glycol and propylene glycol at these ratios is a compromise aimed at maintaining high physical strength whilst improving the hydrophillic character.

6.2 Polymerisation

Again a combination of cobalt octoate promoter and methyl ethyl ketone peroxide initiator at the same concentrations used for COPOLYMER 8 was found to initiate polymerisation at room temperature. The same non-ionic emulsifying agent was also included.

6.3 Composites of COPOLYMER 9

Fig. 47 summarises the technology employed for the preparation of COPOLYMER 9 composites and a typical formulation is shown below

100g of cement (or 16g OPC and 84g Pfa)
60g of resin
6.0g of emulsifying agent
0.3g of promoter (cobalt octoate)
1.2g of initiator (methyl ethyl ketone peroxide)
50g of aqueous solution (simulated waste)

$\frac{Wa}{C} = 0.5$ $\frac{Co}{C} = 0.6$ $\frac{Wa}{Co} = 0.83$

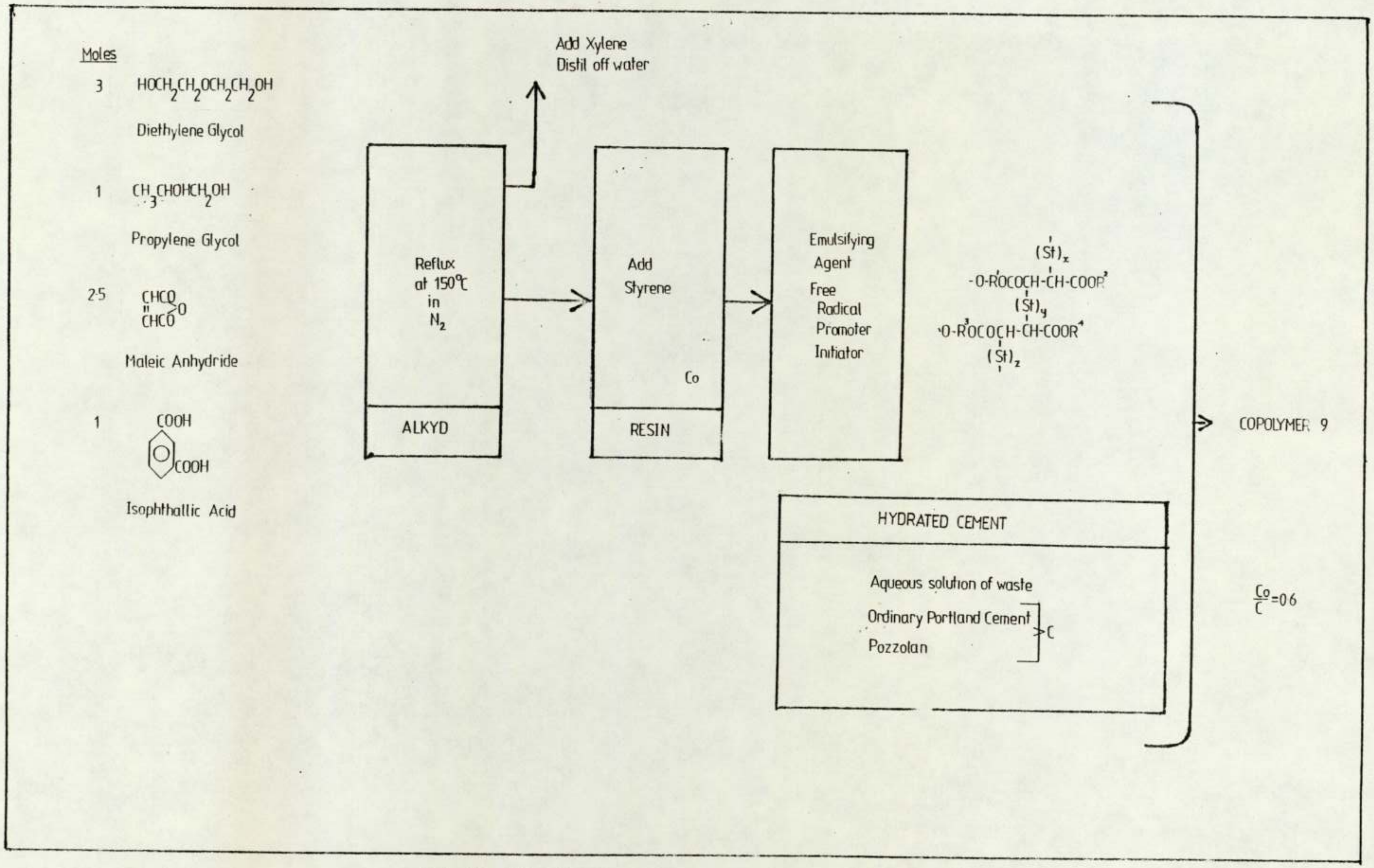


FIG. 47 THE PREPARATION OF COPOLYMER 9 COMPOSITES

The mixing procedure, using 1 M CsCl as the simulated waste, was identical to that described in paragraph 5.3. After curing under standard conditions the leaching characteristics of COPOLYMER 9 composites were determined using the method described in Appendix 2 and results are tabulated in Table 23 of Appendix 3 and shown in Fig. 48.

6.4 Pretreatment

Fig. 49 summarises the technology employed for the preparation of COPOLYMER 9 composites with pretreatment. The mixing sequence was that described in paragraph 5.4. COPOLYMER 9 composites containing 1 M CsCl and pretreatment with $\frac{Wa}{Co} = 0.83$, $\frac{Co}{C} = 0.6$ produced solid monoliths within a few hours of mixing and appeared uniform to the human eye. They did not exhibit any sign of sweating. After curing under standard conditions, the leaching characteristics were determined and the results are shown in Table 24 of Appendix 3 and in Fig. 50.

Caesium immobilisation is not good but the pretreatment technique was again shown to be beneficial. Composites containing pozzolanic cements were found to have higher caesium leach rates than those incorporating OPC alone. This is the reverse of findings for COPOLYMER 8 and no satisfactory explanation for this difference is known at this stage.

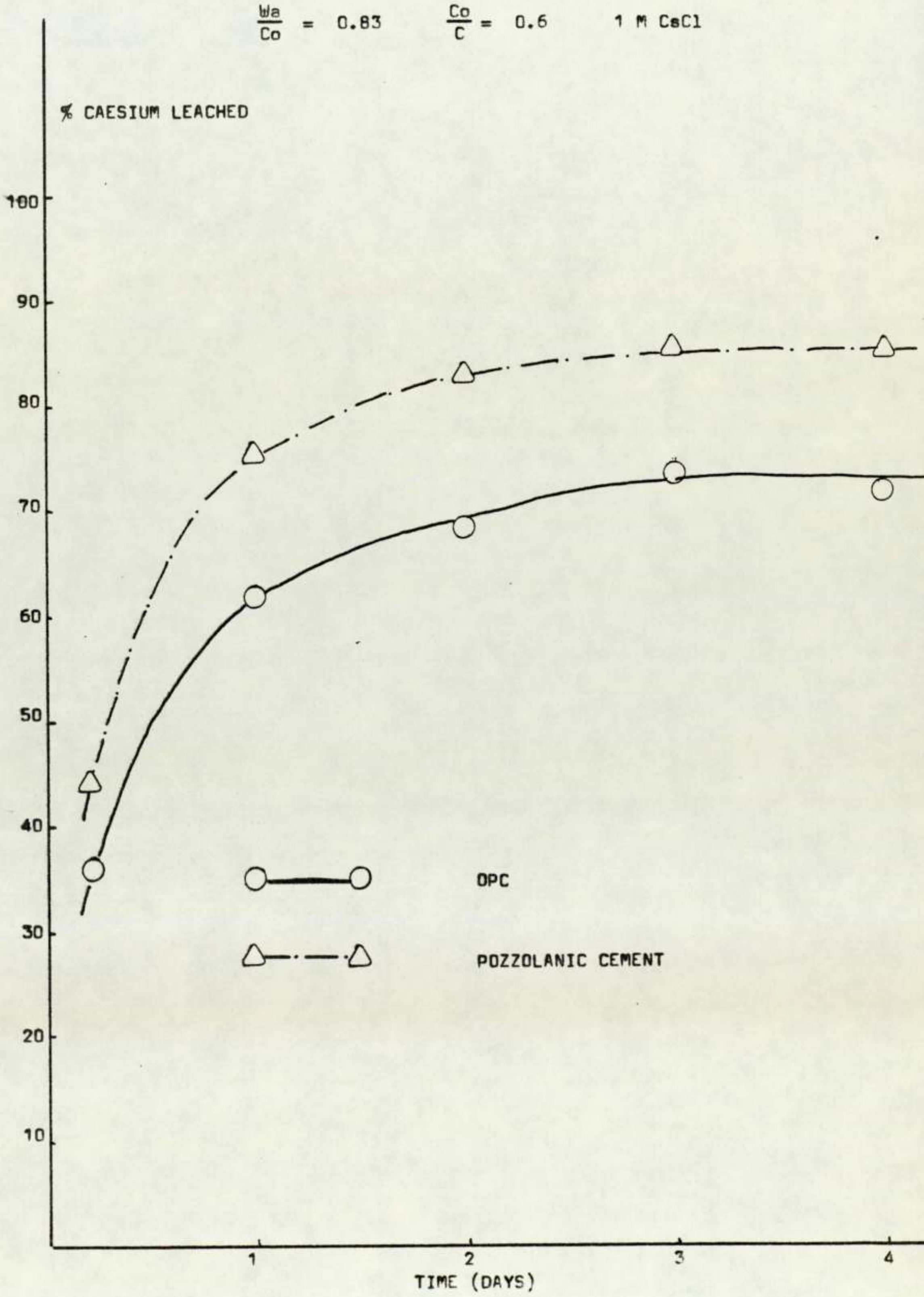
6.5 Strontium Studies

Studies were again made of the leaching characteristics

FIG.48 LEACHING CHARACTERISTICS OF COPOLYMER 9

CONTAINING CEMENTITIOUS INGREDIENTS

$\frac{Wa}{Co} = 0.83 \quad \frac{Co}{C} = 0.6 \quad 1\ M\ CsCl$



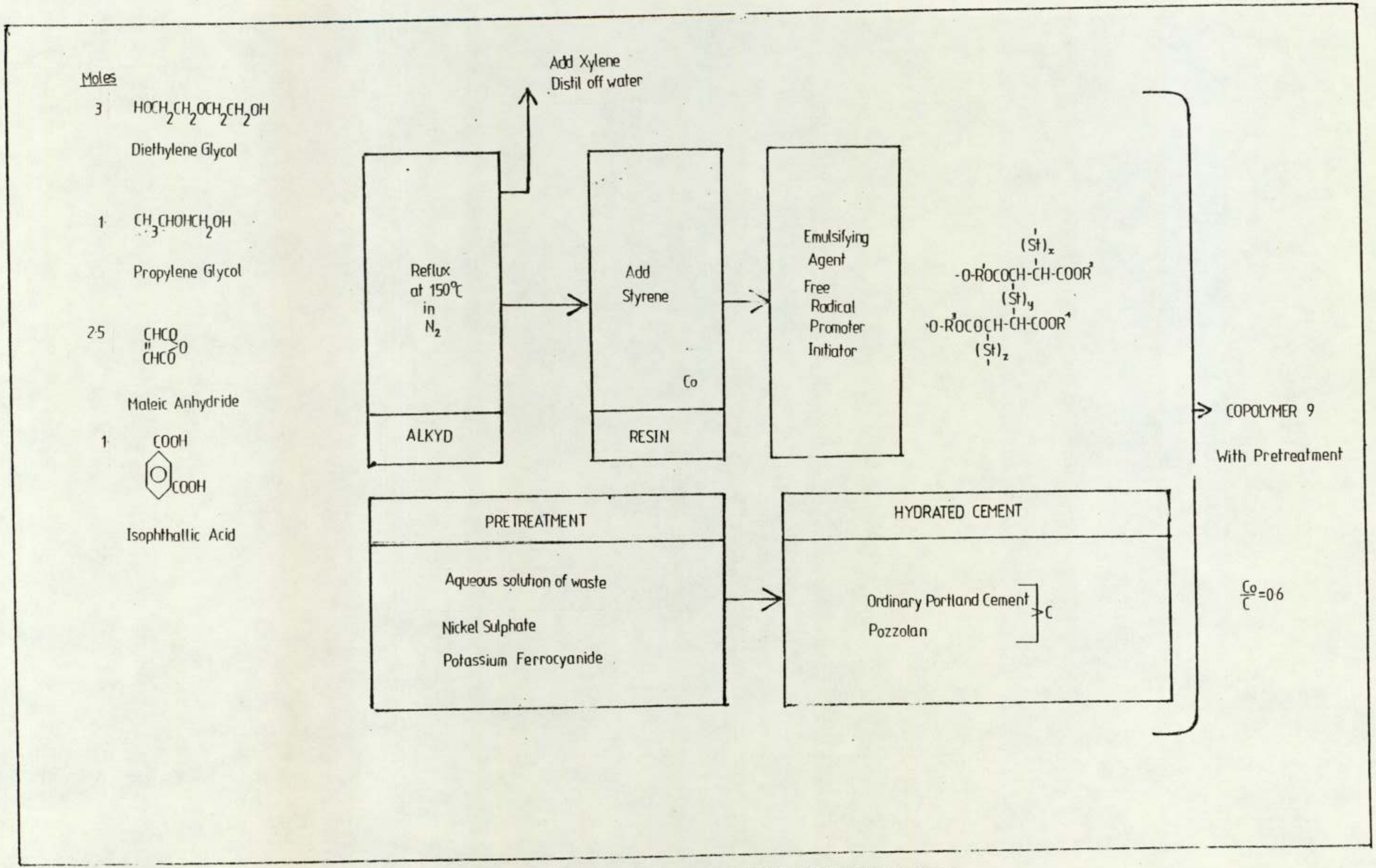
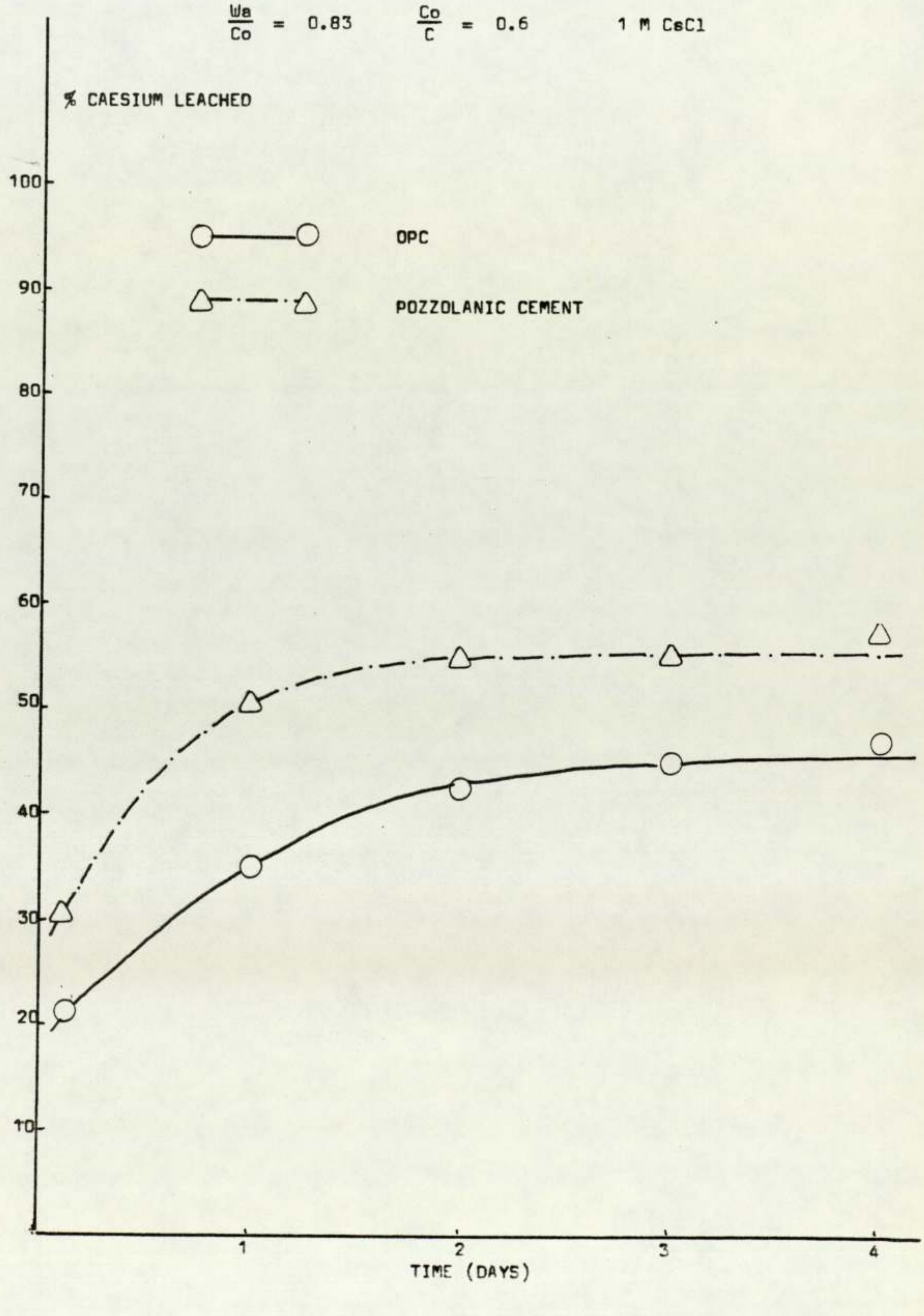


FIG. 49 THE PREPARATION OF COPOLYMER 9 COMPOSITES WITH PRETREATMENT

FIG.50 LEACHING CHARACTERISTICS OF COPOLYMER 9

CONTAINING CEMENTITIOUS INGREDIENTS AND PRETREATMENT

$\frac{Wa}{Co} = 0.83 \quad \frac{Co}{C} = 0.6$ 1 M CsCl



of strontium. COPOLYMER 9 composites were prepared as described in paragraph 6.3 except that a 1 M $SrCl_2$ solution containing 1 mCi of ^{85}Sr was used as the aqueous solution representing simulated waste. Mixing, curing and leaching techniques were unchanged. Table 25 of Appendix 3 and Fig. 51 show the leaching characteristics obtained.

In another series of experiments, the aqueous solution was first subjected to pretreatment as described in paragraph 5.5. Mixing, curing and leaching techniques were again unchanged and leaching characteristics are shown in Table 26 of Appendix 3 and in Fig. 52. The leaching rate of strontium is very low and again shows further reduction when pretreatment is included. Comparing Fig. 50 with Fig. 52 again illustrates the high mobility of caesium when compared with strontium.

6.6 Thermal Stability

A Thermo Gravimetric Balance was again used to study the thermal stability of COPOLYMER 9. Fig. 53 shows the thermal stability of these composites. Comparing Fig. 53 with Fig. 29 shows that COPOLYMER 9 is less thermally stable at temperatures up to about 400°C than COPOLYMER 8. This is presumably due to water loss in COPOLYMER 9 at quite low temperatures which corresponds to its inferior leach resistance qualities. At temperatures above 400°C the thermal stabilities are identical as would be expected.

FIG.51 LEACHING CHARACTERISTICS OF COPOLYMER 9

CONTAINING CEMENTITIOUS INGREDIENTS

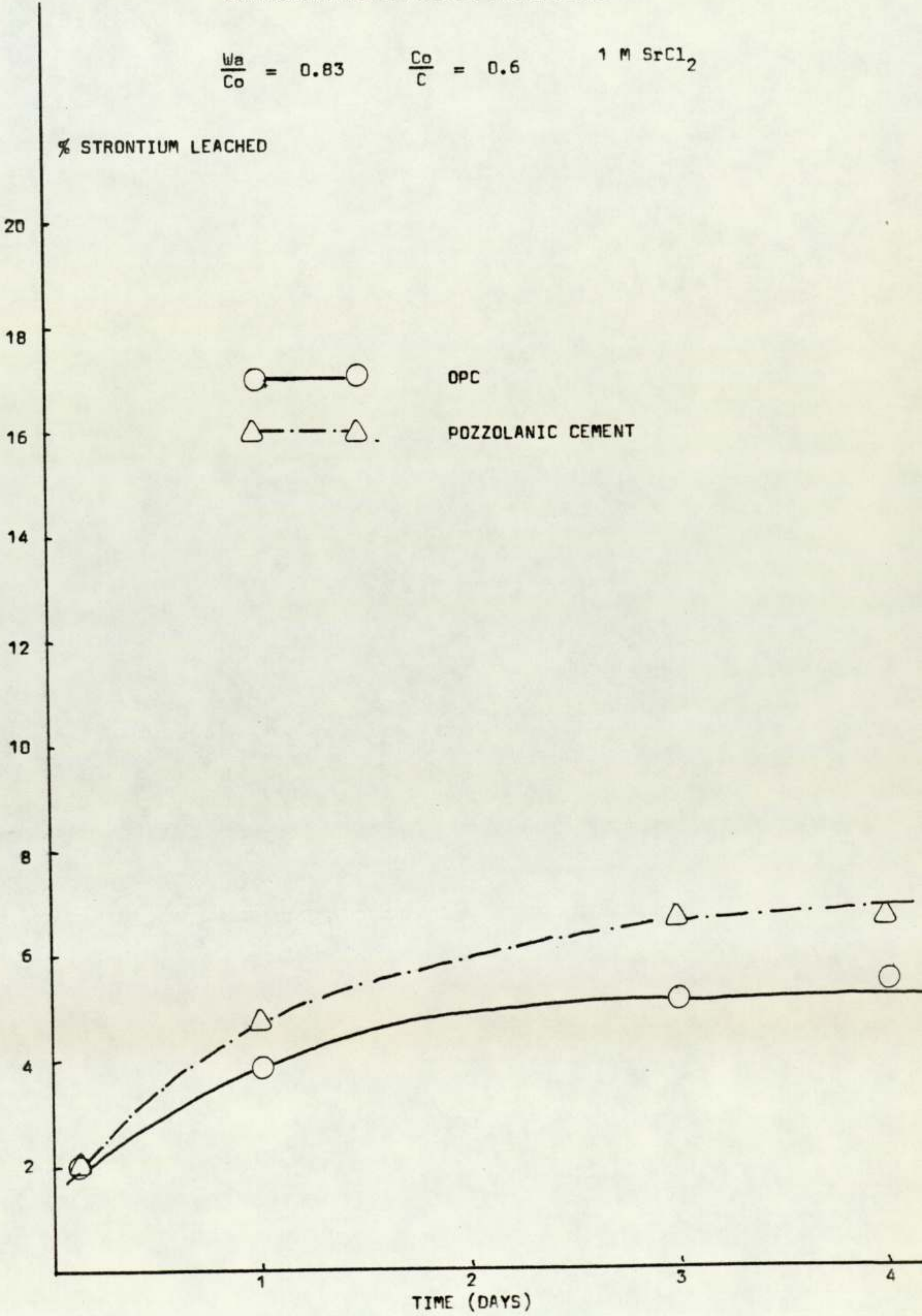


FIG. 52 LEACHING CHARACTERISTICS OF COPOLYMER 9 CONTAINING CEMENTITIOUS INGREDIENTS AND PRETREATMENT

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$ 1 M $SrCl_2$

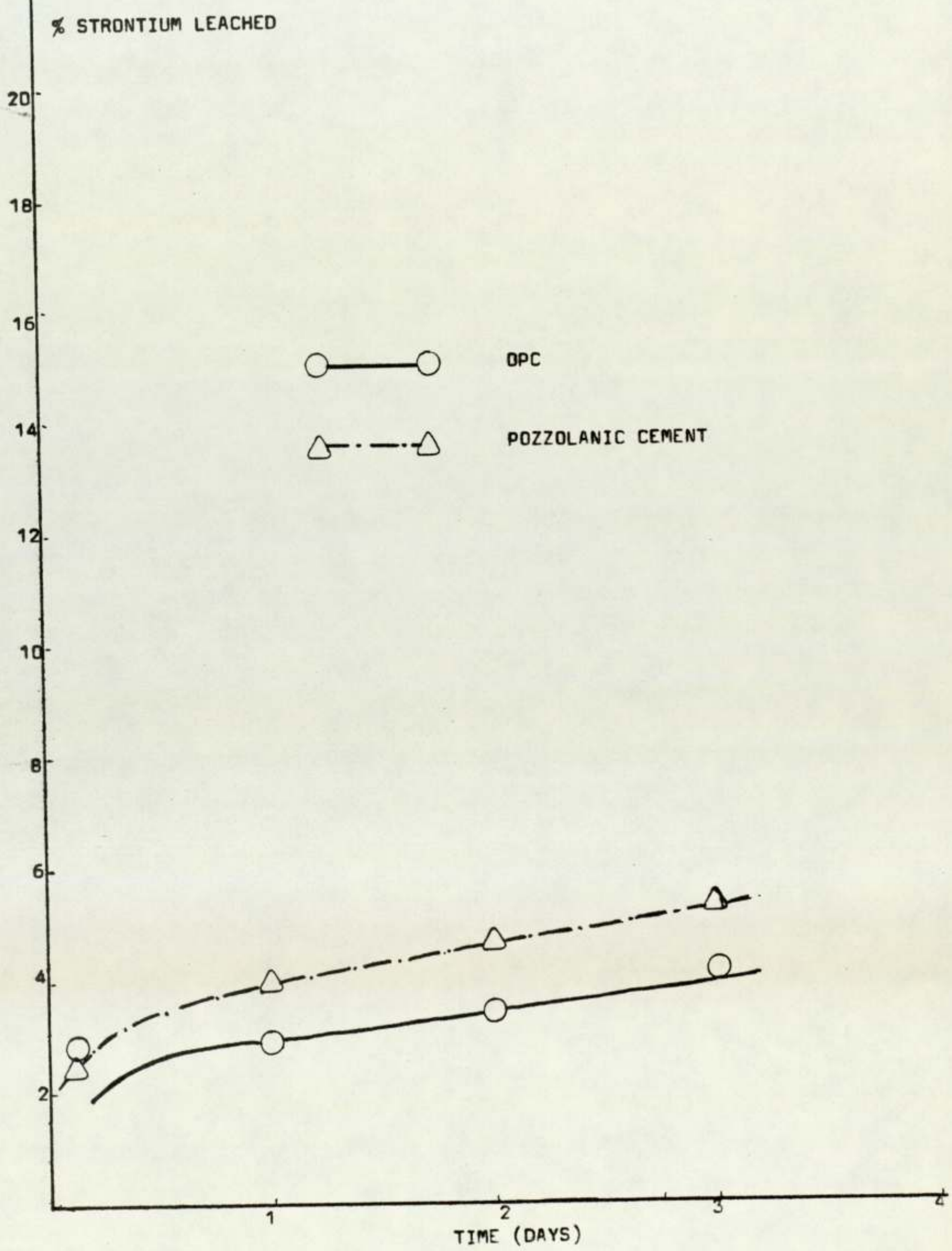
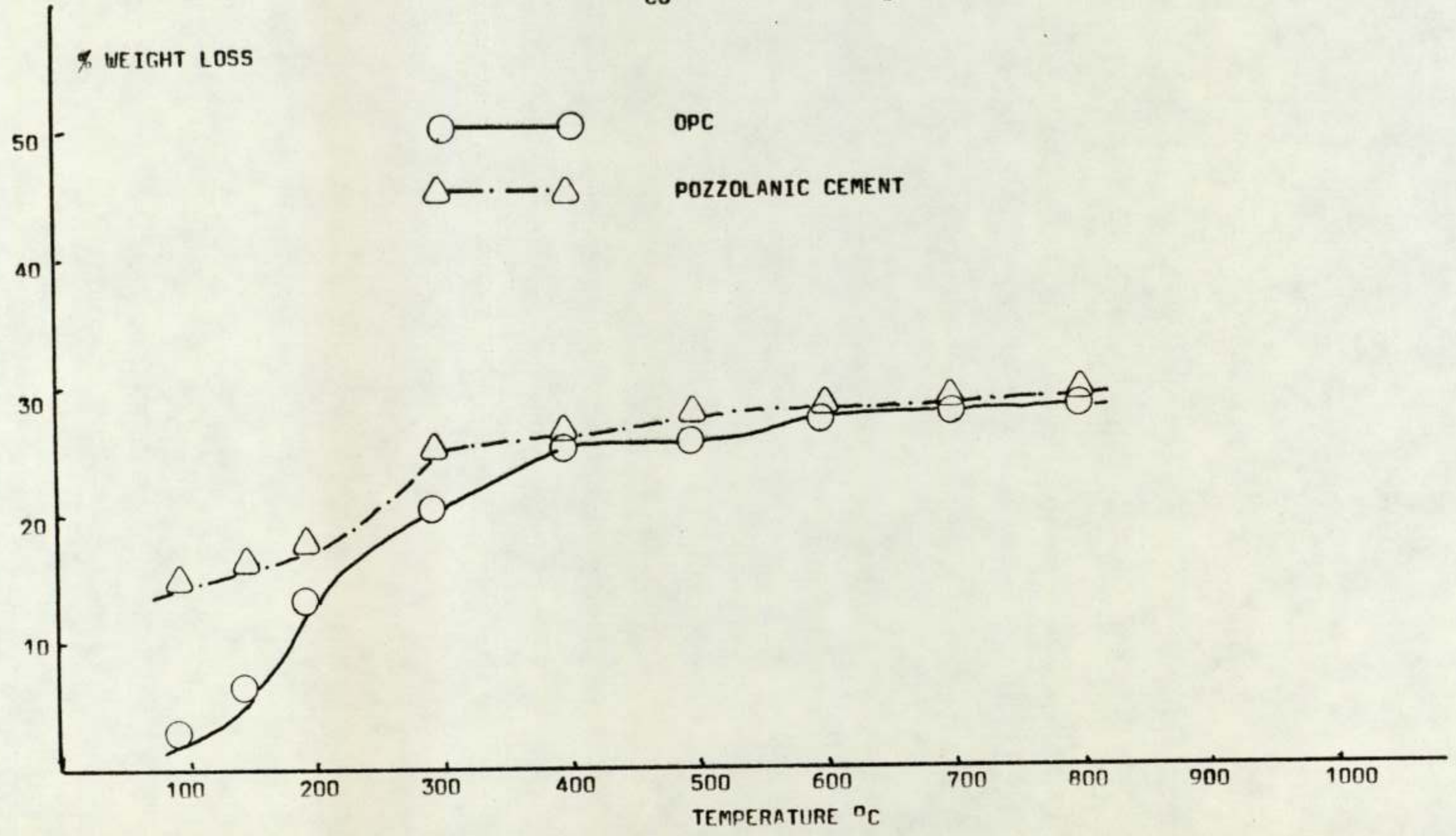


FIG.53 THERMAL STABILITY OF COPOLYMER 9

CONTAINING CEMENTITIOUS INGREDIENTS

$\frac{Wa}{Co} = 0.83 \qquad \frac{Co}{C} = 0.6$



6.7 Radiation Stability

Specimens of COPOLYMER 9 composites were also exposed to a total integrated dose of 500 Mrads gamma radiation and the leaching characteristics of caesium and strontium determined. Table 27 of Appendix 3 shows the results obtained and Figs. 54 and 55 compare this data with non-irradiated specimens. No significant changes in leaching characteristics were detected. Table 10 shows the compressive strengths of these composites before and after irradiation. The increase in compressive strength resulting from irradiation is noteworthy. Subramanian (39, 40, 41, 42) also reported an increase in compressive strength of his polyester products after similar irradiation and ascribed it to additional crosslinking occurring as a result of gamma irradiation.

Table 10 Compressive Strength of COPOLYMER 9 Before and after Irradiation

MN m^{-2}

	Before Irradiation	After 500 M rad Radiation
Copolymer 9 with OPC	3.49	14.98
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$	3.30	15.10
	3.60	14.60
Copolymer 9 with pozzolanic cement	2.99	14.00
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$	2.80	12.80
	2.60	11.50

FIG. 54 LEACHING CHARACTERISTICS OF COPOLYMER 9

BEFORE AND AFTER IRRADIATION

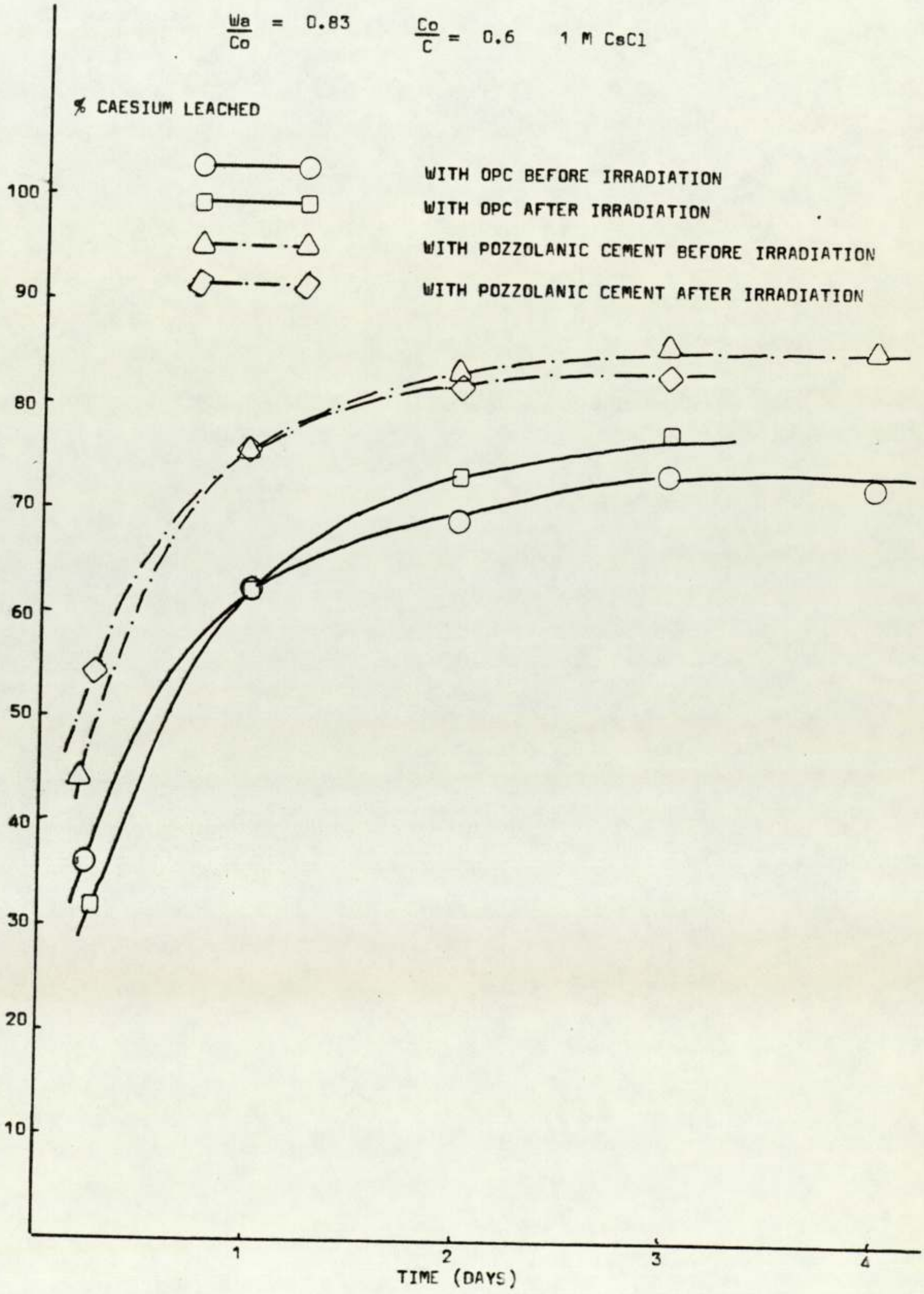
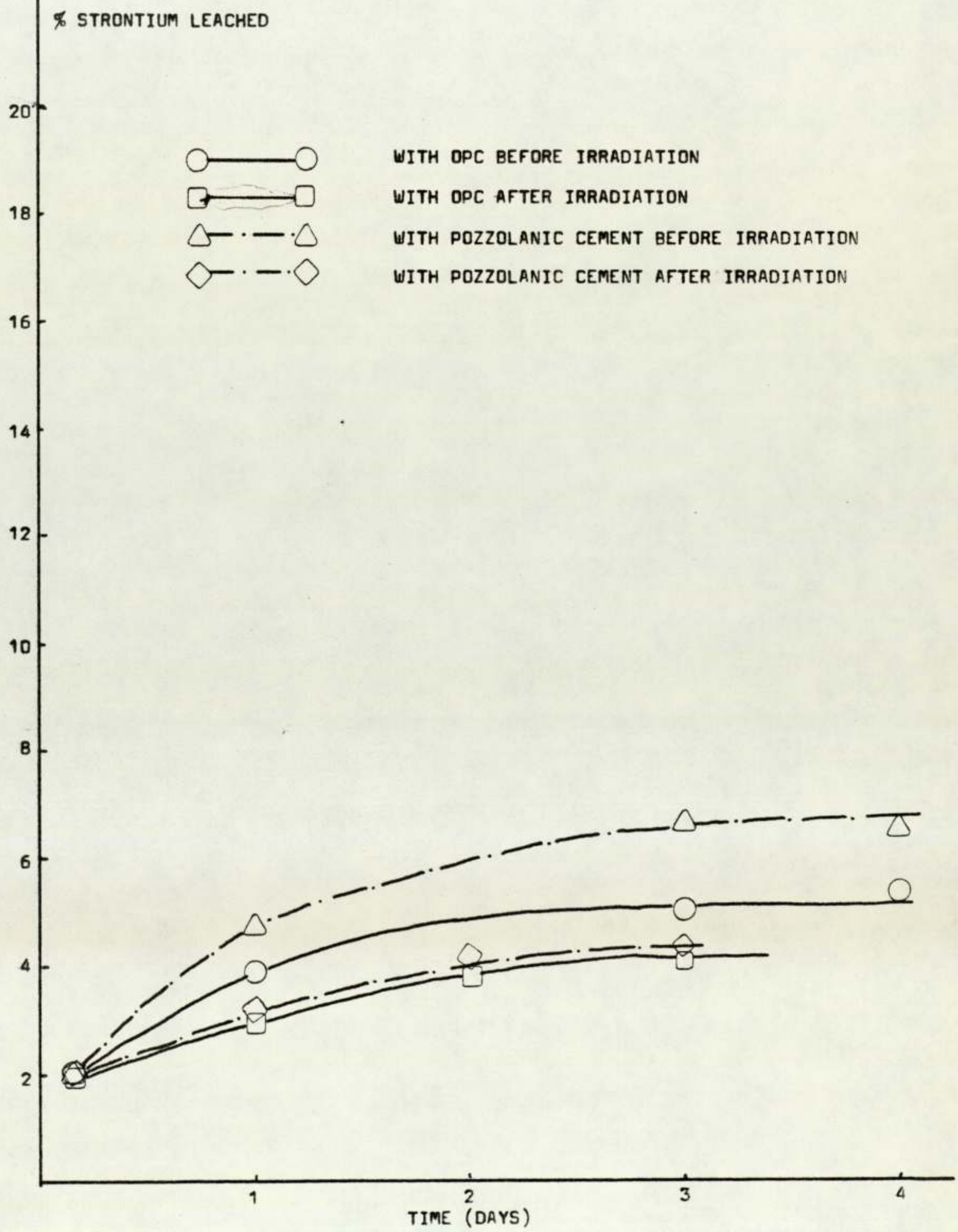


FIG. 55 LEACHING CHARACTERISTICS OF COPOLYMER 9

BEFORE AND AFTER IRRADIATION

$\frac{Wa}{Co} = 0.83 \quad \frac{Co}{C} = 0.6 \quad 1\ M\ SrCl_2$



7.0 COPOLYMER 10

7.1 Organic Synthesis

Brydson (58) describes a method for the preparation of epoxy based polymers which was used to produce polymers different in structure from those described above. 1 mole of Bisphenol A was refluxed at 125°C with 4 moles of epichlorhydrin in an atmosphere of nitrogen. The mixture was continuously stirred for 16 hours whilst 2 moles of 30% NaOH (aq.) was added dropwise. The mixture was maintained alkaline to phenolphthalein during this period. The resulting organic layer was separated, dried with sodium sulphate and fractionally distilled under vacuum. The reaction is shown in Fig. 56 and the product is diglycidylether of Bisphenol A with a molecular weight around 340. Higher molecular weight resins are obtained by reducing the excess of epichlorhydrin. The product was diluted with half its weight of styrene.

7.2 Polymerisation

Diglycidylether of Bisphenol A in styrene can be polymerised with a variety of monomers such as amines or acids. Methacrylic acid was chosen for these experiments. 172g of methacrylic acid were added for each 340g of diglycidylether of Bisphenol A and the mixture was a pale brown non-viscous resin.

0.5g of cobalt octoate and 2.0g of methyl ethyl ketone peroxide were used for each 100g of resin to initiate polymerisation.

7.3 Composites of COPOLYMER 10

Fig. 56 summarises the technology used for the preparation of COPOLYMER 10 composites and a typical formulation is shown below.

100g of cement (or 16g OPC and 84g Pfa)
60g of resin
0.3g of promoter (cobalt octoate)
1.2g of initiator (methyl ethyl ketone peroxide)
50g of aqueous solution (simulated waste)

$\frac{Wa}{C} = 0.5$ $\frac{Co}{C} = 0.6$ $\frac{Wa}{Co} = 0.83$

1 M CsCl solution was used as the simulated waste. The mixing procedure described in paragraph 5.3 was tried and proved to be unsuccessful. The low viscosity of the resin permitted separation into two and sometimes three phases before polymerisation was complete. As a result experimental conditions were changed and the products obtained designated COPOLYMER 11.

8.0 COPOLYMER 11.

8.1 Organic Synthesis and Polymerisation of COPOLYMER 11

The organic synthesis of this product was identical to that described in paragraph 7.1. However, to effect polymerisation the promoter and initiator were changed. 0.5g of NN' dimethylaniline and 4g of benzoyl peroxide (a 50% paste in paraffin) were used for each 100g of resin. The incorporation of 10g of a non-ionic emulsifying agent (a highly oxylated castor oil) per

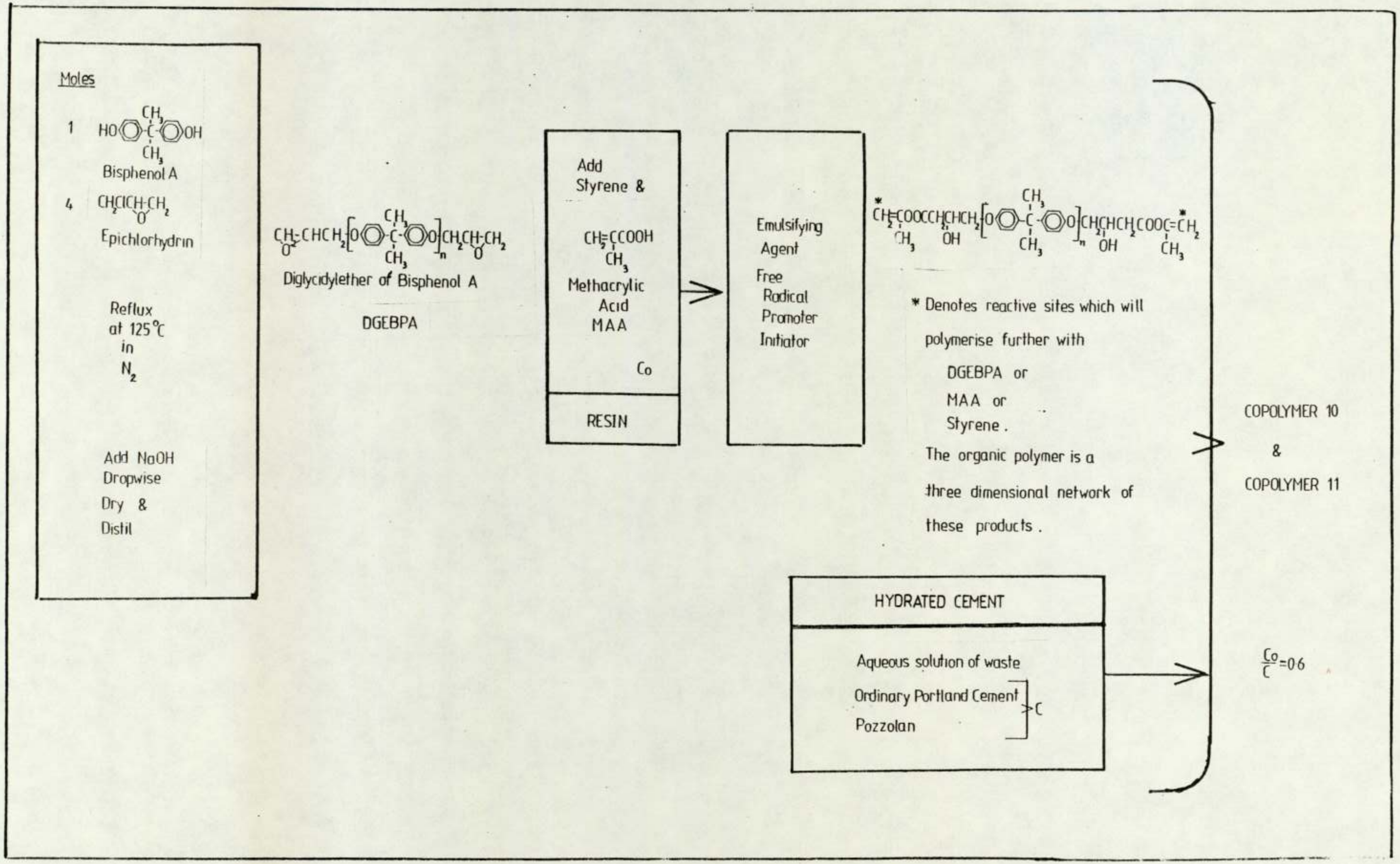


FIG. 56 THE PREPARATION OF COPOLYMER 10 AND COPOLYMER 11 COMPOSITES

100g of resin also proved to be beneficial.

8.2 Composites of COPOLYMER 11

Fig. 56 summarises the technology used for the preparation of COPOLYMER 11 composites and a typical formulation is shown below.

100g of cement (or 16g OPC and 84g Pfa)
60g of resin
6.0g of emulsifying agent
0.18g of promoter (NN' dimethylaniline)
0.72g of initiator (benzoyl peroxide)
50g of aqueous solution (simulated waste)

$\frac{Wa}{C} = 0.5$ $\frac{Co}{C} = 0.6$ $\frac{Wa}{Co} = 0.83$

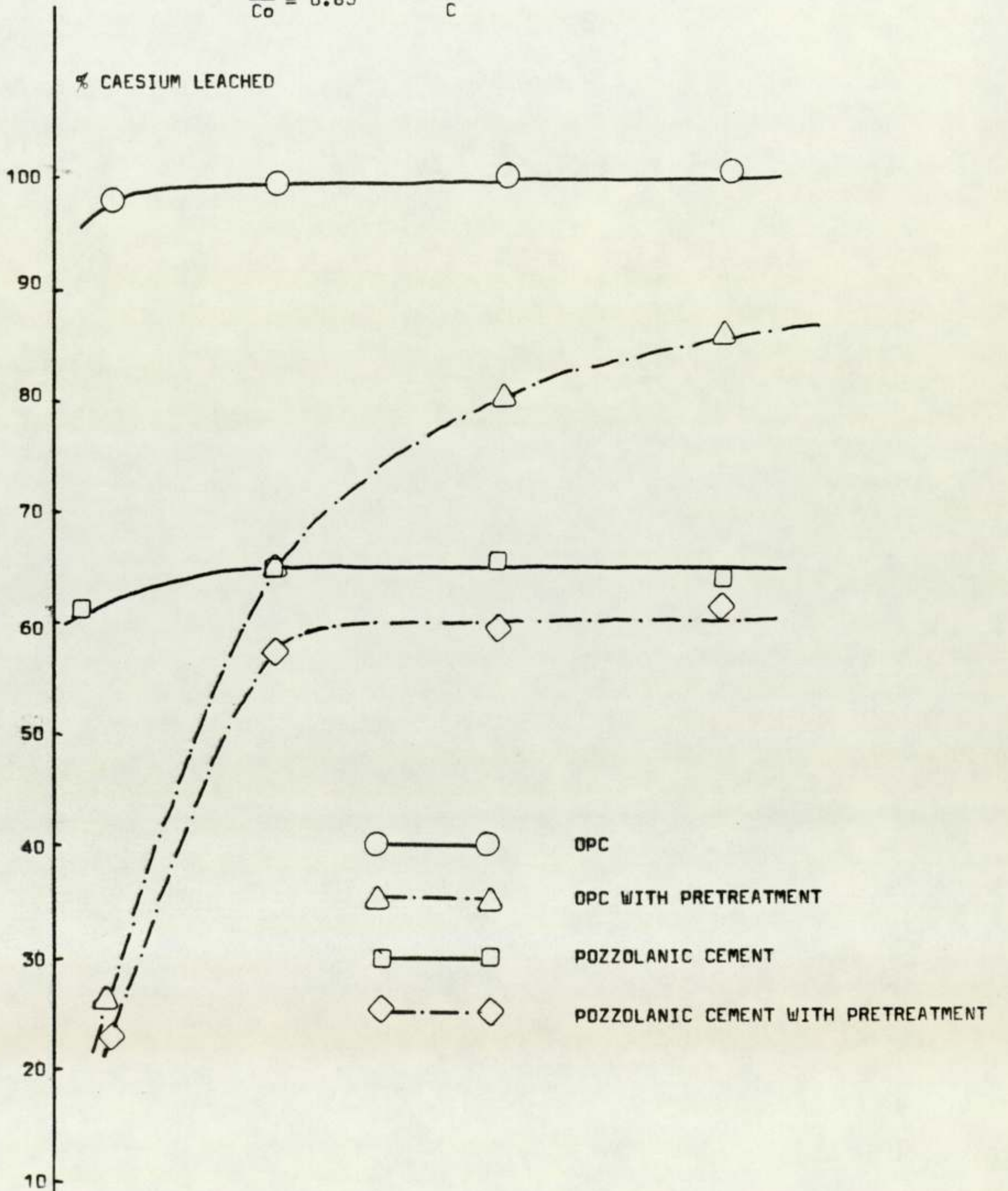
1 M CsCl solution was used as the simulated waste. The mixing procedure described in paragraph 5.3 was employed. Solid, uniform monoliths were obtained within 30 - 90 minutes of mixing. After curing under standard conditions the leaching characteristics of COPOLYMER 11 composites were determined using the method described in Appendix 2. Table 27 in Appendix 3 andFig. 57 show the results obtained. Caesium immobilisation was very poor.

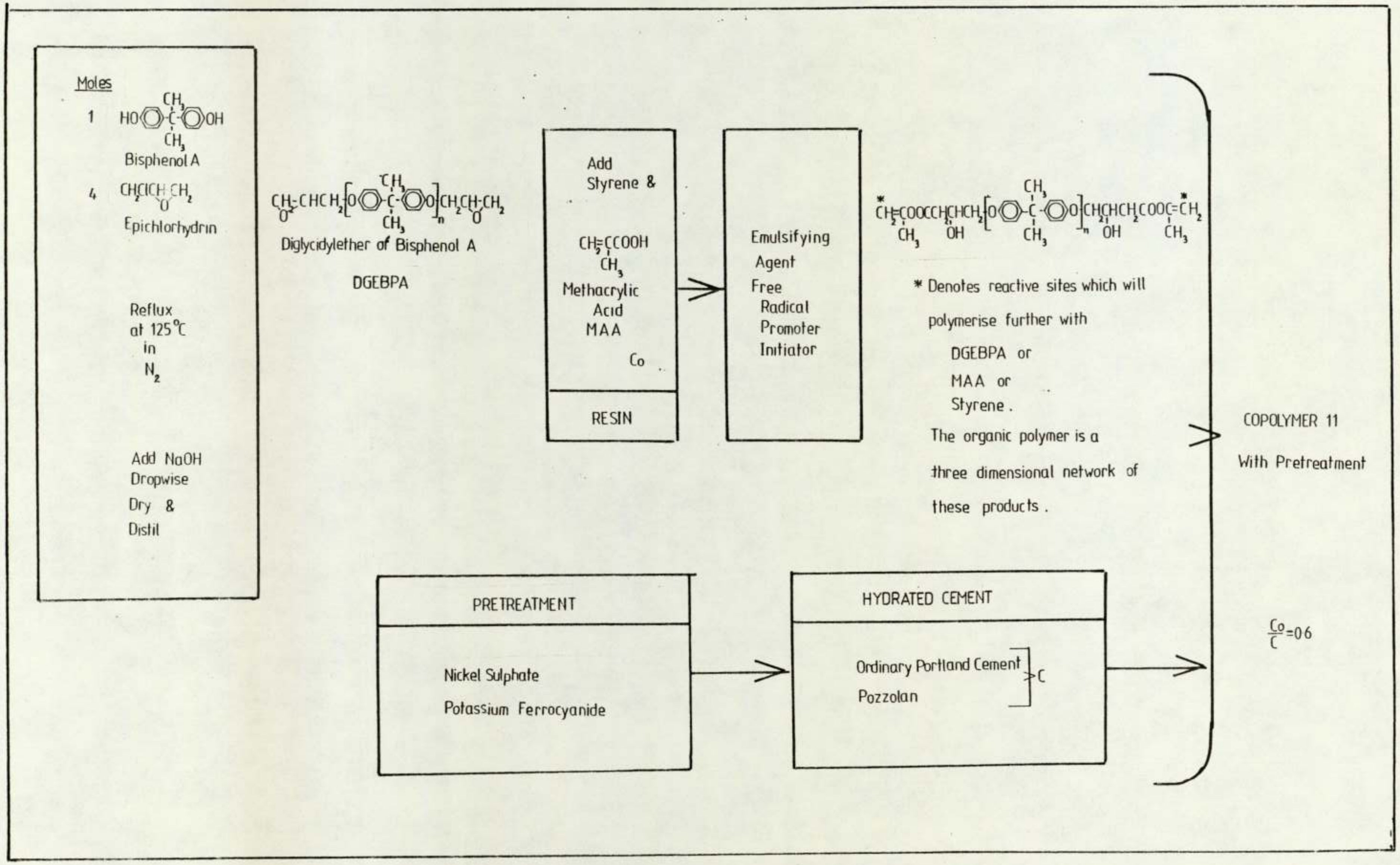
8.3 Pretreatment

Fig. 58 summarises the technology employed for the preparation of COPOLYMER 11 composites with pretreatment. The mixing sequence was that described in paragraph 5.4. 1 M CsCl solution was again used as simulated wastes and solid monoliths were obtained in

FIG. 57 LEACHING CHARACTERISTICS OF COPOLYMER 11 CONTAINING CEMENTITIOUS INGREDIENTS

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$ 1 M CsCl





* Denotes reactive sites which will polymerise further with DGEBPA or MAA or Styrene.

The organic polymer is a three dimensional network of these products.

FIG. 58 THE PREPARATION OF COPOLYMER 11 COMPOSITES WITH PRETREATMENT

less than 2 hours of mixing. Curing and determination of leaching characteristics were carried out by the standard techniques described previously. Table 28 in Appendix 3 shows the leaching characteristics obtained and Fig. 57 compares products with and without pretreatment. The ability to immobilise caesium was very poor and consequently strontium leaching studies and thermal and radiation stability tests were not undertaken.

The poor performance of COPOLYMERS 10 and 11 is not regarded as a conclusive failure of this type of polymeric system since, as mentioned in paragraph 7.0, many variations (and likely improvements) are possible. For example, the molecular weight of the diglycidyl ether can be reduced by increasing the molar ratio of epichlorhydrin used in its preparation. Lower molecular weights would be expected to produce greater cross linking. Additionally, the composition of the acrylic acid used to form the epoxy resin can be altered to produce likely changes in the hydrophillic nature of the resin. Consequently it ought to be possible to optimise the organic synthesis to produce a hard monolith capable of retaining aqueous wastes and the radionuclide pollutants which it contains.

SECTION 4

DISCUSSION AND CONCLUSIONS

1.0 DISCUSSION

Radioactive wastes are generated at many stages in the nuclear fuel cycle. These wastes differ markedly in their characteristic properties and physical form and consequently demand different waste management practices. The techniques used by the British Nuclear Power Industry have been described in this thesis and the need for further research and development in particular areas has been identified. The immobilisation of low and intermediate level aqueous wastes is an area which warrants further development and was chosen for study in this thesis. The concept employed was the solidification of aqueous waste streams within an immobilisation medium without employing a pre-concentration stage such as precipitation, filtration, ion-exchange or evaporation. In order to simplify processing requirements all chemical reactions were required to take place in a single vessel and at ambient temperatures and pressures.

Cement products were selected as the prime candidate immobilisation media since they offer many advantages including wide applicability, ease of processing and low cost. However, a review of the structure of hydrated cement showed that it has a porous nature and that the porosity increases and the compressive strength decreases as the water content increases. Thus the use of high aqueous waste to cement ratios produces a weak product and allows water to permeate readily through the structure. As a result the leaching of polluting radionuclides from a waste repository into the environment seems likely.

The importance of the leaching mechanism has been recognised and a comparison made of the leaching behaviour of natural minerals. From this certain key elements were identified as monitors of waste behaviour. A review of the fission products present in nuclear waste highlighted the importance of caesium and strontium. Theoretical and practical studies of radioactive waste repositories reported in the literature also showed that the key radionuclides are caesium, strontium, cobalt and tritium. Therefore the behaviour of caesium and strontium bearing aqueous wastes has been studied in this work.

Various methods of measuring leaching characteristics have been reviewed and criticised. No single laboratory technique can hope to duplicate the conditions to be found in a nuclear waste repository and therefore the aim of such procedures must be confined to a comparison of the characteristics of candidate immobilisation materials under reproducible conditions. In some reported work in this field, leaching studies have been made by measuring the weight loss of candidate materials. Such weight loss studies are limited by the accuracy of drying and weighing specimens, are difficult to reproduce and are non-specific to particular elements. On the other hand, radioactive tracer studies are specific to the element chosen; no knowledge of the chemical form of the element has to be assumed and they should be more reproducible.

For the purpose of this work, the ISO Soxhlet Leaching Test was chosen and a battery of twelve units constructed. The leaching of caesium and strontium was studied by incorporating aqueous solutions of caesium and strontium salts labelled with ^{134}Cs and ^{85}Sr into the various candidate materials.

Studies of OPC showed high caesium leaching rates and attempts have been made to overcome this deficiency by various techniques. A pozzolanic cement has been studied and improved caesium retention was found. However, caesium leaching rates were increased at high waste to cement ratios and with high concentrations of caesium in the aqueous waste. Strontium leached more readily from the pozzolanic cement than from OPC when products containing aqueous strontium chloride were studied. However, since strontium retention was much greater than caesium retention in all the cases studied, the use of the pozzolanic cement is to be recommended.

An attempt was made to further improve caesium retention by incorporating a styrene-butadiene copolymer into the pozzolanic cement at the wet mix stage. However, leaching characteristics were not improved as was expected and this was attributed to the higher overall water to cement ratios resulting from the addition of the aqueous suspension of the copolymer.

The concept of incorporating monomers into the wet cement phase followed by their polymerisation in situ during the curing phase of the cement is attractive. Polymerisation techniques reported by other researchers were reviewed but none of these processes involved both organic polymerisation chemistry and inorganic cement chemistry at the same time. Laboratory equipment and techniques were developed to produce cement-organic polymer composites. The monomers chosen were required to produce a free standing solid monolith containing aqueous wastes within three hours of mixing and the system had to be compatible with the alkaline conditions which exist within hydrating cement. COPOLYMER 6 was the first composite studied. It was produced using a mixed ester monomer made from phthallic and maleic anhydrides and propylene and diethylene glycols crosslinked with styrene by means of a free radical initiator. Composites containing both OPC and the pozzolanic cement were made. Caesium leach rates were shown to be proportional to the caesium chloride concentration in the aqueous waste.

Under comparable conditions of waste loading, COPOLYMER 6 was shown to immobilise caesium better than both OPC and the pozzolanic cement.

The physical strength of candidate immobilisation products is of interest. They are not expected to be load bearing products so that all that is needed is sufficient strength to maintain the integrity of the product during handling in order to prevent damage and loss of material during transportation and storage. Compressive strength tests on COPOLYMER 6 indicated that the product was satisfactory in this respect and that, as would be expected, the compressive strength decreased as the simulated waste content increased.

COPOLYMER 8 is another cement-organic polymer composite examined in this work. In this case the mixed ester monomer was made from phthallic and maleic anhydrides, propylene glycol and polymerised with styrene. The ratio of maleic to phthallic anhydride in this monomer was increased to 4:1 from the 1:2 ratio employed in COPOLYMER 6 to encourage crosslinking with the aim of improving retention of aqueous waste. COPOLYMER 8 was found to have the ability to solidify large relative quantities of aqueous waste i.e. waste to organic polymer ratios up to 3.8, but caesium leach rates were high. This was attributed to the development of an open structure with high waste loadings.This reasoning was substantiated by the observed lower compressive strengths of these products. Under comparable waste loadings caesium retention in COPOLYMER 8 was better than for OPC and the pozzolanic cement.

The pretreatment technique of co-precipitating caesium with nickel ferrocyanide was studied. Although the method precipitates salts from solution no attempt was made to pre-concentrate the waste by separation or filtration. Pretreatment was applied to COPOLYMER 8 composites and was shown to reduce the leaching rate of both caesium and strontium but even under these conditions caesium still had a leaching rate nine times that of strontium.

Any material incorporating radioactive wastes will be subjected to decay heat and to radiation. Hence the thermal and radiation stability of COPOLYMER 8 was studied. COPOLYMER 8 had a weight loss of less than 5% at temperatures up to 200°C which indicates that it would be suitable for LLW and ILW treatment where temperature rises due to trace contamination of actinides would be expected to be much less than this. Irradiation of COPOLYMER 8 composites to a total integrated dose of 500 M rads showed an increase in compressive strength and no change in caesium or strontium leaching rates. Radiation stability is therefore adequate for LLW and ILW treatment.

An attempt was made to identify the retention mechanism of caesium by carrying out scanning electron microscopy studies on COPOLYMER 8 composites. These studies identified the chemical components of the inorganic matrix and showed that the caesium bearing particles are randomly distributed within the product. Consequently, the improved leaching characteristics of this product could not be explained by the formation of some new insoluble compound. Porosimetry measurements showed that the COPOLYMER 8 composites had smaller pore diameters than the pozzolanic cement and this was attributed to the existence of the organic copolymer within the cement matrix.

It was therefore concluded that the retention of key elements within this composite was due to the creation of a physical barrier of organic polymer which restricted the diffusion of water molecules and dissolved ions within the matrix rather than the formation of any particular chemical species. The improvement in leaching characteristics is therefore due to physical rather than chemical changes in the structure.

Changes in the structure of the mixed ester were made in producing COPOLYMER 9 with a view to increasing the hydrophillic character of the ester. Isophthallic acid was used instead of phthallic anhydride and the ratio of maleic to phthallic was 2.5 to 1. The caesium leaching characteristics of COPOLYMER 9 composites were studied and caesium retention was inferior when compared to COPOLYMER 8. Pretreatment improved the retention of both caesium and strontium. Strontium was again more readily retained than caesium. Thermal stability tests showed that COPOLYMER 9 was less stable than COPOLYMER 8. The effect of 500 M rad radiation increased the compressive strength of COPOLYMER 9 and had a negligible effect on the leaching rates of caesium and strontium. It would seem that the changes in the organic structure of the mixed ester had improved the hydrophillic nature of the composite but this had created a more open structure permitting greater mobility of water molecules and dissolved ions within the structure. It was concluded that COPOLYMER 9 was less satisfactory than COPOLYMER 8.

Epoxy based resins provide an alternative to mixed ester products. COPOLYMERS 10 and 11 have been produced from this base. Although such products have a fundamentally different backbone structure from the mixed ester types they also produce free standing monoliths within a few hours of mixing with simulated wastes and cement products. Although pretreatment improved caesium retention the leach rate is higher than desirable. Nevertheless this range of composites warrants further investigation since many variations aimed at optimising the structure are possible. For example changes in the ratio of epichlorhydrin to bisphenol-A can be made to control the molecular weight and changes in the structure of the acrylic acid used can be made. These changes increase the bonds available for crosslinking thereby offering potential for the improvement of nuclide retention due to the creation of additional barriers within the product. The inclusion of emulsifying agents has indicated that high waste to organic polymer ratios are possible.

2.0 CONCLUSIONS

The need to develop improved waste conditioning techniques for radioactive waste management is apparent and these studies have shown that technical improvements are achievable by a combination of cement chemistry and organic polymer chemistry. Many of the controlling factors which determine the release rate of pollutant species have been identified and standard techniques for production and testing of candidate composites have been developed.

The concept of polymerising organic monomers within the cement matrix as the cement cures offers considerable benefits in the development of an immobilisation medium for use with LLW and ILW. The composites produced possess the desirable properties of cement products and the leaching characteristics are enhanced by the creation of polymer barriers within the matrix which inhibit the diffusion of water molecules into and solutions of nuclides out of the structure.

3.0 SUGGESTIONS FOR FURTHER WORK

COPOLYMER 8 type products warrant further study using other simulated wastes and combinations of aqueous and solid wastes.

COPOLYMER 11 type products should be prepared varying the chemical compositions and studying the effects on leaching of key constituents.

Larger specimens of these products should be produced to permit scale up of laboratory mixing and material handling procedures.

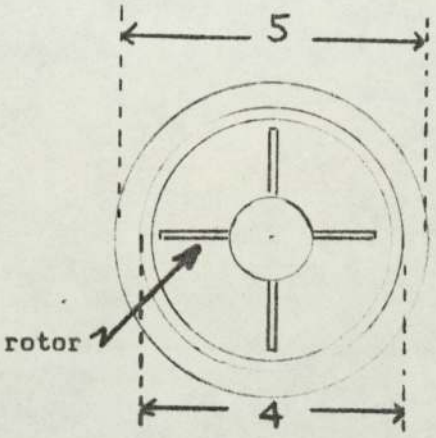
The leaching characteristics of the most promising candidate composites should be compared under standard conditions with other products such as bitumen and urea formaldehyde.

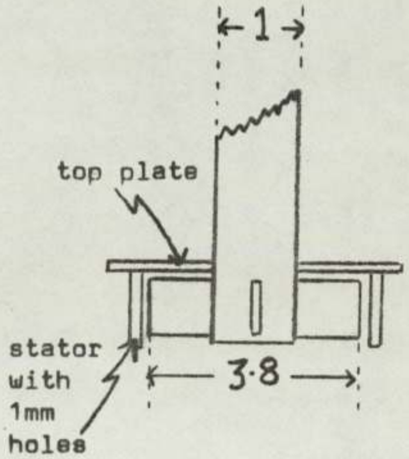
APPENDIX 1

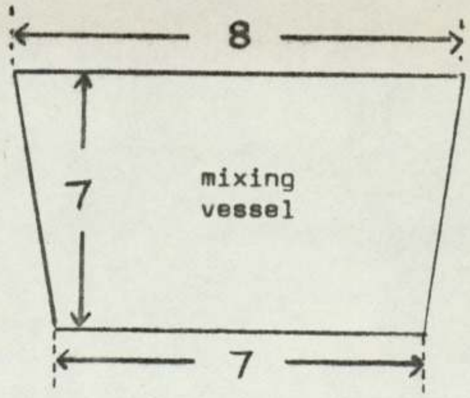
DETAILS OF THE MIXER

The mixer is manufactured by Silverson Machines Ltd., Chesham, being their model LR2 equipped with a high sheer stainless steel rotor and stator. The stator is perforated with 1mm holes. The top plate is stationary. The mixer is driven by a variable speed fractional horse power motor. The full assembly is shown in Fig. 10.

Dimensions are in centimetres







Not to scale.

APPENDIX 2

THE PREPARATION OF SPECIMENS AND THE PERFORMANCE OF LEACHING TESTS

A.1 This procedure is based on a draft proposal issued by the International Standards Organisation (Reference ISO/TC85/SC5/WGSN) and has been chosen to permit comparable leaching information to be obtained in a short period of time. The conditions expose a sample to continuously redistilled water at 100°C. Such conditions tend to accelerate the leach rate so that a product durability can be determined in a short time. The test conditions do not simulate any storage scenario but rather provide a rapid means of intercomparison of solidified waste products with various compositions and methods of preparation.

A.2 The specimen is prepared by transferring weighed ingredients into a paraffin mould 2.4 cm diameter by 3.4 cm height, and allowing it to set. As soon as possible after setting the mould is cut away and the specimen allowed to stand in saturated air at room temperature for a period of twenty-eight days prior to leaching.

A.3 The dimensions and weight of the specimen are determined. The geometric surface area does not exceed $5 \times 10^{-3} m^2$ and the volume does not exceed $2.5 \times 10^{-5} m^3$. In all cases the specimens tested had a volume to surface ratio of 0.44 ± 0.02 cm.

A.4 A commercially available Soxhlet apparatus is used constructed from Pyrex glass. The sample cup contains 1 x 10^{-4} m^3 before siphoning.

A.5 The leachant used is 3 x 10^{-4} m^3 of de-ionised water. The temperature is 100 ± 2°C and the minimum duration of the test is seventy two hours. The reflux rate is such that the siphon cup empties every 15± 5 minutes.

A.6 Care is taken to use a new flask for each run and to decontaminate Soxhlet cups, sample containers and pipettes prior to use.

A.7 At the required sampling time the Soxhlet is switched off and the distallate in the cup returned to the Soxhlet flask. When boiling has ceased a sample of about 20 cm^3 is pipetted out of the flask into a vial. The vial is sealed and cooled to room temperature. The sample is then centrifuged at 6000 rpm for 5 minutes. 10 cm^3 of the supernatant is carefully pipetted out of the vial and transferred to a new vial which is used for counting. The aliquots of leachant are returned to the system prior to the next sampling.

A.8 Counting is done by means of an Automatic Beta Gamma Counter which is capable of accepting up to 400 samples at any one time. The β head is a liquid scintillation counter and the γ head is a NaI (Tl) solid scintillation counter. Each head is equipped with two photomultiplier tubes. The counter is controlled by a CAMAC system and a

Hewlett Packard 2100A computer connected to a teletype and/or disc data storage system. The system incorporates a visual display unit which permits identification of the spectrum.

A.9 ^{134}Cs is a γ emitter with energy peaks at 0.6 and 0.8 MeV. ^{85}Sr is a γ emitter with an energy peak at 0.51 MeV. The computer was programmed to count over these peaks and to compensate for background counts.

A.10 The quantity of metal leached for a given specimen at any particular time was then determined by counting leachant samples and comparing against a standard solution prepared from the same source.

A.11 This is expressed as percentage of metal present in the original sample. A typical calculation is shown below

An aqueous solution representing simulated waste was prepared by dissolving 168.35 g of caesium chloride in distilled water, adding 1 m Ci of ^{134}Cs and making up to 1 litre. This solution is then 1 M CsCl and was used in the preparation of the specimen under test. 25 g of this solution were used to produce a wet mix of 105.6 g which was cast into 3 moulds. The weight of the specimen in each mould was determined and the specimen selected for leach testing weighed 21.61 g.

The specimen therefore contained

$$\frac{25}{105.6} \times \frac{132.9}{1000} \times 21.61 = 0.6799 \text{ g of caesium}$$

On analysing 10 cm^3 of leachant at a particular time the leachant was found to exhibit 118 counts per second. 10 cm^3 of the simulated waste prepared above exhibited 517 counts per second at this time.

The total leachant therefore contained

$$\frac{118}{517} \times \frac{1.329}{1000} \times 300 = 0.0909 \text{ g of caesium}$$

The percentage of caesium leached at this time is

$$\frac{0.0909}{0.6799} \times 100 = 13.4$$

APPENDIX 3

The tables which follow give typical results of the leaching characteristics of the products studied. In the experiments reported in Tables 11, 12, 13 and 14 duplicate specimens of each product were subjected to leaching tests to establish the reproducibility of the test method. The 'percentage leached' figure reported in the tables was within ± 1.7% of the duplicate specimen. Reproducibility was therefore regarded as satisfactory and in subsequent tests only single specimens were studied.

The method of calculating results is illustrated in Appendix 2 paragraph A.11.

APPENDIX 3

TABLE 11

PRODUCT

OPC CONTAINING 1M CsCl

$\frac{Wa}{C} = 0.5$

SPECIMEN CONTAINS 0.146 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	517	520	518	514	
10 cm^3 LEACHATE c.p.s.	78.5	179	186	184	
g Cs IN LEACHATE	0.0606	0.1375	0.1432	0.1431	
% LEACHED	41.5	94.2	98.1	98.0	

PRODUCT

OPC CONTAINING 1M CsCl

$\frac{Wa}{C} = 0.4$

SPECIMEN CONTAINS 0.178 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	517	520	518	514	
10 cm^3 LEACHATE c.p.s.	82.6	182	208	205	
g Cs IN LEACHATE	0.0637	0.1398	0.1606	0.1594	
% LEACHED	35.8	78.3	93.3	89.6	

PRODUCT

OPC CONTAINING 1M CsCl

$\frac{Wa}{C} = 0.33$

SPECIMEN CONTAINS 0.231 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	517	520	518	514	
10 cm^3 LEACHATE c.p.s.	68.8	180	227	228	
g Cs IN LEACHATE	0.0531	0.1383	0.1751	0.1773	
% LEACHED	23.0	59.9	75.8	76.8	

APPENDIX 3

TABLE 12

PRODUCT
POZZOLANIC CEMENT
CONTAINING 1M CsCl
$\frac{Wa}{C} = 0.95$

SPECIMEN CONTAINS 0.139 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1908	1890	1894	1880	
10 cm^3 LEACHATE c.p.s.	428	570	606	601	
g Cs IN LEACHATE	0.0895	0.1202	0.1276	0.1265	
% LEACHED	64.4	86.8	91.8	91.0	

PRODUCT
POZZOLANIC CEMENT
CONTAINING 1M CsCl
$\frac{Wa}{C} = 0.7$

SPECIMEN CONTAINS 0.259 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1908	1890	1894	1880	
10 cm^3 LEACHATE c.p.s.	659	981	1054	1056	
g Cs IN LEACHATE	0.1378	0.2069	0.2219	0.2240	
% LEACHED	53.2	79.9	85.7	86.5	

PRODUCT
POZZOLANIC CEMENT
CONTAINING 1M CsCl
$\frac{Wa}{C} = 0.6$

SPECIMEN CONTAINS 0.299 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1908	1890	1894	1880	
10 cm^3 LEACHATE c.p.s.	731	1084	1166	1172	
g Cs IN LEACHATE	0.1528	0.2287	0.2455	0.2485	
% LEACHED	51.1	76.5	82.1	83.1	

PRODUCT
POZZOLANIC CEMENT
CONTAINING 1M CsCl
$\frac{Wa}{C} = 0.5$

SPECIMEN CONTAINS 0.356 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1530	1530	1525	1520	
10 cm^3 LEACHATE c.p.s.	455	899	1068	1065	
g Cs IN LEACHATE	0.1185	0.2342	0.2795	0.2792	
% LEACHED	33.3	65.8	78.5	78.5	

APPENDIX 3

TABLE 13

PRODUCT
COPOLYMER 3 CONTAINING POZZOLANIC
CEMENT AND 1M CsCl
$\frac{Co}{C} = 0.2 \quad \frac{Wa}{C} = 0.5$

SPECIMEN CONTAINS 0.223 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1530	1530	1525	1520	
10 cm^3 LEACHATE c.p.s.	466	783	843	846	
g Cs IN LEACHATE	0.1215	0.2041	0.2205	0.2221	
% LEACHED	54.5	91.6	98.9	99.6	

APPENDIX 3

TABLE 14

PRODUCT
COPOLYMER 6
CONTAINING 1M CsCl

$\frac{Wa}{C_o} = 0.5$

SPECIMEN CONTAINS 0.222 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1525	1520	1520	1518	
10 cm^3 LEACHATE c.p.s.	125	407	475	482	
g Cs IN LEACHATE	0.0328	0.1068	0.1245	0.1267	
% LEACHED	14.8	48.1	56.1	57.1	

PRODUCT
COPOLYMER 6 CONTAINING
0.2M CsCl

$\frac{Wa}{C_o} = 0.5$

SPECIMEN CONTAINS 0.044 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1525	1520	1520	1518	
10 cm^3 LEACHATE c.p.s.	7	12	13	14	
g Cs IN LEACHATE	0.0016	0.0031	0.0033	0.0035	
% LEACHED	3.6	6.9	7.5	7.9	

APPENDIX 3

TABLE 15

PRODUCT
COPOLYMER 6 CONTAINING POZZOLANIC
CEMENT AND 1M CsCl
$\frac{Wa}{C} = 0.5$ $\frac{Co}{C} = 0.6$ $\frac{Wa}{Co} = 0.83$

SPECIMEN CONTAINS 0.239 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1518	1512	1513	1501	
10 cm^3 LEACHATE c.p.s.	137	439	504	503	
g Cs IN LEACHATE	0.0361	0.1159	0.1329	0.1338	
% LEACHED	15.1	48.5	55.6	56.0	

APPENDIX 3

TABLE 1b

PRODUCT
COPOLYMER 8 ALONE
CONTAINING 1M CsCl
$\frac{Wa}{Co} = 3$

SPECIMEN CONTAINS 0.137 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.25	0.5	1	2	3
STANDARD c.p.s.	3759	3759	3768	3760	3751
10 cm^3 LEACHATE c.p.s.	279	591	1146	1268	1271
g Cs IN LEACHATE	0.0296	0.0627	0.1213	0.1345	0.1352
% LEACHED	21.6	45.7	88.4	98.0	98.5

PRODUCT
COPOLYMER 8 ALONE
CONTAINING 1M CsCl
$\frac{Wa}{Co} = 3.8$

SPECIMEN CONTAINS 0.159 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.25	0.5	1	2	3
STANDARD c.p.s.	3759	3759	3768	3760	3751
10 cm^3 LEACHATE c.p.s.	391	914	1433	1506	1496
g Cs IN LEACHATE	0.0415	0.0970	0.1517	0.1597	0.1591
% LEACHED	26.1	61.0	95.4	100.5	100

PRODUCT
COPOLYMER 8 ALONE
CONTAINING 1M CsCl
$\frac{Wa}{Co} = 2$

SPECIMEN CONTAINS 0.146 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.25	1	2	3	4
STANDARD c.p.s.	3759	3768	3760	3751	3755
10 cm^3 LEACHATE c.p.s.	234	662	963	1164	1375
g Cs IN LEACHATE	0.0249	0.0701	0.1022	0.1238	0.1460
% LEACHED	17.1	48.0	70.0	84.8	100

APPENDIX 3

TABLE 17

PRODUCT
COPOLYMER 8 CONTAINING OPC
AND 1M CsCl
$\frac{Wa}{Co} = 0.83 \quad \frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.159 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	1	2	3	4	
STANDARD c.p.s.	3581	3585	3565	3560	
10 cm^3 LEACHATE c.p.s.	729	873	963	978	
g Cs IN LEACHATE	0.0812	0.0971	0.1078	0.1095	
% LEACHED	51.1	61.1	67.8	68.9	

APPENDIX 3

TABLE 18

10 cm^3 of 0.2M CsCl plus 1 cm^3 of 0.2M $NiSO_4$

STANDARD 0.02M CsCl = 478 cps

cm^3 0.2M $K_4[Fe(CN)_6]$	0.1	0.25	0.5	0.75	1.00
SUPERNATANT cps	439	407	413	356	312
DECONTAMINATION FACTOR	90.8	91.5	91.4	92.5	93.5

10 cm^3 of 0.2M CsCl plus 1 cm^3 of 0.2M $K_4[Fe(CN)_6]$

STANDARD 0.02M CsCl = 478 cps

cm^3 0.2M $NiSO_4$	0.2	0.3	0.5	0.75	1.0
SUPERNATANT cps	417	360	400	390	302
DECONTAMINATION FACTOR	91.3	92.5	91.6	91.8	93.7

APPENDIX 3

TABLE 19.

PRODUCT
COPOLYMER B CONTAINING OPC,
1M CsCl AND PRETREATMENT
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.218 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	4
STANDARD c.p.s.	3590	3581	3585	3565	3560
10 cm^3 LEACHATE c.p.s.	412	682	829	884	883
g Cs IN LEACHATE	0.0458	0.076	0.0922	0.0989	0.0989
% LEACHED	21.0	35.0	42.3	45.4	45.4

PRODUCT
COPOLYMER B CONTAINING POZZOLANIC
CEMENT, 1M CsCl AND PRETREATMENT
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.205 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	4
STANDARD c.p.s.	3590	3581	3585	3565	3560
10 cm^3 LEACHATE c.p.s.	88.2	226	346	401	423
g Cs IN LEACHATE	0.0098	0.0252	0.0385	0.0449	0.0474
% LEACHED	4.8	12.3	18.8	21.9	23.1

TABLE 20

PRODUCT
COPOLYMER 8 CONTAINING OPC
AND 1M $SrCl_2$
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.353 gSr

LEACHATE VOLUME 300 cm^3
STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	2420	2420	2427	2407	
10 cm^3 LEACHATE c.p.s.	78.2	172	248	294	
g Sr IN LEACHATE	0.0085	0.0187	0.0269	0.0321	
% LEACHED	2.4	5.3	7.6	9.1	

PRODUCT
COPOLYMER 8 CONTAINING POZZOLANIC
CEMENT AND 1M $SrCl_2$
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.337 gSr

LEACHATE VOLUME 300 cm^3
STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	2420	2420	2427	2407	
10 cm^3 LEACHATE c.p.s.	174	285	357	383	
g Sr IN LEACHATE	0.0189	0.0310	0.0387	0.0418	
% LEACHED	5.9	9.2	11.5	12.4	

TABLE 21

PRODUCT
COPOLYMER 8 CONTAINING OPC,
1M $SrCl_2$ AND PRETREATMENT
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.287 gSr

LEACHATE VOLUME 300 cm^3
STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	2420	2420	2427	2407	
10 cm^3 LEACHATE c.p.s.	63.5	145	156	157	
g Sr IN LEACHATE	0.0069	0.0158	0.0169	0.0172	
% LEACHED	2.4	5.5	5.9	6.0	

PRODUCT
COPOLYMER 8 CONTAINING POZZOLANIC
CEMENT, 1M $SrCl_2$ AND PRETREATMENT
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.323 gSr

LEACHATE VOLUME 300 cm^3
STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	2420	2420	2427	2407	
10 cm^3 LEACHATE c.p.s.	100	187	188	189	
g Sr IN LEACHATE	0.0109	0.0203	0.0203	0.0207	
% LEACHED	3.4	6.3	6.3	6.4	

APPENDIX 3

TABLE 22

PRODUCT
COPOLYMER 8 CONTAINING OPC,
1M CsCl AND PRETREATMENT.
AFTER IRRADIATION.
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.208 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	3200	3180	3180	3184	
10 cm^3 LEACHATE c.p.s.	272	582	759	814	
g Cs IN LEACHATE	0.0339	0.0730	0.0952	0.1019	
% LEACHED	16.3	35.1	45.8	49.0	

PRODUCT
COPOLYMER 8 CONTAINING POZZOLANIC
CEMENT, 1M CsCl AND PRETREATMENT.
AFTER IRRADIATION.
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.296 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	3200	3180	3180	3184	
10 cm^3 LEACHATE c.p.s.	114	321	486	567	
g Cs IN LEACHATE	0.0142	0.0402	0.0609	0.0710	
% LEACHED	4.8	13.6	20.6	24.0	

PRODUCT
COPOLYMER 8 CONTAINING OPC,
1 M $SrCl_2$ AND PRETREATMENT.
AFTER IRRADIATION
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.265 gSr

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	4
STANDARD c.p.s.	1820	1802	1800	1705	1790
10 cm^3 LEACHATE c.p.s.	32.5	72.6	88.3	87.5	92
g Sr IN LEACHATE	0.0047	0.0106	0.0129	0.0129	0.0135
% LEACHED	1.8	4.0	4.9	4.9	5.1

PRODUCT
COPOLYMER 8 CONTAINING POZZOLANIC
CEMENT, 1M $SrCl_2$ AND
PRETREATMENT. AFTER IRRADIATION
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.245 gSr

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	4
STANDARD c.p.s.	1820	1802	1800	1785	1790
10 cm^3 LEACHATE c.p.s.	24.9	61.7	73.9	73.3	74.9
g Sr IN LEACHATE	0.0036	0.0090	0.0108	0.0108	0.0110
% LEACHED	1.5	3.7	4.4	4.4	4.5

TABLE 23

PRODUCT
COPOLYMER 9 CONTAINING OPC AND
1M CsCl
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.219 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	4
STANDARD c.p.s.	3281	3271	3200	3228	3200
10 cm^3 LEACHATE c.p.s.	645	1094	1196	1298	1265
g Cs IN LEACHATE	0.0784	0.1334	0.1491	0.1603	0.1576
% LEACHED	35.8	60.9	68.1	73.2	72.0

PRODUCT
COPOLYMER 9 CONTAINING POZZOLANIC
CEMENT AND 1M CsCl
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.247 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	4
STANDARD c.p.s.	3281	3271	3200	3228	3200
10 cm^3 LEACHATE c.p.s.	880	1511	1629	1755	1740
g Cs IN LEACHATE	0.1069	0.1842	0.2030	0.2168	0.2169
% LEACHED	43.3	74.6	82.2	87.8	87.8

TABLE 24

PRODUCT
COPOLYMER 9 CONTAINING OPC,
1M CsCl AND PRETREATMENT
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.299 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	4
STANDARD c.p.s.	3281	3271	3200	3228	3200
10 cm^3 LEACHATE c.p.s.	531	853	1010	1079	1103
g Cs IN LEACHATE	0.0645	0.1040	0.1259	0.1333	0.1375
% LEACHED	21.6	34.8	42.1	44.6	46.0

PRODUCT
COPOLYMER 9 CONTAINING POZZOLANIC
CEMENT, 1M CsCl AND PRETREATMENT
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.321 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	4
STANDARD c.p.s.	3281	3271	3200	3228	3200
10 cm^3 LEACHATE c.p.s.	805	1329	1406	1428	1480
g Cs IN LEACHATE	0.0979	0.1621	0.1752	0.1765	0.1845
% LEACHED	30.5	50.5	54.6	55.0	57.5

TABLE 25

PRODUCT
COPOLYMER 9 CONTAINING OPC,
1M $SrCl_2$
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.235 gSr

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	3	4	
STANDARD c.p.s.	1705	1700	1685	1692	
10 cm^3 LEACHATE c.p.s.	30.5	59.5	76.3	83.0	
g Sr IN LEACHATE	0.0047	0.0092	0.0119	0.0129	
% LEACHED	2.0	3.9	5.1	5.5	

PRODUCT
COPOLYMER 9 CONTAINING POZZOLANIC
CEMENT, 1M $SrCl_2$
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.266 gSr

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	3	4	
STANDARD c.p.s.	1705	1700	1685	1692	
10 cm^3 LEACHATE c.p.s.	34.4	78.9	110	109	
g Sr IN LEACHATE	0.0053	0.0122	0.0173	0.0170	
% LEACHED	2.0	4.6	6.5	6.4	

TABLE 26

PRODUCT
COPOLYMER 9 CONTAINING OPC,
1M $SrCl_2$ AND PRETREATMENT
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.227 gSr

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1605	1610	1585	1565	
10 cm^3 LEACHATE c.p.s.	38.5	38.6	44.0	52.9	
g Sr IN LEACHATE	0.0063	0.0063	0.0073	0.0089	
% LEACHED	2.8	2.8	3.2	3.9	

PRODUCT
COPOLYMER 9 CONTAINING POZZOLANIC
CEMENT, 1M $SrCl_2$ AND PRETREATMENT
$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.294 gSr

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1605	1610	1585	1565	
10 cm^3 LEACHATE c.p.s.	40.9	70.4	81.4	92.8	
g Sr IN LEACHATE	0.0067	0.0115	0.0135	0.0156	
% LEACHED	2.3	3.9	4.6	5.3	

TABLE **27**

PRODUCT
COPOLYMER 9 CONTAINING OPC,
1M CsCl. AFTER IRRADIATION

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.225 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.25	1	2	3	
STANDARD c.p.s.	2876	2800	2810	2785	
10 cm^3 LEACHATE c.p.s.	513	971	1135	1230	
g Cs IN LEACHATE	0.0711	0.1383	0.1611	0.1761	
% LEACHED	31.6	61.5	71.6	78.3	

PRODUCT
COPOLYMER 9 CONTAINING OPC,
1M $SrCl_2$
AFTER IRRADIATION

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.315 gSr

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1535	1500	1485	1470	
10 cm^3 LEACHATE c.p.s.	36.8	52.5	67.2	70.5	
g Sr IN LEACHATE	0.0063	0.0092	0.0119	0.0126	
% LEACHED	2.0	2.9	3.8	4.0	

PRODUCT
COPOLYMER 9 CONTAINING POZZOLANIC
CEMENT AND 1M CsCl
AFTER IRRADIATION

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.272 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.25	1	2	3	4
STANDARD c.p.s.	2876	2800	2810	2785	2790
10 cm^3 LEACHATE c.p.s.	1059	1434	1550	1557	1560
9 Cs IN LEACHATE	0.1468	0.2042	0.2200	0.2230	0.2230
% LEACHED	54.0	75.1	80.9	82.0	82.0

PRODUCT
COPOLYMER 9 CONTAINING POZZOLANIC
CEMENT, 1M $SrCl_2$
AFTER IRRADIATION

$\frac{Wa}{Co} = 0.83$ $\frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.333 gSr

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M $SrCl_2$

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1535	1500	1485	1470	
10 cm^3 LEACHATE c.p.s.	39.1	58.7	76.8	80.0	
g Sr IN LEACHATE	0.0067	0.0103	0.0136	0.0143	
% LEACHED	2.0	3.1	4.1	4.3	

APPENDIX 3

TABLE 28

PRODUCT
COPOLYMER 11 CONTAINING
POZZOLANIC CEMENT AND 1M CsCl
$\frac{Wa}{Co} = 0.83 \quad \frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.231 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.125	1	2	3	
STANDARD c.p.s.	1750	1700	1710	1680	
10 cm^3 LEACHATE c.p.s.	624	638	644	623	
g Cs IN LEACHATE	0.1422	0.1497	0.1501	0.1478	
% LEACHED	61.6	64.8	65.1	64.0	

PRODUCT
COPOLYMER 11 CONTAINING
POZZOLANIC CEMENT, 1M CsCl
AND PRETREATMENT
$\frac{Wa}{Co} = 0.83 \quad \frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.219 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.25	1	2	3	
STANDARD c.p.s.	1750	1700	1710	1680	
10 cm^3 LEACHATE c.p.s.	216	542	562	563	
g Cs IN LEACHATE	0.0492	0.1272	0.1312	0.1336	
% LEACHED	22.5	58.1	59.9	61.0	

PRODUCT
COPOLYMER 11 CONTAINING
OPC AND 1M CsCl
$\frac{Wa}{Co} = 0.83 \quad \frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.232 gCs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.25	1	2	3	
STANDARD c.p.s.	1750	1700	1710	1680	
10 cm^3 LEACHATE c.p.s.	987	969	995	982	
g Cs IN LEACHATE	0.2250	0.2273	0.2322	0.2331	
% LEACHED	97.0	98.0	100.1	100.5	

PRODUCT
COPOLYMER 11 CONTAINING OPC,
1M CsCl AND PRETREATMENT.
$\frac{Wa}{Co} = 0.83 \quad \frac{Co}{C} = 0.6$

SPECIMEN CONTAINS 0.277g Cs

LEACHATE VOLUME 300 cm^3

STANDARD 10 cm^3 of 0.01M CsCl

TIME (DAYS)	0.25	1	2	3	
STANDARD c.p.s.	1750	1700	1710	1680	
10 cm^3 LEACHATE c.p.s.	263	627	779	812	
g Cs IN LEACHATE	0.0601	0.1471	0.1816	0.1927	
% LEACHED	26.5	64.8	80.0	84.9	

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