POLYMER IMPREGNATION OF CONCRETE

AS A MEANS OF IMPROVING CORROSION RESISTANCE

by

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CHAPTER 1

1. GENERAL INTRODUCTION

1.1 THE CORROSION OF CONCRETE SEWER PIPES: PROBLEM IDENTIFICATION

1.1.1 Introduction

The service life of concrete in particularly extreme bacteriological environments has long been a problem that has been facing engineers and concrete materials experts. This is particularly relevant for the case of concrete sewer pipes, the useful life of which is critically limited by corrosion due primarily, and ultimately, to sulphide attack.

Sulphides are formed from the sewage sulphates, by bacteria in the slime layers on the walls of the pipe. These diffuse, firstly into the liquid, and then into the sewer atmosphere as hydrogen sulphide, which is then in turn oxidised to sulphuric acid. Hydrogen sulphide gas is well known for its characteristic "rotten eggs" odour, but more important although less known, for its extreme toxicity.(1) The maximum safe concentration in air is only twice that of hydrogen cyanide. It also has the dangerous side effect that the ability to sense it by smell is quickly lost(2) after first encountering the gas, and deaths have occurred in sewers that can be both directly and indirectly attributed to hydrogen sulphide poisoning.

The corrosion discussed in this thesis refers primarily to that caused by this bacteriologically created sulphuric acid attack in the space above the liquid, as opposed to sub-liquid level corrosion due to aggressive chemicals, more commonly associated with industrial effluents. This is all discussed more fully in later sections.

1.1.2 Effects of Hydrogen Sulphide Based Corrosion on Sewers

The results of sulphuric acid corrosion is manifested in sewer pipes in various ways.

(a) A sewer pipe or manhole which has been corroded to such an extent that it has to be replaced can be regarded as a loss of a capital asset.(3) To replace an existing and

operating sewer is always expensive because (i) the flow cannot be stopped and must therefore be diverted by means of mechanical pumping on a continuous basis, and (ii) costs for excavation, pipelaying, materials and reinstatement will, almost certainly, have increased substantially since the pipe was installed. New services, roads and structures may also have been constructed in the vicinity of the sewer in the period between initial construction and the relaying of the pipeline.

(b) The loss of load bearing capacity due to material loss or deterioration in the pipe structure as a result of corrosion often causes the collapse of sections of pipe. Frequently in the event of sudden collapse, the broken pipe pieces cause blockages in the pipeline and the failure of the pipeline is quickly noticed.(3) Occasionally, however, the pipe deteriorates gradually, with the result that soil may be washed into the sewer from above, sometimes leading to the formation of a large cavity in the soil above the pipe, with the eventual collapse of the ground surface and surrounding roads, sidewalks or structures.

(c) A typical example of severe corrosion of concrete structures in the local sewerage system can be seen in the harbour residential area of Hout Bay, near Cape Town. This reticulation system has been in operation for some 19 years and carries purely domestic sewage. The system consists of a series of interconnected septic tanks and concrete manholes, and the severity of the corrosion on these structures is graphically illustrated in plates 1.1 to 1.5.

The typical results of corrosion such as the deterioration and eventual disappearance of concrete, or mortar, are clearly evident in plates 1.1, 1.2 and 1,4, as well as expansion of mortar in the brick structure, plate 1.5 and (but less clearly) plate 1.1. The mortar material, between the brickwork, after such corrosion, is of a soft mushy or flaky nature of the consistency of wet cake or fresh cement paste, and has no strength at all. This can be seen in plates 1.1, 1.2 and is very easily removed or dislodged, as can be seen in the spade in plate 1.3. Often, with the removal of this scum layer, for example by hydraulic action or gravity, the underlying aggregate and indeed steel reinforcing of concrete structures, is sometimes exposed - plate 1.4.

It has been estimated that the replacement of only the manholes and roof slabs of the septic tanks of this system will cost approximately twice the amount of the original full construction costs!

These and other types of situations are obviously very undesirable as severe disruption is caused and rectification of the situation is costly and time consuming.

A far more preferable situation would be to use, in the first place, a pipe which is designed to have extremely high corrosion resistance so that it does not need any maintenance, repair or replacement during its design life but which is still economically attractive. This study on deeply impregnated polyurethane concrete is aimed at contributing to this field with a view to at least extending the useful life of concrete sewer pipes.

To this end the thesis reviews current solutions to the concrete sewer corrosion problem including the physical and chemical treatment of the sewage and the use of sacrificial layers in pipes; alternative or better materials selection; PVC and vitrified pipes; and composite "pipes within pipes". Coatings and linings are also examined and their deficiencies in terms of cost and serviceability exposed. The need for a polymer coating which is impregnated to form an integral part of the pipe wall is developed and the specific effectiveness of this, using a moisture curing polyurethane co-polymer, is discussed.

In addition the thesis deals with improvements of strength, degree of penetration, and corrosion resistance as necessary and successful adjuncts prior to the development of the use of these composite materials on a commercial scale. Future tests still to be undertaken are also discussed together with recommendations of how present techniques can be optimised, and of alternative polymer materials.

1.2 BIOCHEMICAL BASIS OF SEWER CORROSION

1.2.1 Sources of Sulphides in Sewers

In domestic wastewaters sulphur compounds are derived

from human metabolism of foodstuffs and from household detergents.(2) In addition there are naturally occurring sulphates as well as those added to water as flocculants during the water treatment process such as aluminium, ferrous or ferric sulphates.

Certain industries such as abattoirs, tanneries and oil refineries may discharge relatively larger amounts of sulphides into the sewers. It is, however, possible to implement some control over these discharges.

However, the commonest source of sulphides is biological activity in the sewer itself(2) and the principal sulphur compound in wastewaters is the sulphate ion. Provided there are dissolved oxygen and/or nitrates present, little change in sulphur compounds will take place. When organic material is present and both dissolved oxygen and nitrates are absent, then bacteria of the species Desulphovibrio desulphuricans (or Desulphatomaculum desulphuricans) and others will reduce the sulphate to sulphide, using the oxygen made available to oxidise organic matter:

$$SO_4^{=} + 2C + 2H_2O \longrightarrow 2HCO_3^{-} + H_2S$$

For sulphate to be reduced to sulphide, it is necessary that the medium be completely devoid of free oxygen(1) and other active oxidising agents such as nitrates(2, 4) and chlorine. The stream of wastewater in a partially-filled sewer is not completely anaerobic because it is exposed to the sewer atmosphere. Oxygen absorbed at the surface of the stream generally reacts quite rapidly, and in large sewers its concentration may be quite low, say 1 mg/litre, yet enough is present to prevent sulphate reduction in the stream.

All sewers have a layer of slime on sections of the walls which are submerged.(1, 4) If dissolved oxygen is present in the stream, it diffuses rapidly into the slime layer, but the aerobic bacteria will use it so rapidly that the oxygen penetration is only about 0,25 mm. Further in than this, the slime layer is anaerobic and it is here where the reduction of sulphate to sulphide takes place. The sulphide generation layer is also about 0,25 mm thick. At deeper levels the slime

layer is largely inactive because of a lack of nutrient supply. As long as the surface of the slime layer is aerobic, sulphide diffusing out of the anaerobic zone will be oxidised (see fig. 1.1). If the dissolved oxygen content of the wastewater drops to less than about 1 mg/litre then incomplete oxidation of the sulphide may occur. Anaerobic conditions are however needed before all the sulphide produced can pass into the stream. Figure 1.2 illustrates this.

The rate at which sulphide can be produced by a slime layer is generally determined by the rate that the reactants, i.e. sulphate and organic nutrients, can reach the sulphate reducing bacteria. When the slime layer contains a maximum population of these bacteria, and when their metabolic rate is high because of favourable temperature and other conditions, the reactants do not have so far to diffuse and the rate of sulphide generation reaches a maximum.(2) By contrast, if the population is sparse or the metabolic rate is lower for some reason, the reactants must diffuse further; as a result, the sulphide generation rate is slower.

The effect of temperature on the rate of sulphide production is complex.(2) The increased metabolic rate of the bacteria reduces the distance that the reactants need to diffuse, and at the same time the diffusion coefficient increases. It appears that the overall effect is about 7% increase per $1^{o}C$ rise in temperature.

The absorption of oxygen into a wastewater stream can take place at the surface of the stream and at points of high turbulence. At the surface of the stream the rate of oxygen transfer is proportional to the oxygen deficit, i.e. the difference between the actual concentration of oxygen in the wastewater stream and the saturated concentration of oxygen in the wastewater stream at the same conditions of temperature and pressure, also the relative difference in oxygen concentrations of the air and the stream. The rate of transfer will be affected by the presence of any surface active films caused by fats, oils and detergents.(2, 5) In addition to surface aeration much oxygen can be dissolved in the wastewater at drops and high velocity junctions, i.e. places of high turbulence.

Sulphides may be lost in two ways:(5)

(a) By reaction of sulphide with oxygen

Under the conditions usually found in partly filled sewers, a major part of the sulphide passing from the slime layer into the stream is subsequently destroyed by oxidation. This reaction may be either chemical or biochemical. In wastewaters that are biologically inactive because of toxic materials, the sulphide is oxidised chemically to sulphate by complex reactions. The reaction rates vary with sulphide and dissolved oxygen concentrations.

The biological reaction is more rapid with thiosulphate being formed:

$$2HS^- + 2O_2 \rightarrow S_2O_3^= + H_2O$$

The rate of sulphide oxidation in this reaction varies with the biological activity of the wastewater, e.g. the rate may be 1 mg/litre/hr in fresh wastewater, or 10 mg/litre/hr in stale sewage. The rate is independent of dissolved oxygen and sulphide concentrations provided these are not less than 1 mg/litre.

(b) By escape to the atmosphere

For sulphide to enter the atmosphere it must be in the form of a gas. The relevant sulphides here exist in two forms:

(i) Insoluble metallic sulphides - mainly iron sulphide except where industrial wastes include zinc, copper, lead and cadmium.

(ii) Dissolved sulphides, being a mixture of the H_2S molecule, the HS^- ion and a trace of the $S^=$ ion. The ionisation reactions are $H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2H^+ + S^=$.

There is always a balance between the proportions of these dissolved sulphide forms,(1) the proportions depending on the temperature of the sewage, the pH, and the presence of metallic ions. The proportion of molecular H_2S is very dependent on the pH, being 50% at pH = 7 and 90% at pH = 6. Thus the sudden discharge of any acid wastes will result in a release of a high concentration of H_2S gas. At pH values

above 8 nearly all the sulphide is held in the form of the HS^- ion, and cannot be lost to the atmosphere. See fig. 1.3.

1.2.2 Bacterial Activity

It has been proved that certain species of bacteria are responsible for the oxidisation of H_2S gas in the sewer air to H_2SO_4 on the crowns and sides of sewer pipes.(4)

Nature of the Bacteria

The bacteria which effect the oxidation of sulphur or sulphur compounds to sulphuric acid are autotrophic,(4, 5) i.e. they require CO_2 as a source of carbon, NH_3 as a source of nitrogen, and various mineral salts such as magnesium, iron, potassium and manganese. It appears that these salts are readily available from solution of the concrete salts. Near the sewage surface, these and other salts are drawn up from the sewage in the concrete walls by capillary action.

The energy requirements for bacterial metabolism are derived from oxidation of sulphur or nitrogen compounds, using atmospheric oxygen as the acceptor ion.(6) For example, in the breakdown of the H_3COOH molecule, the hydrogen bonds are broken by the bacterium to form CO_2 molecules and H^+ ions. This breakdown releases energy which is used by the bacterium in its metabolism, and the H^+ ions are attached to O_2, NO_3^-, NO_2^- or S ions, in that order of preference. Thus it can be seen that H_2S will be formed only if there is no oxygen present, as happens when H_2S is produced in anaerobic sewage, provided no nitrates are available for use as acceptor ions.

The organisms significantly active in the advanced highly acidic high-rate stages of concrete corrosion in sewers are the species Thiobacillus concretivorus.(4, 5) The pH range in which this species is active is 1 to 6, and before this species can proliferate, the pH of the concrete surface must first be lowered to approximately 6. It has been suggested that this reduction in pH is brought about as follows:(4)

The pH of freshly hardened concrete is determined by the $Ca(OH)_2$ liberated and lies between 11 and 12,5. Due to carbonation by CO_2 in the atmosphere, the exposed surface becomes converted to calcium carbonate and the pH drops to 10. In the

presence of moisture, which is usually the case in sewers, some of the carbonate is dissolved as bicarbonate (HCO_3^-) and an equilibrium is set up between the calcium carbonate ($CaCO_3$), the saturated bicarbonate solution and the CO_2 in the atmosphere. Depending on the CO_2 concentration, the pH drops further (to pH 8,4 for normal 0,03% CO_2 concentration in air, and to pH 7,4 for sewer air containing 1% CO_2 concentration). The pH may drop even further if H_2S is dissolved on the moist surface. At this point the bacteria Thio. concretivorus (and Thio. thiooxidans) become established and proceed to produce sulphuric acid under favourable conditions; the pH can then drop to as low as 1.

It is also thought that bacteria species Thio. thioparus(4) and sulphur oxidising fungi Aspergillus niger, Penicillium cyclopium and others, which are less acid tolerant, may also assist in reducing the pH by way of limited acid production before Thio. concretivorus takes over.

Growth Requirements

For the chain of bacteriological processes to commence and continue to the final stage, and for the final stage to remain active, certain environmental conditions must be satisfied:(5)

(a) Source of Infection:

There must be a primary source of infection of the concrete surface with the necessary bacteria. It is known that the organisms actively involved in the corrosion process are commonly found in water supplies, soil, and in stormwater (from running over and through soils thereby picking up the various organisms). These organisms then find their way up the walls of the concrete pipe presumably by capillary action, splashing, or by simply being carried up in moisture globules evaporating from the surface of the sewage.

(b) Moisture on the Concrete Surface:

The various bacteria cannot proliferate if the concrete surface is insufficiently moist. This occurs when the relative humidity of the sewer air falls below 85%, at which point the evaporation of water from the acid solution on the surface is so great that the high acid concentration kills off the acid

producing bacteria, the remaining acid being quickly neutralised by the basic cement products.

The moisture on the concrete surface arises from evaporation from the sewage and then condensation on the normally cold walls, through capillary action at the sewage surface, and sometimes, if the external ground water level is high enough above the pipe, by direct infiltration through the concrete walls of the pipe.

(c) Nutrient Supply to the Bacteria:

Important nutrients are

Sulphur	-	from H_2S in the sewer air
Nitrogen	-	from NH_3 gas or ammonium salts
Carbon	-	from CO_2 in the sewer air
Mineral salts	-	from the cement in the concrete and from the sewage water.

It should be noted that no corrosion occurs if H_2S is not present, also, the amount of acid produced is directly proportional to the Nitrogen and Phosphate content in the nutrient supply.

(d) Temperature:

The temperature at which acid production by the bacteria effectively starts is $\pm$ 15°C, rising to a maximum rate at $\pm$ 30°C. Outside of these temperatures, production decreases and may even cease. The normal sewage temperature of 25°C unfortunately fits well into the active temperature range.

1.2.3 The Mechanism of Corrosion

Introduction

The chemical corrosion of concrete sewer pipes results from the breaking down primarily of the cement paste and to a lesser extent aggregate by chemical action of the aggressive agents,(4) in this case sulphuric acid and sulphates. Attack by sulphates may result from the presence of sulphates in the sewage or from sulphates formed as products of sulphuric acid attack on the concrete.

Corrosion of sewer pipes made of cement-bonded materials is not uniform.(1) Lack of uniformity is due in part to the

air currents that control the rate of transfer of hydrogen sulphide to the pipe wall. The greatest corrosion is generally observed at the soffit of a manhole outlet because that is where there is the greatest shear between the air stream and the pipe material. Structures projecting into the air stream suffer more rapid corrosion than the pipe wall. Test specimens hung in a sewer may provide information on the relative corrodability of different materials, but they will not show how fast a pipe wall will corrode.

There is normally a flow of air down the sewer, but in addition, transverse currents are set up by temperature differences. The pipe wall is normally cooler than the water, especially in the summer when sulphide concentrations are at a maximum. The air that is cooled by the walls moves downwards, and slightly warmer air rises from the centre of the stream surface. As a result, the maximum rate of transfer of hydrogen sulphide to the pipe wall is at the crown (see fig. 1.4).

Uneven distribution of corrosion also results from the migration of acid-containing condensate down the pipe wall, particularly when there is a high rate of acid production. In the zone that is intermittently washed by the sewage, the pasty decomposition products are cleaned away. As a result, the pipe wall is laid bare to the attack of the acid when the water level is low. Deeper penetration may therefore be observed in this zone (see fig. 1.5).

Sulphuric Acid Attack

Sulphuric acid will attack both the aggregate and cement portions of concrete.(4)

(a) Aggregate

Silicious aggregates which are often used for normal concrete pipes are relatively unaffected by sulphuric acid and cannot therefore provide any neutralising basic material. Once the cement bonding matrix around the aggregate has been corroded away, the aggregate falls off, thereby exposing fresh concrete to attack (see section 1.3.3.5).

Calcareous aggregates such as limestone are attacked by the sulphuric acid although they do provide a larger chemically

active surface area and hence the rate of corrosion of the pipe is less than that for silicious aggregate pipes. The corrosion products formed are calcium and magnesium sulphates, which may further aid the general sulphate corrosion of the cement matrix.

(b) Hydrated Cement

Hydrated calcium silicates, aluminates and ferrites are broken down to form the various sulphates of calcium, aluminium and iron, together with amorphous silica in the case of calcium silicate hydrates, the principal hydration product of cement. Calcium hydroxide reacts with sulphuric acid to form gypsum ($Ca\ SO_4 . 2H_2O$). This in turn reacts with some of the hydrated calcium aluminates to form $C_3A . 3Ca\ SO_4 . 31H_2O$ or $C_3A . Ca\ SO_4 . 12H_2O$. Due to the large amount of water of crystallisation, the calcium sulphate and tri-calcium sulpho-aluminate have larger volumes than the substances from which they are formed, and this resultant increase in volume(4, 7) can cause expansion of the concrete accompanied by cracking and deterioration (see plates 1.2, 1.3, 1.5).

Sulphate Attack

As can be seen from the section above, the sulphate attack on concrete is a function of the tricalcium aluminate (C_3A) content of the cement. Certain sulphate resisting cements with low C_3A contents are available.(7, 8) These, however, only provide a certain amount of protection against sulphate, as opposed to sulphuric acid, attack, although they are not resistant to magnesium and ammonium sulphates.

The rate of sulphate attack increases with sulphate concentration,(7) up to 0,5% for magnesium sulphate ($MgSO_4$) and 1% for sodium sulphate (Na_2SO_4). A saturated solution of magnesium sulphate leads to serious deterioration of concrete, although with a low water/cement ratio this takes place only after 2 - 3 years. Alternate wetting and drying accelerates the rate of sulphate damage owing to an accumulation of crystallised salts in the pores of the concrete.

In designating cement compounds, a shortened notation is conventionally used where

$C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$ and $H = H_2O$

A summary of the relevant chemical reactions is given below.(5, 7)

(a) Sodium Sulphate with Calcium Hydroxide

$$Ca(OH)_2 + Na_2SO_4 \cdot 10H_2O \rightarrow CaSO_4 \cdot 2H_2O \text{ (Cryst.)} + 2NaOH + 8H_2O$$

(b) Sodium Sulphate with Calcium Aluminate Hydrate

$$2(3CaO \cdot Al_2O_3 \cdot 12H_2O) + 3(Na_2SO_4 \cdot 10H_2O) \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O \text{ (Cryst.)} + 2Al(OH)_3 + 6NaOH + 17H_2O$$

(c) Calcium Sulphate attacks only Calcium . Al. Hydrate, forming $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ (Cryst.)

(d) Magnesium Sulphate with Calcium Silicate Hydrate

$$MgSO_4 \cdot 7H_2O + 3CaO \cdot 2SiO_2 \text{ aq.} \rightarrow CaSO_4 \cdot 2H_2O \text{ (Cryst.)} + Mg(OH)_2 \text{ (ppt)} + SiO_2 \text{ (aq.)}$$

(e) Magnesium Sulphate also attacks Calcium Hydroxide

$$MgSO_4 \cdot 7H_2O + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O \text{ (Cryst.)} + Mg(OH)_2 + 5H_2O$$

1.3 ANTI-CORROSION MEASURES IN SEWER PIPES AND SEWERAGE SYSTEMS

1.3.1 Introduction

The structural deterioration of concrete sewer pipes due to corrosion in service is primarily a function of the pipe material and of the sewage itself. Modification of either or both these parameters can lead to reduced corrosion and a longer life for the system. The limiting factors in these two parameters appear to be, respectively, the cement matrix bonding material of the pipe and the presence of hydrogen sulphide generated in sewage and in the slime layers on the pipe walls, as mentioned in section 1.2. Hydrogen sulphide, on oxidation by the bacteria present above the water level in the sewer, yields sulphuric acid which attacks primarily the cement matrix. Efforts to inhibit, or at least retard the corrosion process are thus divided into two areas, (i) treatment of the sewage to prevent critical levels of sulphides developing, and (ii) improved pipe materials which have both an inherent higher resistance to corrosion as well as making it more difficult for bacteria to settle and proliferate on the pipe wall.

1.3.2 Sewage Treatment

Sewerage systems and sewage can be treated, with a view to preventing corrosion, by mechanical means or by the direct introduction of chemicals to the sewage.

1.3.2.1 Forced Ventilation

An essential environmental requirement for the proliferation of acid-producing bacteria is moisture on the surface of the pipe wall. If the relative humidity of the sewer atmosphere falls below 85%,(2, 5) the rate of evaporation of water from the acid on the walls of the pipe is such that the increased acid concentration tends to kill off the acid-producing bacteria (see section 1.2.2).

The walls of the pipe can be dried to this degree by means of mechanically induced forced air ventilation.(4, 5) The main drawbacks are, however, the high installation, running and maintenance costs, as well as increased problems with odours

that are blown out at manhole lids along the sewer line. This method is also generally only suitable for large diameter sewers where the air requirements are less than that for small diameter pipes, because of the smaller internal wall surface area to pipe volume ratios.

1.3.2.2. Injection of Air or Oxygen

Often, in the early stages of the operational life of sewerage pump stations, long retention periods can occur if the flow into the pump station is well below the design capacity. Such long retention periods cause a rapid depletion of dissolved oxygen levels and a severe build up of hydrogen sulphide gas,(3) resulting in corrosion of concrete structures in the pump station sump and at the outfall of the pressure main.

By injecting air into the pressure main,(2, 3, 4) the oxygen content of the sewage can be maintained at a sufficiently high level to prevent the evolution of hydrogen sulphide (i.e. in excess of approximately 1 mg/litre - see section 1.2). A more efficient dissolution of oxygen in the sewage can be achieved if the air is injected at the lowest point in the pressure main where the hydrostatic pressure is at its maximum.(2)

A more effective level of dissolved oxygen concentration can be obtained if pure oxygen is injected into the sewage. Wastewater is capable of carrying up to 20 mg/litre of dissolved oxygen if turbulence is avoided, whereas the injection of air as opposed to pure oxygen into the main will result in a residual level of oxygen of not more than 4 mg/litre (consistent with the elemental composition of the atmosphere).

This process is generally only suited to full pressure mains, but has the added advantage of bringing about a partial purifying treatment of the sewage because of the relatively high oxygen levels. The remarks on capital and running costs as mentioned in the section on forced ventilation above also apply.

1.3.2.3 Chemical Treatment of the Sewage

The addition of chemicals(2) to sewage can reduce hydrogen sulphide evolution and subsequent sulphuric acid production by either (i) killing off the sulphide-producing bacteria, or (ii) by limiting the very evolution of free hydrogen sulphide (H_2S)

gas.

Chemicals that have been used with varying degrees of success (1, 4, 6, 9) are calcium hypochlorite, zinc sulphate, sodium hydroxide, potassium permanganate and activated carbon. More successful results have been obtained with chlorine, lime, nitrates and hydrogen peroxide, the processes of which are more fully described below.(2, 9)

(a) Chlorine and Hypochlorite

Chlorination can be effected by the use of liquid or gaseous chlorine, as well as calcium and sodium hypochlorite. Chlorine reacts with sulphide, according to the reactions indicated below, and other organic sulphides to form sulphur and hence sulphate ions. The reaction with chlorine is immediate, whereas the reaction with injected air or oxygen is slower. Theoretically nine parts by weight of chlorine are required for one part of sulphide, but in practice about twelve parts by weight are required due to side reactions.

$$HS^- + Cl_2 \rightarrow S + H^+ + 2\ Cl^-$$

followed by

$$HS^- + 4\ Cl_2 + 4\ H_2O \rightarrow SO_4^{=} + 9\ H^+ + 8\ Cl^-$$

For maximum effectiveness the chlorine must be uniformly distributed in the sewage, preferably introduced just above an hydraulic pump or any point of high turbulence. If the sewer is long, rechlorination at points further down the line may be necessary as the chlorine is quickly consumed by the sulphides and other chemicals in the sewage.

(b) Lime

Slaked lime or calcium hydroxide may be added continuously to the sewage at a suitable point of turbulence or as a periodic bulk "shock" loading. By liming on a continuous basis, the pH of the sewage is increased to about 8,5 at which point the emission of hydrogen sulphide is virtually stopped since approximately 97% of the sulphide is present as the non-volatile HS^- ion(1, 2) (see fig. 1.3). The dosage of lime required is usually about 150 mg/litre. This treatment does not reduce the total amount of sulphide present but merely holds it in the liquid phase. Raising the pH to 8,5 appears to reduce the activity of the sulphate-reducing bacteria.

In shock dosing of a sewer, the pH is temporarily raised to about 11. The intention of this procedure is to neutralise or render inactive the slime layer and effectively arrest or seriously inhibit sulphide generation. This is only a temporary measure as generation can start within a few days and can be back to pre-treatment levels within a week. Higher pH values reached during shock dosing will generally have a more lasting effect, but the critical effects of cost effectiveness play a part, as well as the ability of the treatment works to handle the high pH sewage and limit its widespread use.

A disadvantage of using calcium hydroxide is the quantity of sand(3) (up to 15% by weight) commonly found in industrial lime. If lime is used on a continual basis, the effects of sand build up in the sewers and pump station sumps must be considered and is often limiting.

(c) Nitrates

As mentioned in section 1.2.2, sulphates will not be reduced if nitrates are present in the wastewater.(2, 4) The use of commercial nitrates is uneconomical, but if a cheap source of nitrates can be found, such as humus tank effluent, it may be well worth while leading this effluent back to a sewerage pump station.(2, 3) Pump stations are usually located at a level below that of treatment works outfalls, so that additional pumping will not be necessary. When the pump station is underloaded and excessive retention times occur in the pressure main, this additional flow will help to reduce the retention time, and by diluting the wastewater, will reduce its oxygen demand at the treatment works, as well as also reducing the total oxygen demand in the sewer.(2)

(d) Hydrogen Peroxide

Hydrogen peroxide dissolved in water in a 50% concentration can be used to oxidise hydrogen sulphide completely. The oxidation products vary depending on the pH of the sewage. In acid or neutral sewage, water and elemental sulphur are formed: (2, 6, 9)

$$H_2O_2 + H_2S \rightarrow S + 2\ H_2O$$

In alkaline sewage, water and sulphates are formed:

$$4\ H_2O_2 + H_2S \rightarrow SO_4^{=} + 4H_2O + 2\ H^+$$

In practice a ratio of 3 : 1 of hydrogen peroxide to sulphide is required in the first reaction to allow for side reactions, and a ratio of 6 : 1 in the second reaction.

Hydrogen peroxide mixed with the sewage has an advantage in that it does not produce any problematical by-products that may affect the subsequent treatment processes since it decomposes to form water and oxygen.(9) It also helps to reduce odour problems!

The practice of mixing hydrogen peroxide with sewage to reduce hydrogen sulphide evolution has been successfully employed in Texas, U.S.A.,(9) where severe corrosion of a 1050 mmø, 6 km long concrete sewer pipe has been effectively halted. Hydrogen peroxide treatment proved to be the cheapest solution in comparison with relaying of the sewer and sliplining as well as significantly reducing odour problems.

1.3.3 Improved Pipe Materials

1.3.3.1 Steel

If the pipe is completely full, and if the pH of the sewage is above 6,5, and the chloride content less than 500 mg/litre, little serious corrosion will occur. However, most sewers run less than full, typically half full, and a steel pipe will suffer both sulphuric acid corrosion and hydrogen sulphide corrosion if oxygen is present in the sewer atmosphere, producing bulky iron sulphide deposits. Corrosion due to oxidation under the water level is, however, small. If the steel pipe has 10 mm or thicker cement mortar lining, it will be protected(1) as long as the lining is not exposed to sufficient acid to destroy the protective lining.

The great variety of chemicals found in industrial wastewaters would appear to limit the beneficial effects of galvanising of steel pipes, although this method is very successfully used in buried galvanised steel water supply pipes, where the zinc coating provides adequate electrolytic protection under most groundwater conditions.(6)

A major advantage of steel pipes is that they need only to be manufactured with relatively thin walls (6 - 10 mm) as

opposed to concrete pipe walls (50 - 100 mm) and although of denser material, are therefore lighter in weight. Steel pipes can also be manufactured in lengths limited only by handling considerations, thereby greatly reducing installation time, effort and hence, ultimately, cost.(3)

1.3.3.2 Cast Iron

Cast iron pipes generally last longer than steel because the pipe wall is thicker(1) and the corrosion process slower. The corrosion of cast iron exposed to water commonly proceeds by "graphitization", in which the true iron crystals are dissolved, leaving a porous mass of carbides and silicides of iron.(1) The surface of iron often appears unaltered, thus giving a false impression of the true condition of the pipe. Like steel, cast iron gives good service when completely filled with wastewater at a pH of 6,5 or above, together with an absence of high chloride content.

Fabrication costs of cast iron pipes are understandably greater than those of steel or concrete pipes, particularly so in the larger diameters, and typically also require a thicker wall than steel to maintain the same structural strength and toughness.

1.3.3.3 Vitrified Clay

These pipes appear to be completely immune to sulphuric acid attack,(1, 2, 3) but suffer from several disadvantages, namely

(a) they cannot easily be manufactured in sizes greater than 450 mm diameter;

(b) clay pipes are generally twice as expensive as concrete pipes in the 300 - 450 mm sizes;

(c) clay pipes are more brittle than concrete pipes, are easily cracked or broken during transport and laying, and have a lower structural strength when load bearing capacity is considered, e.g. maximum 22 kN/m(10) as against 45 kN/m(11) for a class C concrete pipe;

(d) because of the limited structural strength, clay pipes are also not manufactured in lengths longer

than 1,5 m, leading to significantly increased laying costs;

(e) where sulphides are expected, the use of cement mortar joints is unsatisfactory,(1, 4) because the action of sulphuric acid on the cement causes expansion, which may break the socket joints and may even crack the pipe. A new development is the use of rubber ring joints which are substantially unaffected by sulphuric acid.

Another disadvantage of cement mortar caulked joints is that tree roots(3) can relatively easily penetrate cracks in the mortar and eventually cause a total blockage of the pipe in their search for water and nutrients, both of which are supplied abundantly by sewage. The use of rubber ring joints should dramatically reduce the occurrence of this type of problem.

1.3.3.4 Asbestos Cement

Owing to an 85% cement content, the alkalinity of asbestos cement pipes is higher than that of dolomitic aggregate pipe (see section 1.3.3.5) and this can therefore neutralise much of the sulphuric acid which normally causes corrosion.(12) Asbestos cement pipes have a high compaction value which is considered an important factor in reducing the rate of corrosion,(8, 12, 13) and the felted layer of magnesium silicate asbestos fibres remains in position after the cement has been corroded.(13) This matrix contains a gel of silica, and precipitated calcium sulphate, both of which interfere strongly with the diffusion of acid into the deeper layers of the asbestos cement pipe wall.

This tends to extend the service life in comparison with an equivalent size and strength concrete pipe, although generally being more expensive. They are manufactured in lengths up to 6 m and are easily cut on site to the desired length. If, however, the cut section has to be coupled to another pipe, the end of the pipe must be machined at a factory to fit the coupling joining the two pipes.

Asbestos cement pipes are also generally lighter in weight than concrete pipes, due to a thinner wall, although this may

again limit the service life of the pipe under corrosive conditions.(1)

1.3.3.5 Dolomitic Aggregate Concrete

Conventional concrete pipes are made with a siliceous aggregate which is relatively inert, so that the only neutralising material available is the cement.(14) Sulphuric acid attacks the cement binder around the large and small aggregate particles, and the aggregate eventually falls off, exposing a fresh and deeper section of pipe wall to the corrosion. Because of this, concrete sewer pipes are often made with large and small calcareous (dolomitic or limestone) aggregates(1, 2, 3, 8) which substantially prolong the service life of the pipe by providing additional alkalinity and hence enhanced neutralising ability.

Concrete pipes can also be made with aluminous cement and sulphate resisting cement, but these only impart resistance to sulphate attack, not sulphuric acid attack. Aluminous cement will also be attacked by caustic alkalis(7) if these are present in the sewage.

Concrete pipes are often constructed with a thicker pipe wall,(1, 3, 11) the object being to provide a sacrifical layer of concrete on the inner wall which will prolong the life of the pipe. In addition, being sacrificial, the layer is not taken into account as a load bearing structural element of the pipe. This understandably makes the pipe heavier and more expensive, and also reduces the internal diameter and hence the flow capacity.

1.3.3.6 Protective Coatings

Polymer and other non-corroding linings are available (1, 9, 15 - 18) and have been extensively used, but a problem exists in obtaining a satisfactory bond between the lining and the wall of the concrete pipe. In many circumstances where the pipe is laid below the water table, infiltration of water through the pipe walls under the external hydrostatic head lifts the lining off the concrete surface. In addition, pinholes and any damaged areas of the lining, however small, can cause the sulphuric acid to penetrate behind the lining and cause serious

corrosion of the pipe, leading to peeling off of the lining. A strong physical joint or bond is required to ensure that the lining will not be forced to separate from the concrete, and there is always the danger of damage to the lining during transport and laying and also by debris in the sewage, such as stones, logs of wood, bricks and scrap metal.(6) Damage can also be caused by cleaning equipment which is of necessity harsh and sharp.(1, 3)

A useful analogy here is to regard the polymer skin as being useful only so long as its integrity is maintained, i.e. the "plastic bag" concept. A plastic bag full of water, for example, will only continue to hold that water while there are no holes in it - once it is punctured it becomes effectively useless. A thin polymer skin lining a sewer pipe may be regarded in a similar light.

An extension of the pipe liner concept is that of a pipe within a pipe,(9, 3) where a corrosion-resistant pipe (e.g. PVC high density polyethylene) of sufficient wall thickness (10 - 20 mm) to support itself is drawn through a concrete pipe, the concrete pipe acting as the main structural portion of the pipe. This method of corrosion control is expensive as firstly, thickwalled PVC pipes are very costly, and secondly, the user is effectively paying for two pipes while only obtaining the benefit of the flow carrying capacity of one of them.

1.3.3.7 Impregnated Linings

A far more satisfactory type of lining promises to be where the protective coating is impregnated into the pores of the concrete pipe(16, 17) either at the time of manufacture of the pipe (Polymer Portland Cement Concrete - PCC - see section 2.3.1) or by impregnating an already cast and cured concrete pipe with a polymer or monomer (Polymer Impregnated Concrete - PIC - see section 2.3.3). This would imply that the polymer forms an integral part of the pipe wall and as such cannot be torn away or result in any spreading corrosion damage due to small local pinholes or scratches. Impregnation depths up to several centimetres are obtainable(16, 17) with monomer impregnations which are subsequently polymerised, and

also but more rarely with freshly polymerised polymer impregnation.(12, 19) This is fully discussed in section 2.6.

This thesis seeks to examine the feasibility of this latter technique, i.e. polymer impregnated concrete, as a means of strengthening sewer pipes and of overcoming the effects of the severe conditions which are present and which have been extensively discussed in this chapter. This is done initially as a laboratory scale investigation, but it is envisaged that data obtained in this way will be correlated with, and extended by, parallel studies with in service pilot systems in actual sewers.

The approach taken has been to examine the parameters which control the impregnation characteristics of polymer into the concrete. Chief among these are reportedly(17) (a) evacuation prior to soaking, (b) application of pressure during soaking, (c) drying temperature, (d) curing and impregnation time (i.e. "soaking"), as well as (e) viscosity and (f) polymer properties. At the same time it has been necessary to develop techniques for measuring impregnation depth, strength, porosity and durability.

Other areas which are considered worth examining but which have not been included in this thesis because of time considerations include the effects of sulphate attack, toughness measurements, long term corrosion tests, shear and adhesion and in-situ corrosion in sewer pipes.(24)

The polymer used for this study has been a moisture curing polyurethane co-polymer of the type used for factory floors as supplied by a commercial company. As will be seen in later chapters, this material is very effective in achieving the desired properties and fulfilling the necessary requirements. However it is not felt that this is necessarily the "ultimate" polymer material and future studies will almost certainly examine other possibilities, for example, poly methyl methacrylate (PMMA), if only to confirm the present work. Before the experimental techniques are discussed in detail, a review of the use of polymers in concrete is in order.

FIG. 1.1.
PROCESSES OCCURRING IN SEWERS WITH SUFFICIENT OXYGEN TO PREVENT SULFIDE FROM ENTERING THE STREAM REF (1)

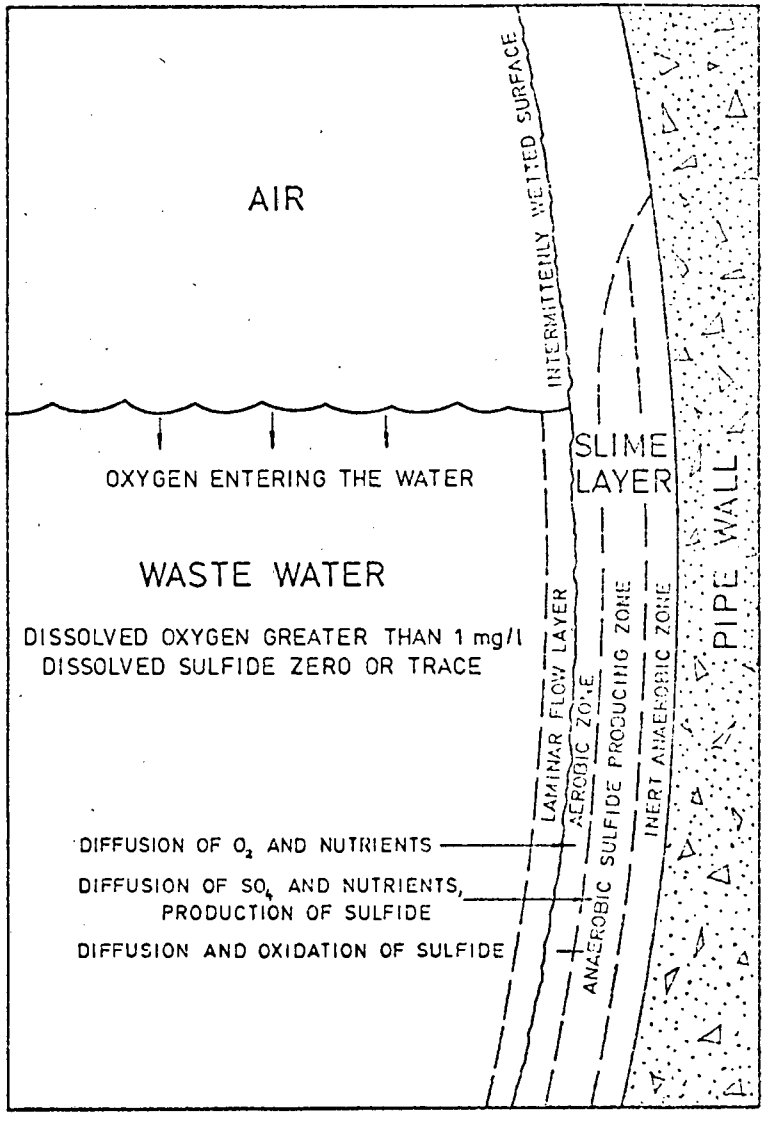

FIG. 1.2.
PROCESSES OCCURRING UNDER SULFIDE BUILDUP CONDITIONS REF (1)

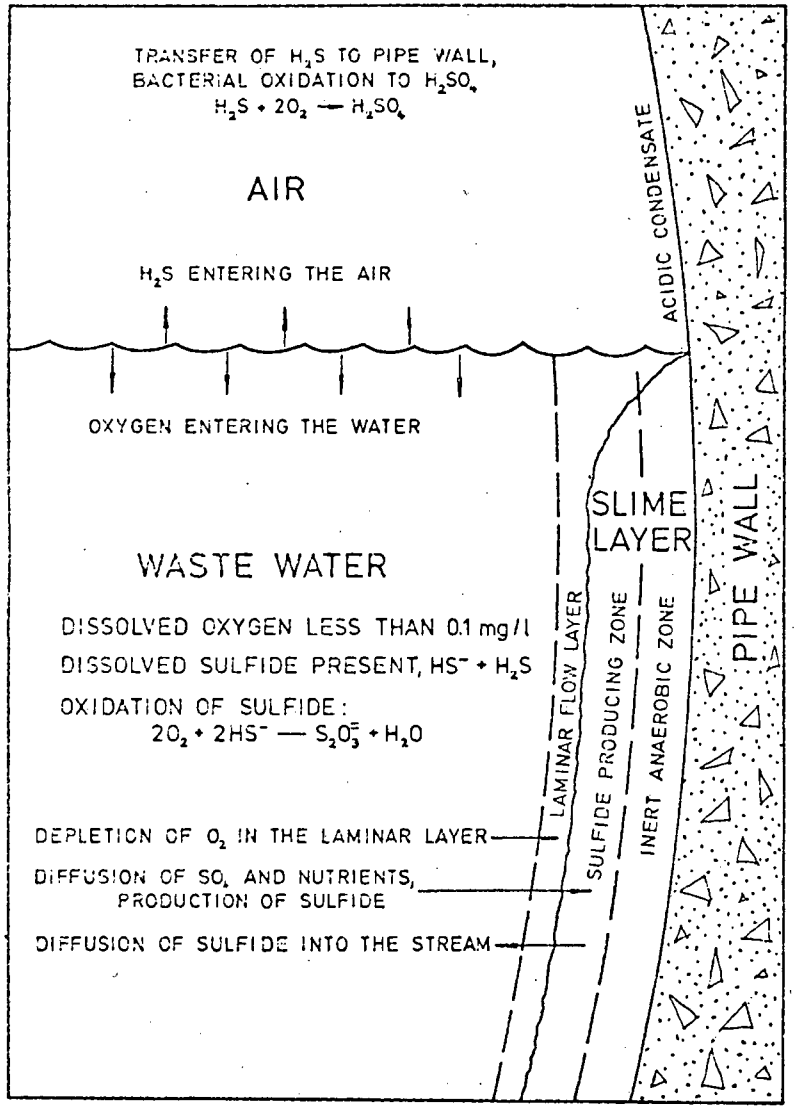

FIG. 1.3.
PROPORTIONS OF H_2S AND HS^- IN DISSOLVED SULFIDE
REF (1)

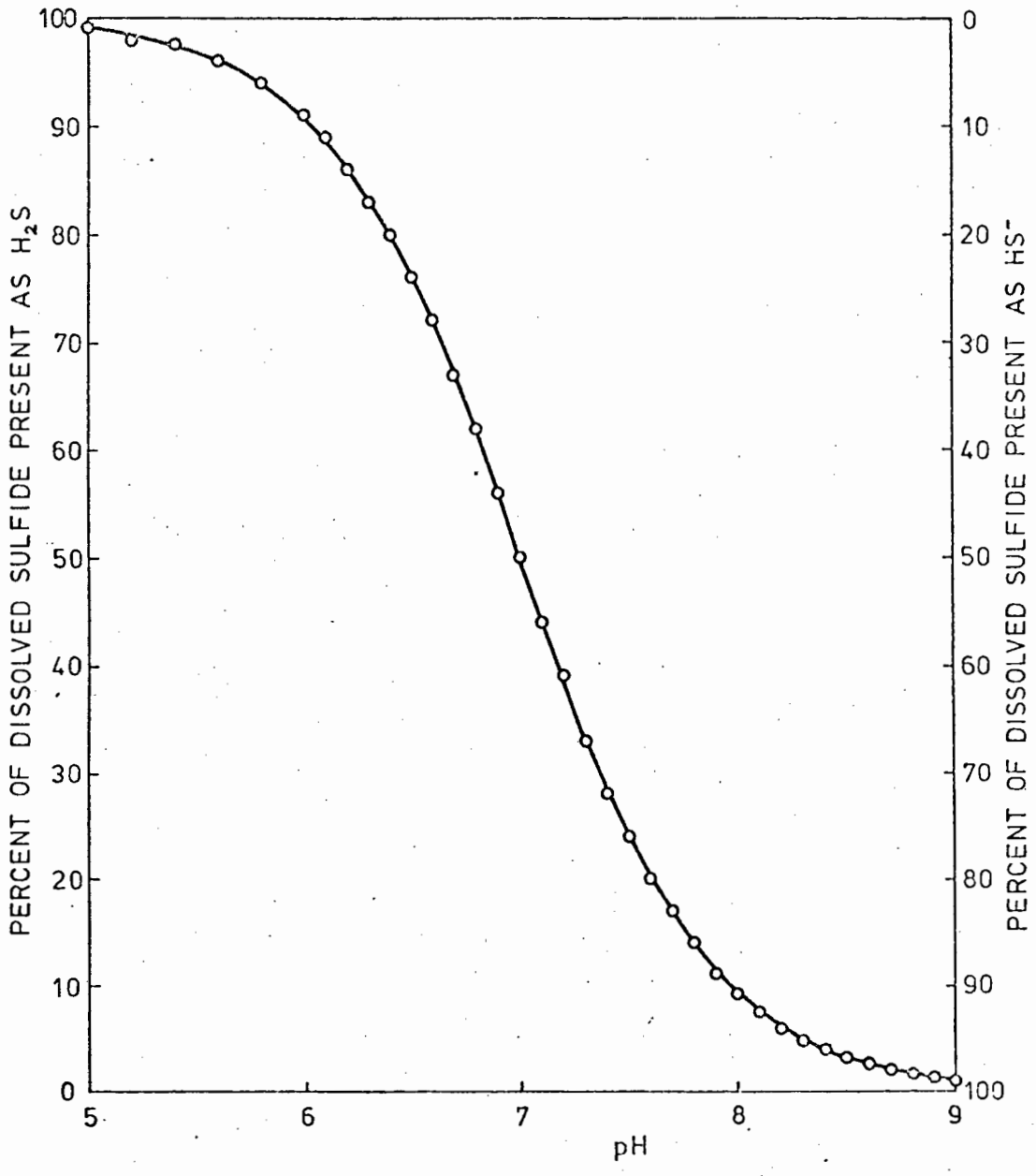

FIG. 1.4.

UNEQUAL DISTRIBUTION OF CORROSION IN A CONCRETE SEWER

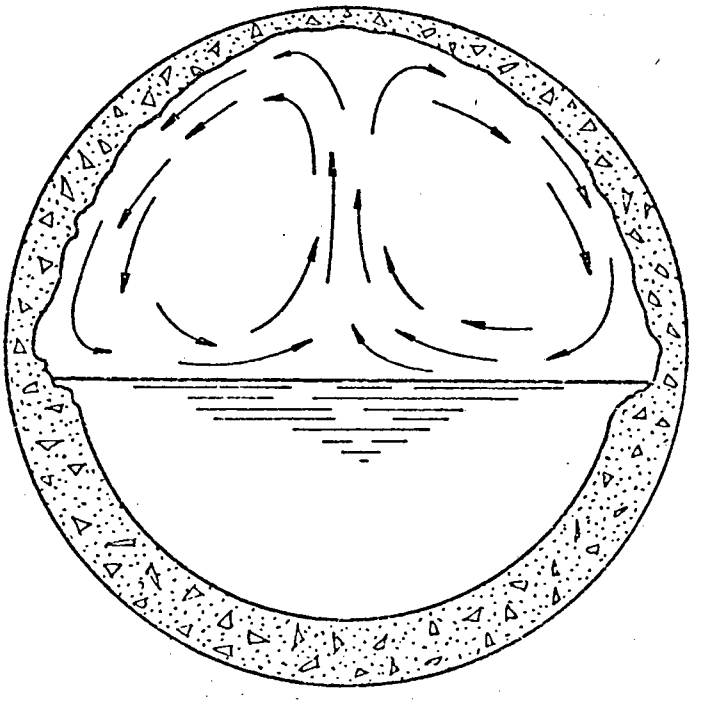

FIG. 1.5.

DIAGRAMATIC CROSS SECTION OF SEWER PIPE UNDER TYPICAL CORROSION CONDITIONS

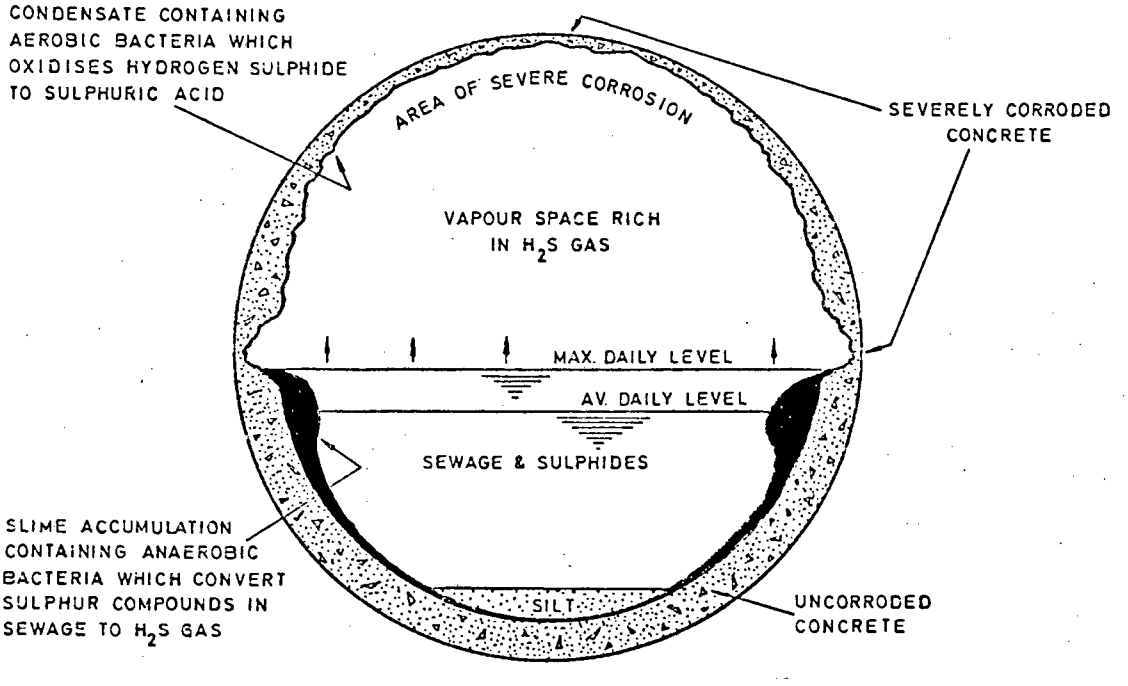

PLATE 1.1: Severe disintegration of the concrete roof slab of a septic tank and severe deterioration of the cast iron cover frame

PLATE 1.2: Corrosion of the concrete roof slab yielding soft mushy material of negligible strength. (See vicinity of top left hand corner of the spade.)

PLATE 1.3: An example of the extremely corroded soft concrete material taken from the benching of the manhole in Plate 1.2.

PLATE 1.4: After cleaning with a water jet, corrosion of the concrete roof slab of the septic tank to approximately 80 mm was apparent and bottom reinforcing steel was exposed.

PLATE 1.5: Expansion and corrosion of the mortar in the joints of the brickwork in a wall of a septic tank. (See also plate 1.1.)

CHAPTER 2

2. THE USE OF POLYMERS IN CONCRETE

2.1 INTRODUCTION

The development of much of concrete-polymer composites is relatively new. Research on polymer concrete (PC) and polymer cement concrete (PCC) (see section 2.3) has been in progress since the 1950s and much of the early data are contained in the three symposia held by RILEM* and the American Concrete Institute between 1965 and 1967.(18 - 20) Extensive work on the technology and use of PCC and PC was carried out in Russia during this period and much of the data are well documented by Solomatov(21) and Moschanskii and Paturoev.(22) An excellent review of polymers in concrete, particularly polymer impregnated concrete (PIC), is given by Swamy(17) and for a more comprehensive study readers are referred to this and other references.

A monomer can be regarded as a molecular species which is capable of combining chemically often by means of cross linking of chains with molecules of like kind, or with other species of monomers, to form a high molecular weight material known as a polymer.(16, 17) Such a polymer consists of repeating units derived from the monomers which are linked together in a chain-like structure. The chemical processes through which these linkages occur is known as polymerisation. If more than one chemical species is used as the monomer, then a co-polymer results.(16, 17)

2.2 POLYMERISATION

When the monomer is polymerised, it sets or cures to a solid gel-type material, and this may be brought about, depending on the type of monomer used, by three methods:(16)

(a) Thermal Catalytic

Small amounts of certain compounds called initiators can be added to the monomer which will generate free radicals on heating and thereby cause the monomer to polymerise.

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*Réunion Internationale des Laboratories D'essais et de Recherches sur les Materiaux et les Constructions.

(b) Promoted Catalytic

Polymerisation can also be brought about without heat by chemical promoters which cause the initiators to decompose and release free radicals, leading to polymerisation of the monomer.

(c) Radiation

Some monomers which absorb radiation, for example, gamma rays, will polymerise without the use of initiators. The main advantage of this method is that polymerisation can be brought about when it is required and at low air temperatures. At low temperatures the chain length of the polymer is increased, leading to less loss of monomer from the impregnated specimen due to seepage.

2.3 CLASSIFICATION OF POLYMER CONCRETES

There are generally three types of concrete materials which utilise polymers to form composite materials,(16 - 22) as described below.

2.3.1 Polymer-Portland Cement Concrete (PCC)

PCC is a premixed material in which either a monomer or a polymer is added to a fresh concrete, mixed in, and subsequently allowed to cure, and, if necessary, polymerised in place.

2.3.2 Polymer Concrete (PC)

A polymer concrete is a composite material formed by polymerising a monomer and aggregate mixture. The polymerised monomer acts as a binder for the aggregate, performing the same function as the cement matrix in cement concrete.

2.3.3 Polymer Impregnated Concrete (PIC)

PIC is an hydrated Portland cement concrete which has been impregnated with a monomer, and subsequently polymerised in situ.

A variation of PIC is polymerised polymer impregnated concrete.(19) One such polymer is a polyurethane co-polymer which is polymerised during manufacture with short initial chain lengths but which requires moisture to bring about the final curing or setting of the polymer, i.e. substantial cross linking and chain lengthening. The polymer is impregnated into the open pores of the concrete thereby sealing the pores and bridging gaps between adjacent aggregate and hydrated cement particles

(see fig. 2.1).

2.4 PROPERTIES OF POLYMERS IN CONCRETE

The impregnation of concrete with polymers in general results in a new composite material which is significantly superior to ordinary concrete in both physical and chemical properties, such as increased compressive, tensile and flexural strengths and abrasion resistance, increased durability and resistance to chemical attack and reduced shrinkage, creep and water absorption.(16 - 23, 26 - 29)

2.4.1 Strength

High strengths in compression, tension and flexure can be achieved with PIC, with increases being as much as four times that of control specimens(16) (see fig. 2.2). These improvements appear to be due to several factors, viz. the empty pores of the concrete are filled with load bearing polymer, the polymer fills and heals microcracks, and the polymer improves the bond between the aggregate and the cement paste (see fig. 2.1). This is shown during compression failure tests.(17, 18) Normal concrete specimens will fail but retain their shape, whereas PIC specimens shatter, and fracture cracks can be seen to pass through, not around, the large aggregate particles.(23) The strength improvements are very dependent on the degree of impregnation, the type of polymer used, and the quality of polymerisation.(16 - 18) (See fig. 2.2.) A lower grade, more porous concrete will require a greater polymer loading than a denser, high grade, concrete, but the final strength values will be similar.(16, 17)

Tests have been carried out on impregnating non-reinforced concrete pipes which showed that three point loading and internal hydrostatic strengths were twice those of non-impregnated control pipes.(28)

2.4.2 Durability and Corrosion Resistance

PIC demonstrates significantly less water absorption and permeability than does conventional concrete.(16 - 18) As a result, the durability of PIC to most forms of environmental attack, including resistance to freeze-thaw, sulfates and acids, is significantly improved. The reason for this appears to be

that the open pores of the concrete are effectively sealed,(16) thereby preventing the intrusion of water and other deleterious substances.

The sulphate resistance test usually consists of a 24-hour cycle in which the concrete is soaked in 2,1% sodium sulphate solution for 16 hours, then dried in hot air for 8 hours. A net expansion of 0,2% is considered a failure. In sulphate resistance tests,(23) because of the sealed pores, PIC typically indicates an expansion of about one-tenth that of normal concrete.

Tests on the resistance of PIC(17, 23) to sulphuric acid indicated a somewhat reduced rate of corrosion in 15% sulphuric acid solution, although this test is considered very severe.(15, 23) Considerable improvement in the acid resistance results when the concrete is given two layers of polymer coating. This may be due to the fact that during the first impregnation, polymer (or monomer) may be drawn into the smaller diameter pores from out of the larger pores by the high capillary forces. (20). When polymer cures, a certain amount of shrinkage of the polymer takes place.(16, 29) The effect of this on pore volume is not fully understood, and a preliminary attempt in the present study to evaluate the performance of both single and double polymer impregnated concrete specimens with respect to acid corrosion resistance and strength was undertaken. The rate of corrosion was observed by monitoring volume changes and weight loss,(15) fully discussed in section 4.8. Significant improvement in corrosion resistance was observed, but the data on double impregnation tests was too sparse to draw final conclusions. This is considered a promising area for future study.

2.5 PRESENT DAY USES OF POLYMERS IN CONCRETE

Although much empirical evidence needs to be accumulated on the impregnation and utilisation of polymers in concrete before a full understanding of this field can be developed, this relatively new composite material has already been successfully used,(16, 17 20 - 22) and the following examples highlight some of these areas.

2.5.1 Highway Bridge Deck Impregnation

Certain highway bridges in the U.S.A. have suffered from severe freeze-thaw deterioration and de-icing salt corrosion due

to the water and salt being able to penetrate the open pores of the concrete deck surface, causing disruption and corrosion of the concrete.(16, 29) The Federal Highway Administration arranged for the impregnation of four bridge decks with polymer, using the following procedure:

(a) drying a section of the concrete surface with hot air heaters, and then cooling;

(b) allowing a monomer to soak through a layer of dry sand and into the deck surface for several hours; and finally,

(c) applying heat to the deck surface to polymerise the monomer in the concrete.

Although optimum impregnation depth is usually obtained in the laboratory by the use of vacuum and pressure (see section 4.4) dense impregnation depths of up to 125 mm were achieved. It was also found that the salt already present in the pores only slightly reduced the rate of impregnation.

2.5.2 Desalting Structures

One of the first projects in which polymers were used in concrete was in the design and construction of prestressed concrete tanks for a desalination plant.(16, 28) In this particular instance the ability of polymer to provide increased corrosion protection and a long maintenance free service life, in a highly corrosive environment was made apparent. In addition, it was possible to use thinner walls because of the increased structural strength of PIC, which is of the order of three to four times that of conventional concrete.

Other uses have included(16) polymer impregnation of concrete surfaces in dams to repair and prevent cavitation damage, and polymer impregnation of both reinforced and non-reinforced concrete pipes which were then placed in service in a sewage farm where they were subjected to high H_2S concentrations. After two years of service no measurable depth of attack was observed. In the light of the present situation as regards corrosion of sewer pipes, this is very promising.

2.6 FACTORS AFFECTING IMPREGNATION

The success and quality of impregnation of polymers into concrete depends on several factors, such as porosity of the concrete, dryness of the concrete, age and dilution of the polymer, application of vacuum and pressure, and other factors all more fully described below.

2.6.1 Porosity of the Concrete

The amount of polymer used in the impregnation of any cured concrete specimen is dependent on the volume of the open pores, a more porous concrete requiring a proportionally greater volume of polymer than a denser concrete, for the same depth of impregnation.(16)

The average pore size also affects the efficiency of impregnation. It has been found that concrete cured under both high and low steam pressures and then impregnated resulted in higher strengths at lower polymer loadings than comparable concretes moist cured at room temperature.(16, 17) This was attributed to the fact that the steam cured concrete had larger pore sizes (although similar total porosity) than moist cured concretes, leading to a more efficient impregnation.

The change in porosity (or net volume) of any concrete specimen before and after impregnation, as well as the depth of impregnation, can be measured to determine the effectiveness of the impregnation. Apparatus and techniques developed for this project, to measure the change in porosity and depth of impregnation, are described in sections 3.6 and 3.4 respectively.

2.6.2 Dryness of the Concrete

The strength and durability of PIC are strongly affected by the proportion of pore volume occupied by the polymer,(16, 17) which in turn depends greatly on the degree of drying of the concrete before impregnation,(16, 17, 23, 27) the two main reasons for this being that (a) impregnation into the pores may be hindered by the physical presence of water, and (b) the bond between the concrete and the polymer may be adversely affected by moist pore surfaces. In the case of the polymer used in this project, which is moisture-curing, the polymer may begin to cure prematurely before maximum impregnation is achieved.

If the pore water is to be removed by heating, it appears that a drying temperature just above boiling point (say 110°C) is insufficient,(16, 17) yet heating the concrete to temperatures above 200°C adversely affects the strength of the concrete(8, 16) (see fig. 2.3). Although a temperature of 100 to 150°C has been reported as optimum,(16) tests were carried out during this project to determine the optimum drying temperature, based on drying temperature vs. concrete strength, as well as to determine the exposure time required to dry the concrete to constant mass (see section 4.2).

2.6.3 Time Effects

(a) Age of the Polymer

It has been reported(12, 16) that the "freshness" of the polymer affects its impregnation characteristics. This freshness is related to the time between polymer manufacture and impregnation, but is also related to storage conditions and temperature and affects the effective size of the polymer (or monomer). Monomers are normally supplied with an inhibitor added to prevent premature polymerisation. The inhibitors become used up with time, and must be replenished periodically until the monomer is used and polymerised. Tests conducted in this project used commercially manufactured polymer, the age of which was variable. Often polymer cannot be made on a small scale (in the laboratory) without resulting in a wide variability in viscosity, setting and curing time,(12) because of the normally large volumes required to maintain the exothermic reaction.

(b) Soaking Time

In addition, the duration of soaking, or the length of time the concrete is subject to polymer impregnation, also has a significant effect on impregnation depth.(17) Generally longer impregnation or soaking times yield greater impregnation depths or polymer loadings. This can be seen, for example, in asbestos cement in fig. 2.4.(20)

2.6.4 Vacuum and Pressure

The depth of impregnation is affected by the pressure applied to the polymer(12, 16 - 18, 20, 23) during impregnation,

as well as by pre-evacuation of air from the pores of the concrete, and also the length of time which the concrete is allowed to soak in the polymer, under pressure or vacuum.

Contrary to expectations, it has been found(12, 16) that "forcing" the polymer into the concrete pores under pressures of less than 690 kPa (100 psi) is not as effective as evacuating the concrete and then simply allowing it to soak in the polymer under atmospheric pressure (see fig. 2.5).

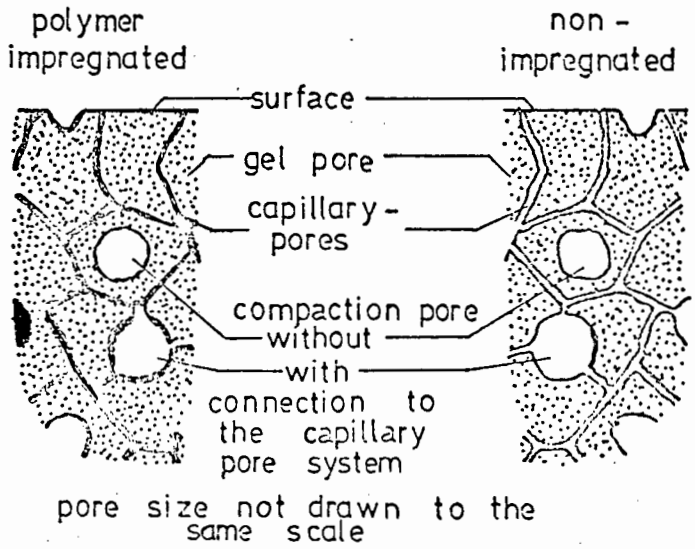
Soaking the concrete in polymer at atmospheric pressure for 24 hours results in partial impregnation,(12, 16) the depth depending on the porosity of the specimen and the viscosity of the polymer. The effect of capillary forces, which can be very high for small diameter pores,(26) must also be considered.

Apparatus and techniques developed in which concrete specimens can be impregnated under various pressures (up to 250 kPa) and vacuums (down to -85 kPa), or combinations thereof, as well as under a pressure gradient, are described in sections 4.4 - 4.6.

2.6.5 Dilution of the Polymer

The dilution of a monomer or polymer by its solvent greatly affects the rate and depth of impregnation due to the change in chain length and hence viscosity.(12, 16) Capillary forces are directly proportional to the surface tension of the fluid entering the pores,(26) and surface tension is presumably a function of the dilution of the polymer. It can therefore be expected that any change in the viscosity of a monomer by the addition of certain amounts of solvent(12) or of polymer,(16) will affect the impregnation characteristics of the impregnating medium.

Tests have been carried out in this project to determine the effect of dilution of the polymer with its solvent, Xylene, on the rate and depth of impregnation. See section 4.7.

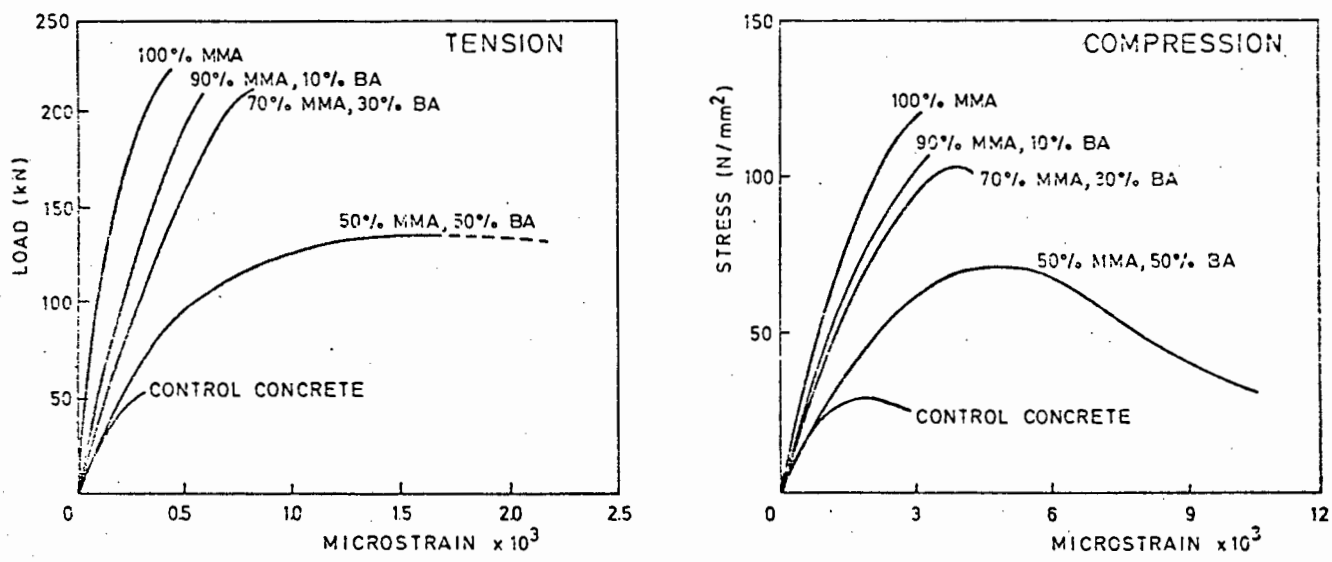


SCHEME OF PORES IN HARDENED CEMENT PASTE

FIG. 2.1.

FIG. 2.2.

INFLUENCE OF CO-POLYMER ON THE STRESS - STRAIN BEHAVIOUR OF PIC IN TENSION AND COMPRESSION (17)



MMA: METHYL METHACRYLATE
BA : BUTYL ACRYLATE

FIG. 2.3.

EFFECT OF TEMPERATURE ON ULTIMATE FLEXURAL STRESS OF MORTAR BEAMS

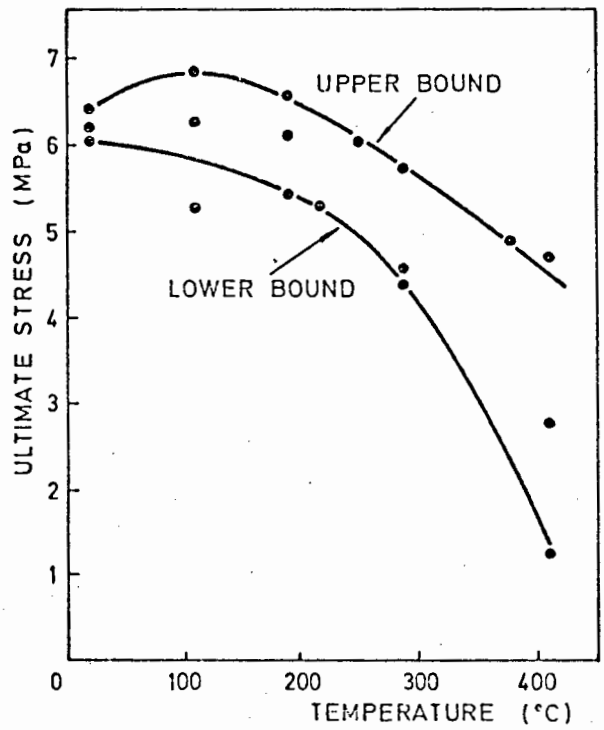


FIG. 2.4.

IMPREGNATION vs. TIME (ASBESTOS CEMENT) (REF. 20)

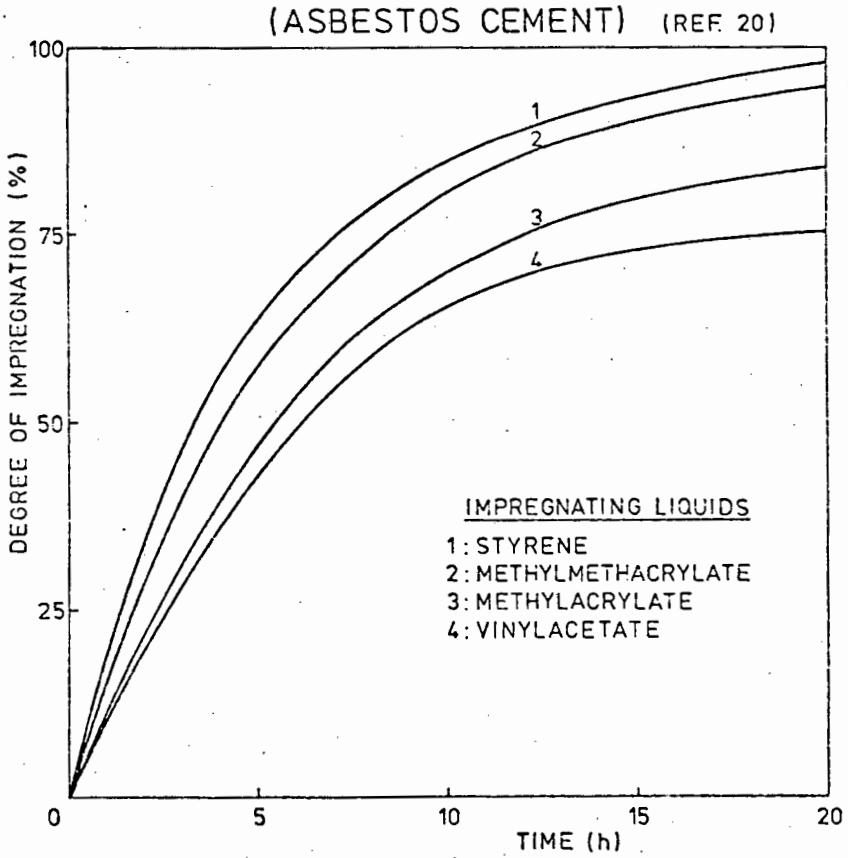
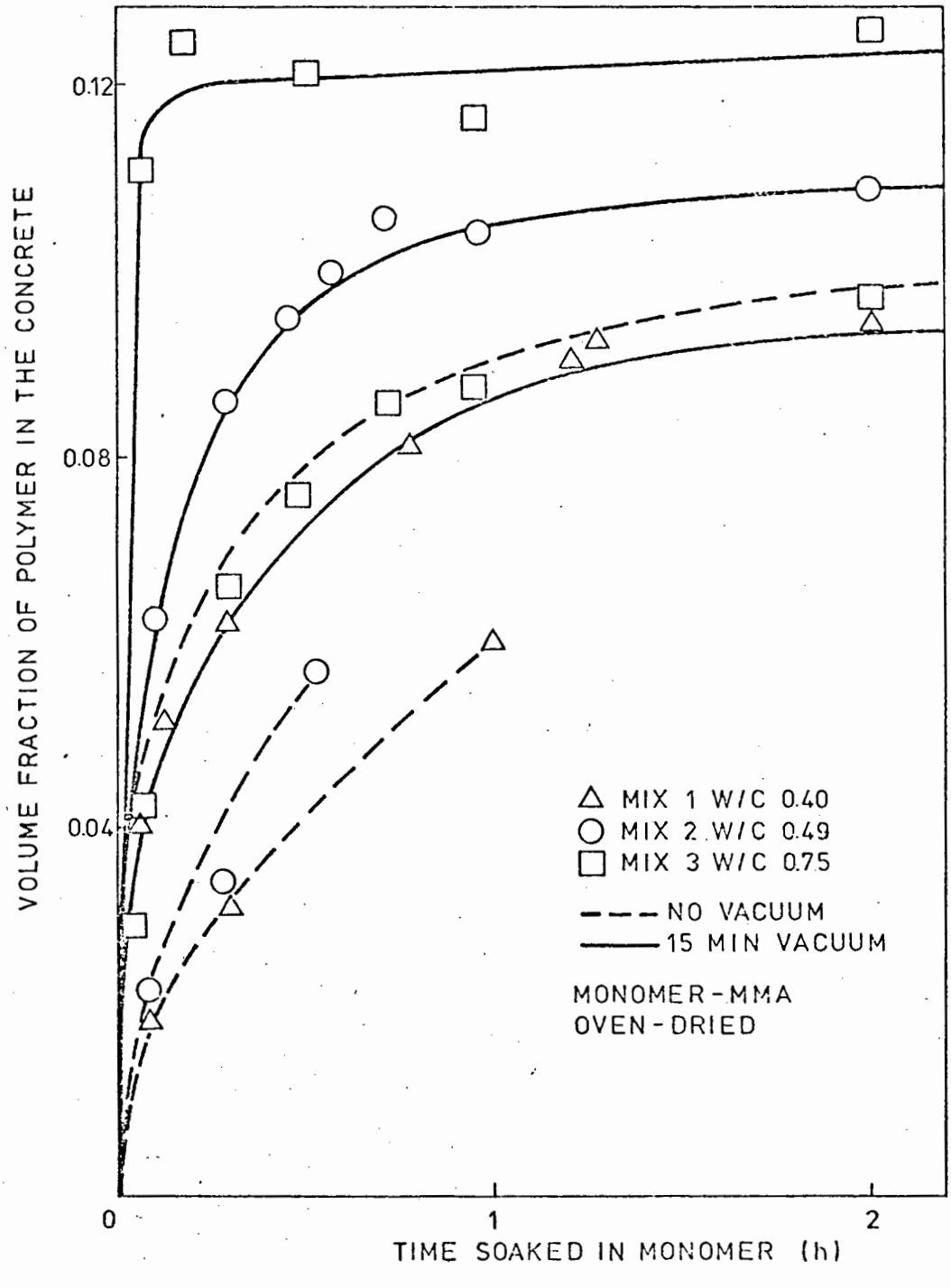


FIG. 2.5.

INFLUENCE OF WATER-CEMENT RATIO AND VACUUM TREATMENT ON POLYMER (MMA) LOADING (17)



CHAPTER 3

3. EXPERIMENTAL MATERIALS, APPARATUS AND TECHNIQUES

3.1 MATERIALS: CONCRETE AND POLYMER

3.1.1 Introduction

Investigations were restricted, in this initial stage of the investigation, to concrete specimens of limited aggregate contents. This was done as it was felt that an understanding was first required of the primary constituents, sand and cement, and impregnation of polymer into the mortar, before future studies were conducted using coarse aggregate, the specification of which is more difficult to standardise and control.

3.1.2 Sand

For all the test series, specimens were prepared using local sieved Cape Flats sand with a Fineness Modulus between 2,3 and 2,62. The Fineness Modulus was prepared using standard techniques(8) and the results of the sieve analysis are shown in table 1 and fig. 3.1, the sand grading curve. As can be seen, there were small changes in the sand grading as the result of fluctuations in supply for the duration of the project, but these differences were considered small and acceptable.

To minimise variations caused by differing sand moisture contents, all sand was dried in an oven at 115^{o}C for at least 24 hours, and cooled in a desiccator prior to specimen preparation.

The Fineness Modulus of the sieved sand was determined to lie between 2,3 and 2,62 with a weighted mean of approximately 2,50 (see fig. 3.1, parts (i) and (ii)), a value which indicates that the sand is within the fine to medium range of generally accepted sizes for fine aggregates.(8)

3.1.3 Cement

Rapid Hardening Portland Cement or type III(7) was used throughout this investigation, the particulars of this batch being as follows:

Tricalcium Silicate 49,7% (C_3S)
Dicalcium Silicate 19,6% (C_2S)
Tricalcium Aluminate 12,1% (C_3A)
Tetracalcium Aluminoferrite 7,3% (C_4AF)
(Blaine) Nominal Specific Surface Area = 5000 $\pm$ 200 cm^2 g

Because of the smaller average cement particle size in Rapid Hardening Portland Cement, the curing process is accelerated and approximately 85% of the 28 day strength of ordinary Portland Cement can be achieved within 7 days.

Since there are only relatively small increases in strength development following the first 7 days after coating, the experimental programs were planned to utilise specimens of this age, and proved to be very suitable. Before mixing, all cement was sieved through a 1,2 mm sieve to remove hard lumps.

3.1.4 Water

The water used was that obtained from the domestic mains supply and was typically between 18^{o} and 22^{o}C prior to mixing and specimen fabrication.

3.1.5 Polymer

The polymer used in this project was a polyurethane co-polymer commercially manufactured under the name UPC. This polymer is polymerised during manufacture and requires moisture to cure fully. It is used predominantly at present to impregnate concrete factory floors, showrooms, cold rooms and hospitals (floors and walls) to increase wear resistance, minimise dust development, improve sterilisation conditions as well as significantly reducing permeability.

An accelerator was available to speed up the curing process and was used in the initial experiments where soaking times of concrete specimens in the polymer were relatively short, typically 30 minutes. Later experiments of longer soaking times (24 hours) were conducted without the presence of the accelerator to avoid the possibility of the polymer curing before the specimens could be properly impregnated, or before they could be removed from the soaking bath.

Before use, the polymer was stored in sealed steel or glass containers to minimise contact with moisture in the air and thus

effectively prevent premature curing.

3.2 SPECIMEN MANUFACTURE

3.2.1 Introduction

The shape of each specimen was in the form of a rectangular prism, 18 mm X 18 mm X 120 mm, these dimensions being selected for convenience of: impregnation, pressure and vacuum work, cost of materials, reproducibility, suitability for the specimen chamber of the porosimeter and modulus of rupture tests using a Monsanto Hounsfield tensometer (see sections 3.6 and 3.5 respectively).

3.2.2 Moulds

Two mould boxes each with 10 compartments and one mould box with 6 compartments were constructed from interlocking panels cut and milled from 5 mm and 10 mm flat perspex sheet. A sketch of portion of a mould box is shown in fig. 3.2 and plate 3.1.

Perspex was chosen as the most practical material for the moulds for the following reasons:

(a) Perspex, unlike steel or wood, is only minimally affected by the water in the wet specimens, and for practical purposes can be regarded as ideal;

(b) The ease of cutting and machining of perspex;

(c) Because perspex is transparent, at least three faces of each mould compartment could be visually checked for voids or large air bubbles (during casting and after vibration) and subsequently removed if necessary;

(d) The very smooth and flat characteristics of perspex lead to a high quality off-shutter finish with sharp corners easily obtainable. To capitalise on this characteristic and to optimise reproducibility for porosity measurements, the moulds were very lightly coated with a film of petroleum jelly (Vaseline grease) to facilitate the removal of specimens from the moulds without damaging the smooth surfaces of the specimens.

3.2.3 Mix

Several trial mixes were made to determine the most suitable workability for vibration of the cast specimens on a small electric vibrating table.

Initially the water/cement ratio was fixed at 0,42, this value being the minimum required for maximum hydration of the cement.(7, 8) With this water/cement ratio and the particular sand used, the optimum cement/sand ratio was determined as being between 1 : 2½ and 1 : 3. A ratio of 1 : 2,75 was initially chosen, although this was later changed to 1 : 2,5 to improve the workability of the mix.

For the preparation of a batch of 26 specimens in the initial series of tests the materials as described in sections 3.1.2 to 3.1.4 were measured out as follows:

Sand:	1815 g	± ½ g	sand/cement ratio = 2,75 : 1
Cement:	660 g	± ½ g	water/cement ratio = 0,42
Water:	277,2 g	± ½ g	

To compensate for water lost due to evaporation during mixing and for wetting of the steel base on which the mortar is mixed, a further 2,8 grams (1%) of water was added to bring the total mix water up to 280 grams.

In the later series of tests, specimens were prepared from a mix as follows:

Sand:	1800 g	± ½ g	sand/cement ratio = 2,5 : 1
Cement:	720 g	± ½ g	water/cement ratio = 0,42
Water:	302 g	± ½ g	
	+ 3g (1%)		

3.2.4 Casting

After coating all parts of mould boxes with petroleum jelly, they were assembled and each box was firmly held together with 3 strong rubber bands. These also served the useful purpose of keeping the moulds out of direct contact with the vibrating surface of the vibrating table, thereby permitting a more gentle vibration of the mortar than would normally be obtained on that particular type of machine, and also protecting the perspex from chipping.

The sand and cement components were thoroughly mixed by

hand for 3 minutes using a small steel trowel on a flat steel surface, and then water was added, followed by hand-mixing for a further 3 minutes.

Each component of the mould boxes was filled with the mortar and hand tamped to a level slightly above the top of the mould. Each mould box was vibrated for half a minute while the top surface was smoothed over and levelled with a small steel trowel.

3.2.5 Curing and Storage

Initial specimens were cured in the moulds for 12 hours in a humid room (RH = 95 - 100%, temp. = 23 - 25°C) and then removed from the moulds and cured under water for 7 days, air dried for 12 hours, oven dried for 24 hours at a temperature of 115°C (± 5°C), and cooled and stored in an evacuated desiccator. See section 4.2.3.

Later specimens were cured in the moulds in the humid room for 18 hours as it was found that those specimens cured for only 12 hours were more susceptible to breakage on stripping of the moulds. The oven drying was also extended to 24 hours at 110°C and then 24 hours at 150°C. See section 4.2.4. This followed as the result of developments concerning the importance of correct drying techniques.

3.3 POLYMER IMPREGNATION - GENERAL PROCEDURE

3.3.1 Introduction

Two methods of impregnation were adopted in this project, namely, soaking the specimens in polymer for relatively short periods of time (up to 30 minutes), and for longer periods (typically 24 hours).

3.3.2 Short Soak (Initial Tests)

After drying and cooling as described in section 3.2.5, specimens were completely immersed in the polymer for a short period and subsequently removed and placed inside the pressure chamber for pressure/vacuum impregnation for periods up to 30 minutes, as required.

Before immersion of the specimens, an accelerator was added to, and thoroughly mixed with, the polymer in the proportion of

3 ml/litre.

After impregnation, specimens were removed from the pressure chamber, wiped clean with absorbent paper, and allowed to cure in the air for seven days.

3.3.3 Long Soak (Later Tests)

The polymer used in the later tests did not contain the accelerator as the impregnation times were up to 24 hours and the effect of small errors in accelerator measurement was more significant. After impregnation, specimens were similarly cleaned and cured in the same manner as the short soak specimens.

3.4 MEASUREMENT OF IMPREGNATION DEPTH

3.4.1 Introduction

Of fundamental importance to the success of this project was the development of a facility to determine quantitatively the depth of impregnation of polymer in the concrete specimens.

When a freshly impregnated specimen is broken in flexure, the polymer impregnated area is easily seen by eye as a wetted area. When the polymer cures, however, the wet appearance disappears and is almost indistinguishable from the non-impregnated centre core of the specimen. Various attempts(12) to colour the polymer with dye were largely unsuccessful and gave limited results. However, a very simple and successful technique of colouring the non-impregnated sections of a broken specimen was developed and is described below.

3.4.2 The "Ink Staining Technique"

A water-based black printer's ink was diluted with water to approximately the consistency of fountain pen ink, and the fractured face of a specimen was dipped into the diluted ink for a few seconds, removed and wiped dry with absorbent paper (i.e. briefly "blotted"). The ink penetrated the non-impregnated concrete, colouring it black, while the impregnated portion remained effectively untouched. A permanent and clearly defined demarcation between the two portions of pure mortar and polymer impregnated mortar was thus relatively easily achieved (see plate 3.2). This process constituted the first stage of quantitative impregnation depth measurements. To quantify the depth of the now readily apparent impregnated

areas reasonably accurately, while at the same time achieving some degree of statistical averaging, the following procedure was developed.

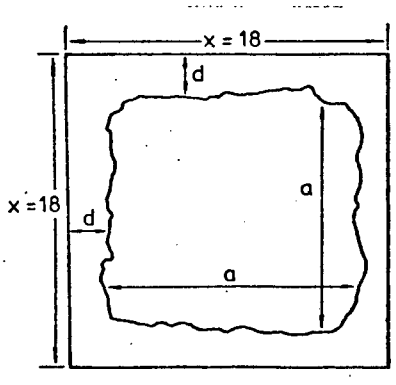
Flexural fracture surfaces were almost always approximately normal to the longitudinal axis of the specimens but did not readily lend themselves to direct and easy measurement of impregnation depth by such means as rulers, callipers or a travelling microscope. These latter techniques also suffered from low accuracy and large scatter, depending where the measurement was taken. For a reasonable statistical mean, multiple readings would have to be made which was unrealistic, bearing in mind the large number of tests planned.

Alternatively, it was considered preferable to obtain an accurate picture of the fractured face of the specimen on paper, for record purposes, and also for further evaluation and measurement of the impregnation depth. Photographic techniques (e.g. plate 3.2), while acceptable, were ruled out because of the high cost in both materials and time, particularly in view of the large number of tests.

A quick and easy method of achieving reproductions on paper was developed in this Department and involved placing a batch of broken specimens (one half of each complete specimen) in the projector chamber of an epidiascope with the fractured face facing the projecting lenses (see plate 3.3). A sharply focused image of the specimens was thus projected onto a paper screen from which a tracing could readily be made (see fig. 3.3).

The average impregnation depth can be derived from the ratio R of the annular impregnated area to the full cross-sectional area of the specimen, as shown below.

Calculation of Impregnation Depth



ASSUMPTION: The core area is square.

x = length of one side

d = impregnation depth

R = ratio of impregnated/total area

a = core dimension

unimpregnated core

impregnated annulus

From the sketch

$$x - 2d = a \qquad \ldots\ 1$$

dividing by x and squaring

$$(1 - \frac{2d}{x})^2 = \frac{a^2}{x^2}$$

Now R = ratio of $\frac{\text{impregnated area}}{\text{total area}} = \frac{x^2 - a^2}{x^2}$

$$R = 1 - \frac{a^2}{x^2} = \frac{4d}{x} - \frac{4d^2}{x^2} \qquad \ldots\ 2$$

Let: $\frac{d}{x} = p$ $\qquad \ldots\ 3$

where p = half percentage penetration depth (i.e. the specimen is fully impregnated when p = 0,5)

Substituting (3) in (2), $R = 4p - 4p^2$

Therefore $4p^2 - 4p + R = 0$

So that: $p = \frac{1}{2} \pm \frac{1}{2} \quad 1 - R$

And from (3) d = px, therefore impregnation depth, d, can be obtained by multiplying p by the sample dimension x, in this case 18

e.g. if R = 0,732
p = 0,241
and d = 4,34 mm

The basic assumption made is that the unimpregnated core of the specimen remains approximately square. This is reasonable in most cases, but implies that the depth of impregnation is uniform on all sides, which is not quite the case for large depths. It should be remembered, however, that this method gives an <u>average</u> depth, and that even though the core perimeter is somewhat irregular, on average the depth calculated will be representative. The fact that the depth is calculated from a ratio of areas means that this very area ratio, R, and hence impregnation depth, is independent of the magnification created by the epidiascope and this, experimentally, is very convenient and influenced the choice of this technique.

The areas are conveniently measured using a Tektronics 4051 Summagraphics Digitiser, in effect a digital electronic

planimeter coupled to a computer. An existing computer program was modified for the above task and the printout indicated the two areas (annular and total) as well as the ratio of the areas. By repeating the measurements three or four times, the values of the ratios could be checked and confirmed, and the operator's accuracy therefore assessed.

Elementary operating instructions for the computer are given in the appendix and a typical printout is shown in fig. 3.4. As can be seen, this is the counterpart of fig. 3.3 and refers to vacuum impregnation tests.

3.4.3 Confirmation of the Accuracy of the Ink Staining Technique

Although the ink technique appeared to indicate accurately the position of the interface between impregnated and unimpregnated areas of the specimen, it was thought worthwhile to confirm the accuracy of this method by comparing epidiascope tracings with measurements taken using a Cambridge S180 Scanning Electron Microscope (SEM), as described below.

Procedure

An impregnated specimen was broken in half, yielding two mirror cross-sections. One cross-section was prepared for the SEM by mounting on a large (30 mm diameter) specimen stub, and coated in the usual way with layers of carbon and gold/palladium. The other was dipped in ink and its impregnated area manifested by the ink staining procedure described above.

After SEM scrutiny of the specimen, it became apparent that parts of the cross-section appeared in a tight flat matt form analogous to a "lace tablecloth" (see figs. 3.5, 3.7(a)). Other areas appeared to have petal-like flakes peeling away from the surface, rather like paint or "chocolate flakes" (see figs. 3.6, 3.7(c)). Further observation revealed that the "lace tablecloth" regions unequivocally represented unimpregnated concrete which had simply been ink stained, while the "flakes" regions represented polymer impregnated concrete. The "flakes" can be thought of as a peeled paint surface which has come about as the result of the extreme vacuums that specimens are subjected to both in preparation for, and in the operation of, the SEM. This can be seen to some extent, in context, in

fig. 3.8(a) and at higher magnification (of the same area) in fig. 3.8(b).

Having identified a feature on the fracture surface to facilitate subsequent relocation, and bearing in mind that "flakes" represented polymer impregnated areas and the "lace" merely ink-stained areas, it was possible to perform a mechanical line scan from one side of the specimen to the other. This was conducted parallel to one edge and achieved by means of the normal X-shift micrometer screw on the goniometer stage of the SEM. It was important to arrange the correct tilt angles, in two rotational degrees of freedom, to ensure that the mechanical line was (i) parallel to one edge, and (ii) in the same plane as the fracture surface (otherwise one is viewing and measuring on a foreshortened picture which was continually going out of focus. In this latter case, an alternative but less desirable solution would be to multiply by the secant of the effective measured tilt angle.)

Results and Discussion

Scanning along this line and taking digital readings on the counter of the micrometer screw gauge scale, it was possible to record the positions of the edges of the sample as well as the interface between impregnated and unimpregnated concrete (see fig. 3.9(a), (b)). These are, for example, 14,9, 6,1 and 11,1 respectively, indicating an impregnation depth of approximately 5,0 mm. Several runs were performed and, for clarity, only three of these are shown in fig. 3.9(a). A comparison of these indications of polymer interface with those obtained by means of the standard ink staining technique is shown by means of the overlay in fig. 3.9(b). As can be seen, extremely good correlation of the two techniques was obtained, thus confirming the validity of the ink staining technique as a representative means of obtaining impregnation depth.

3.5 MEASUREMENT OF STRENGTH

3.5.1 Introduction

In order to determine the effect of polymer impregnation on the flexural strength of impregnated specimens, Modulus of Rupture tests were conducted on all specimens prior to measurement of the depth of impregnation. The Modulus of Rupture is

defined as the maximum stress on the outermost fibres at failure.

3.5.2 Procedure

Specimens were tested in flexure to destruction in a three point loading rig of a Monsanto Hounsfield Tensometer with a span of 80 mm between supports, and loaded at a rate of approximately 600 N/minute. In the first few test specimens, the direction of loading was parallel to the bleeding pores of the specimens (see fig. 3.10). This particular positioning of the specimen in the rig meant that either the knife-edge supports or the knife-edge load point were applied to the open side of the specimen, i.e. the upper side of the specimen as seen from the top of the perspex mould box. This open face was not in contact with any straight sides of the mould box, and its surface was therefore not as straight and regular as the other three longitudinal sides. To ensure that the loading points of the rig were evenly applied, all other later specimens were positioned with the bleeding pores perpendicular to the direction of loading.

The load/deflection curves were recorded on an automatic rotating drum and heat sensitive pen plotter attached to the Tensometer (see fig. 3.11, plate 3.4).

3.6 POROSITY AND VOLUME MEASUREMENT

3.6.1 Introduction

The ease with which polymer can impregnate into concrete was thought to be a function, among other parameters, of concrete porosity. Porosity in concrete can be related to the relative amount of open pores or spaces within the concrete or mortar matrix, and may be classified as of three types,(25) viz.:

(a) External Pores: Those present on the surface of the concrete;

(b) Open Pores: Those that are inter-connected and linked to the external pores;

(c) Closed Pores: Those that are not linked to open pores or external pores, i.e. sealed cavities locked inside the matrix.

This project is concerned with those pores that can be impregnated with polymer, viz. the external and open pores (the so-called "effective porosity") (see fig. 2.1).

In order to make measureable comparisons of this "porosity" (or strictly external solid volume), a measuring device was required. This is described in the next section and had the added advantage of being suitable for measuring volume loss as the result of corrosion in the series of corrosion tests (see section 4.8).

3.6.2 Porosimeter

Ramana and Venkatananayana(25) describe an instrument which is suitable for the measurement of such external pore volume, a so-called Porosimeter. A model was constructed along the lines of that described in Ref. 25 and a detailed description and method of operation of such a porosimeter is given in that reference. The porosimeter constructed for this work is shown in fig. 3.12 and its operation in fig. 3.13. The principle of operation of the porosimeter relies on the linear relationship between the level of the mercury column in the 2 mm diameter tube and the volume of free air in the specimen chamber (fig. 3.12). Any change in this volume due to the introduction of solids within the specimen chamber is reflected in the level of the mercury column. Thus, for example, a change in the effective external porosity (or solid volume) of a specimen before and after impregnation of polymer is shown by a change in this mercury level.

Calibration of the Porosimeter

Prior to each series of tests, the instrument was calibrated by making use of six steel specimens of the size and shape of the proposed mortar specimens (see section 3.2.1). Assuming the porosity of steel to be zero with respect to this measurement technique, different artificial porosities of these calibration specimens was achieved by drilling several holes of known diameters into each. The "porosity" or solid volume of each specimen could then be calculated from volume determinations subsequent to vernier calliper measurements.

Porosimeter Calibration Tests: Results and Discussion

Preliminary tests for a range of specimen volumes from

0 to 40000 mm^3 indicated that the relative change in mercury level of the porosimeter was not very great, typically 50 mm, and the sensitivity could be increased by reducing the so-called "dead space" surrounding the specimen in the specimen chamber. This was achieved by filling a portion of the "dead space" with paraffin wax which included a 4 mm diameter hole to allow for free movement of air (see fig. 3.12). This had the effect of increasing sensitivity by approximately 40%.

The results shown in table 2 are drawn graphically in fig. 3.14. Within experimental error, the level of the mercury can be seen to be linearly dependent upon the volume of the free air in the specimen chamber, or inversely linearly dependent upon the solid volume of the specimen, where:

solid volume = overall volume minus
effective pore volume

3.7 SUMMARY

This chapter has described the basic materials and apparatus needed for the general study of the suitability of polyurethane polymer as an impregnating material for concrete with a view to improving its corrosion resistance.

The fundamentals have been discussed in this chapter and include choice of materials, specimen fabrication and general procedures for polymer impregnation. All the measurement techniques have also been discussed and cover impregnation depth measurement by means of an ink staining technique followed by epidiascope plots for subsequent digitiser analysis; the verification of the validity of this technique using the scanning electron microscope; and measurements of flexural strength (Modulus of Rupture) and solid volume (or so-called external "porosity").

Specific tests and their associated apparatus that needed to be developed during the course of the investigation, however, are not mentioned here but in the next section. This includes such parameters as the effect of temperature, pressure (and vacuum), differential pressure studies, polymer/solvent dilution, duration of impregnation and corrosion tests. All this is fully discussed in the next chapter.

GRADING ANALYSIS RESULTS

FOR BOTH SAND BATCHES (i) AND (ii)

Sieve Size (m)	Mass Retained on Sieve (gm)		Percentage Retained		Cumulative Percentage Retained	
	(i)	(ii)	(i)	(ii)	(i)	(ii)
2360	0	0	0	0	0	0
1180	47	28	4.7	2.8	4.7	2.8
600	642	455	64.2	45.5	68.9	48.3
300	206	331	20.6	33.1	89.50	81.40
150	95	168	9.5	16.8	99.0	98.20
Pan	14	19	1.4	1.9	-	-
TOTALS	1004	1001			262.1	230.

FINENESS MODULUS (i) 2.62 and (ii) 2.30

TABLE 1

VOLUME OF STEEL SPECIMENS AND CALIBRATION READINGS

Specimen	Overall Volume mm^3	"Pore" or Hole Volume mm^3	Nett Solid Volume mm^3	Porosimeter Reading mm
No holes	38680	0	38680	186.7 187.0
5 X 5.1 mm holes	38703	1838	36865	189.8 190.3
10 X 5.1 mm holes	38507	3677	34830	193.3 193.6
5 X 10.2 mm holes	38680	7350	31330	200.6 201.0
Block 19 X 19 X 66.2	23900	0	23900	212.2 213.0
Cylinder 94.7 X 25.35	47800	0	47800	170.4 167.0

TABLE 2

FIG. 3.1.

SAND GRADING CURVE

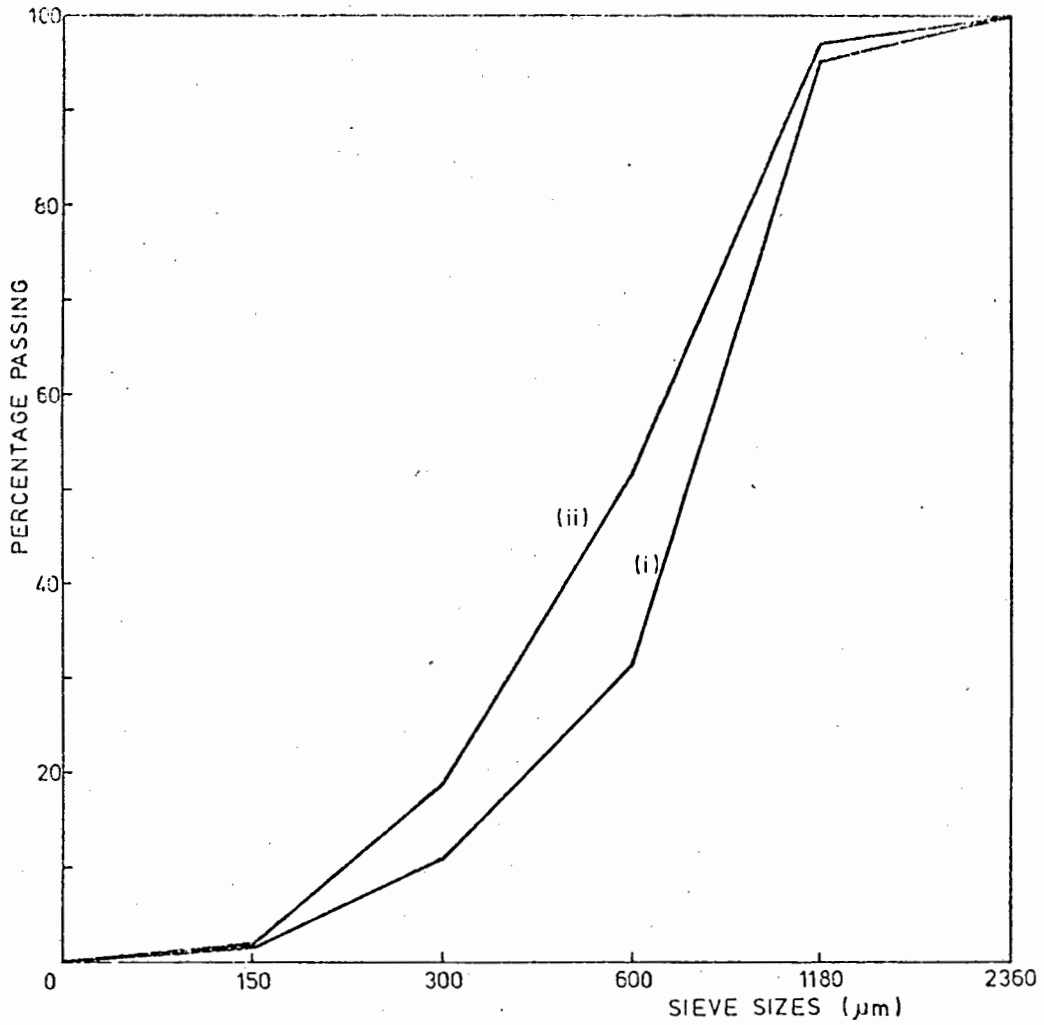


FIG. 3.2.

PORTION OF PERSPEX MOULD

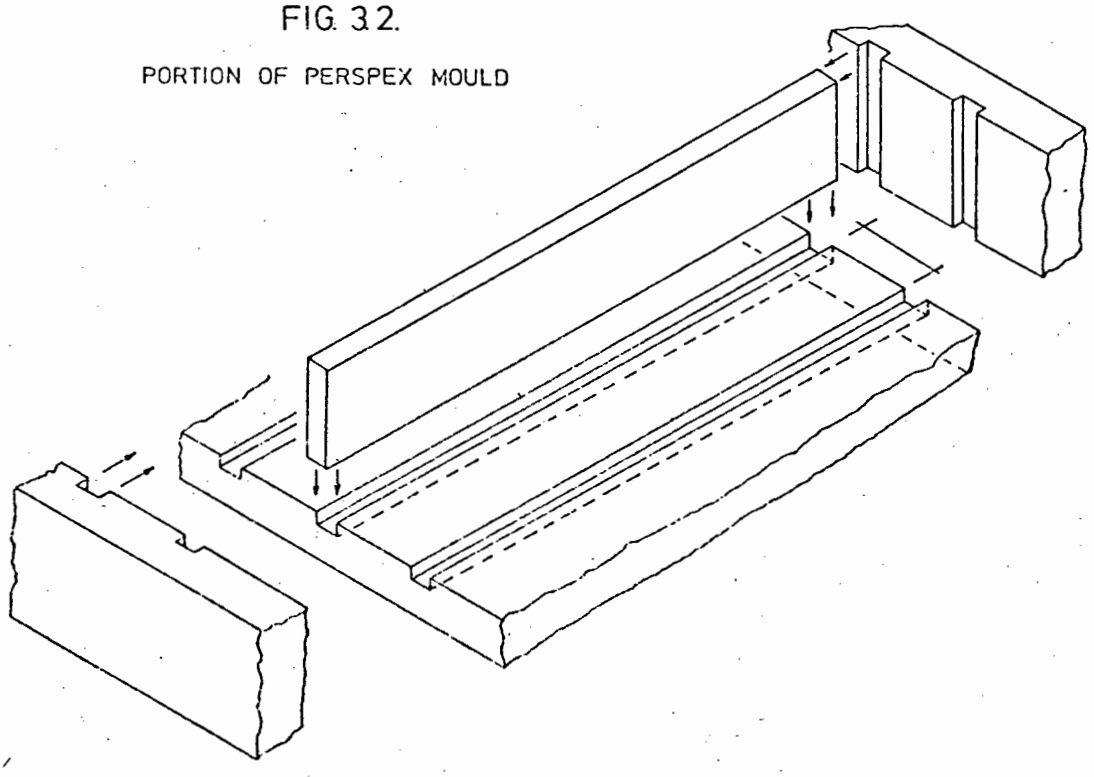


FIG 3.3.

TYPICAL EPIDIASCOPE TRACES

VACUUM IMPREGNATION 2 1/2 mins.

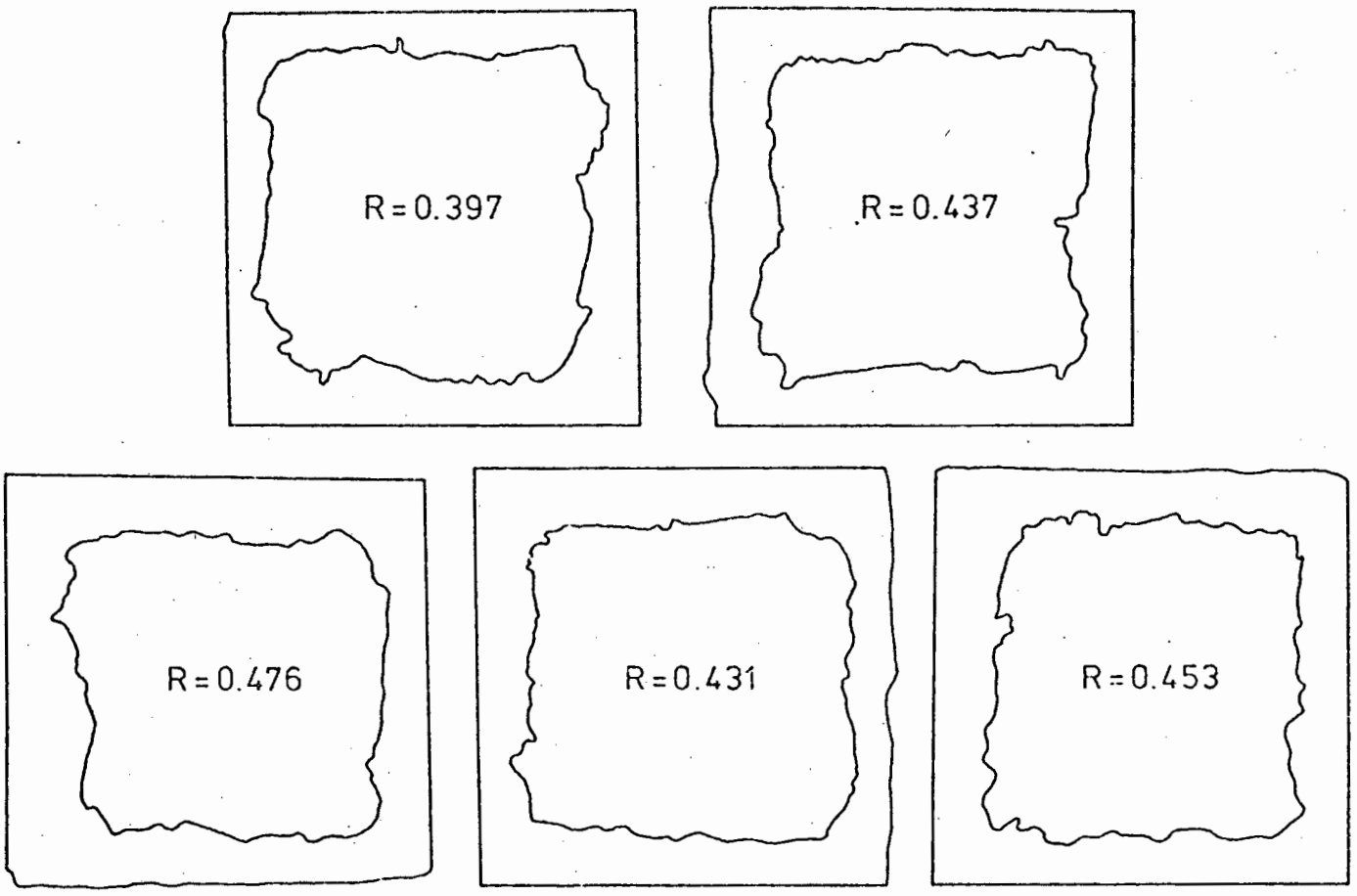


FIG. 3.4.

TYPICAL COMPUTER PRINTOUT FOR IMPREGNATION DEPTH DETERMINATIONS (see FIG. 3.3.)

```
THE DIGITIZED AREA IS :     7911   MM*2
THE DIGITIZED AREA IS :     4769   MM*2
THE RATIO OF EXTERNAL TO INTERNAL AREAS IS:   0.397
THE DIGITIZED AREA IS :     8170   MM*2
THE DIGITIZED AREA IS :     4599   MM*2
THE RATIO OF EXTERNAL TO INTERNAL AREAS IS:   0.437
THE DIGITIZED AREA IS :     7908   MM*2
THE DIGITIZED AREA IS :     4140   MM*2
THE RATIO OF EXTERNAL TO INTERNAL AREAS IS:   0.476
THE DIGITIZED AREA IS :     8097   MM*2
THE DIGITIZED AREA IS :     4608   MM*2
THE RATIO OF EXTERNAL TO INTERNAL AREAS IS:   0.431
THE DIGITIZED AREA IS :     7941   MM*2
THE DIGITIZED AREA IS :     4345   MM*2
THE RATIO OF EXTERNAL TO INTERNAL AREAS IS:   0.453
```

FIG. 3.5: SEM Micrograph of Unimpregnated Plain Concrete Simply Ink-Stained (Note the "lace tablecloth" effect)

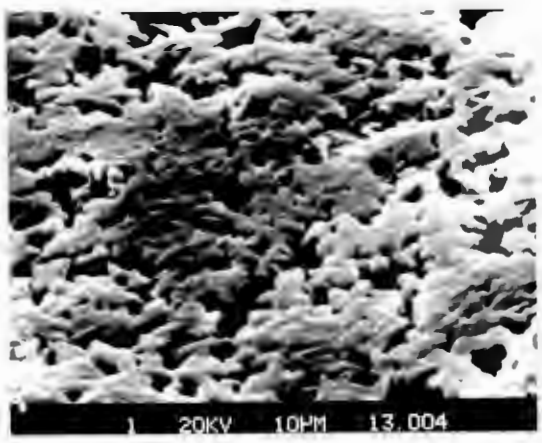


FIG. 3.6: SEM Micrograph of Polymer Impregnated Concrete. "Flakes" of Polymer on the surface like peeling paint are characteristic

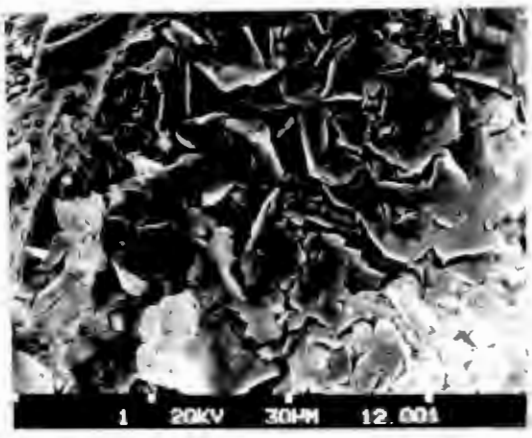
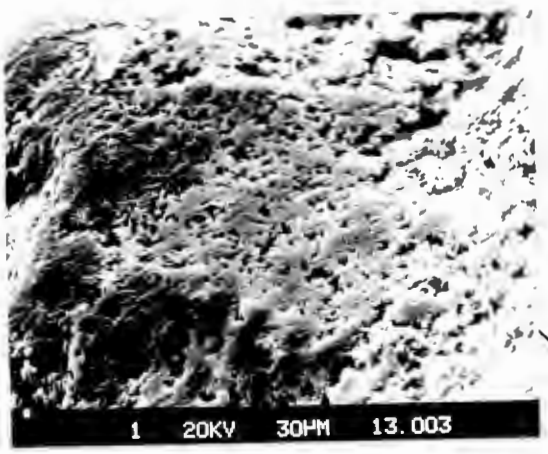
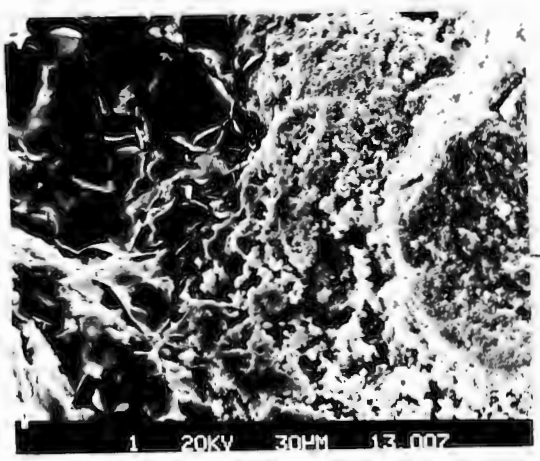


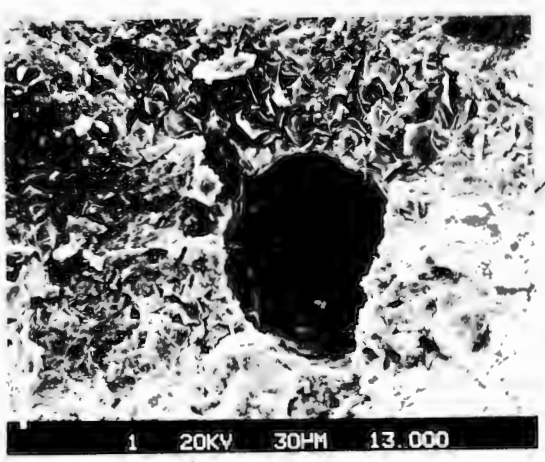
FIG. 3.7: Electron Micrograph illustrating: (a) Unimpregnated Concrete and "lace" due to ink staining; (b) The Interface between Impregnated ("flakes") and Unimpregnated ("lace") Concrete; and (c) Polymer Impregnated Concrete showing "flakes" and a small Porosity



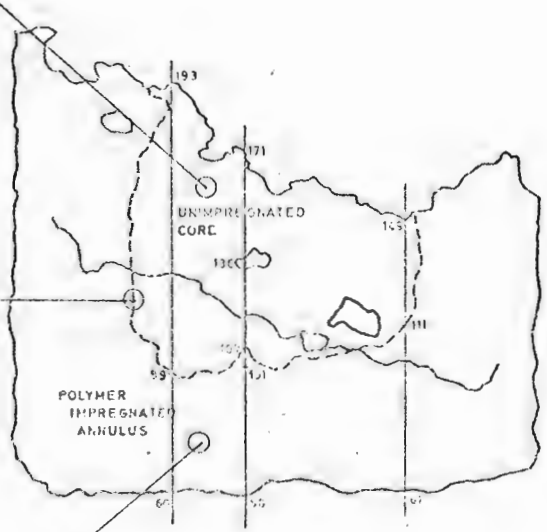
(a)



(b)

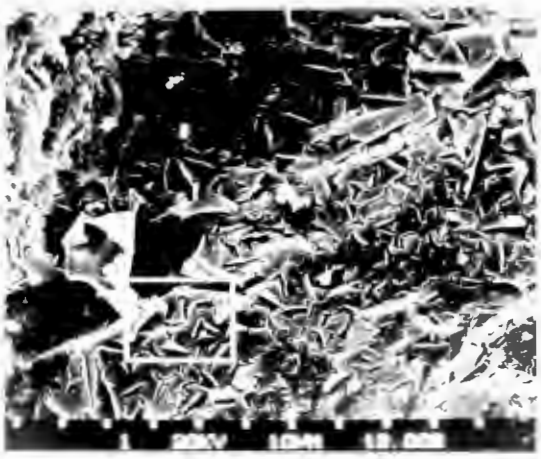


(c)

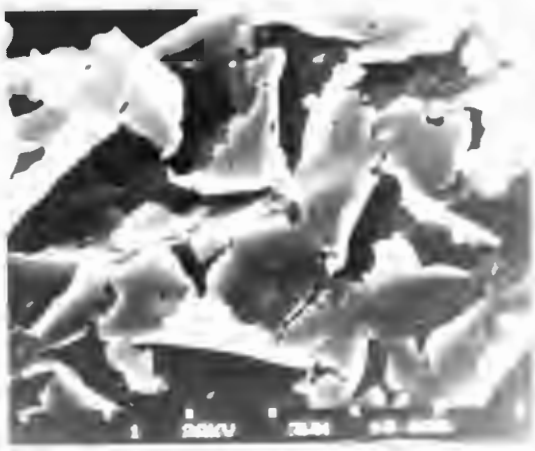


SURFACE SCANNED UNDER ELECTRON MICROSCOPE

FIG. 3.8: SEM Micrographs of Impregnated Concrete illustrating typical "flakes" both (a) in context and (b) at higher magnification



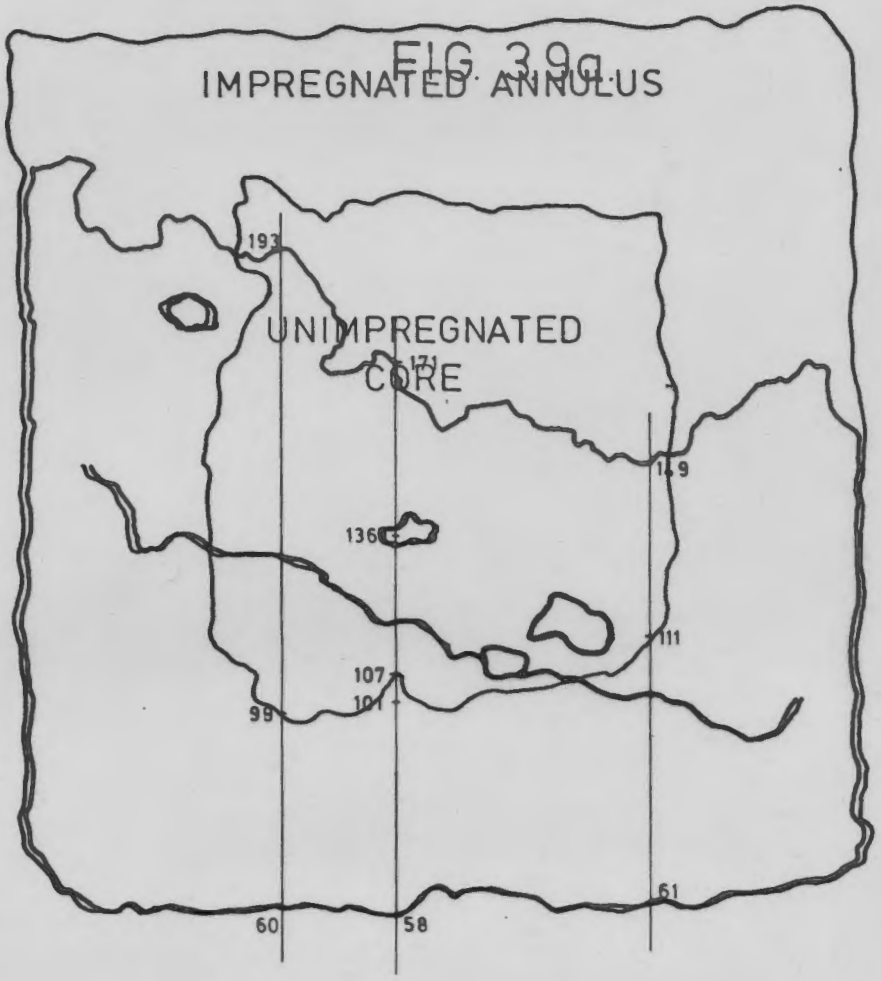
(a)



(b)

FIG. 3.9b.

CORRELATION BETWEEN STANDARD INK STAINING TECHNIQUE AND SCANNING ELECTON MICROSCOPY TO VERIFY EXTENT OF POLYMER IMPREGNATION



SURFACE SCANNED UNDER ELECTRON MICROSCOPE

SURFACE SCANNED UNDER ELECTRON MICROSCOPE

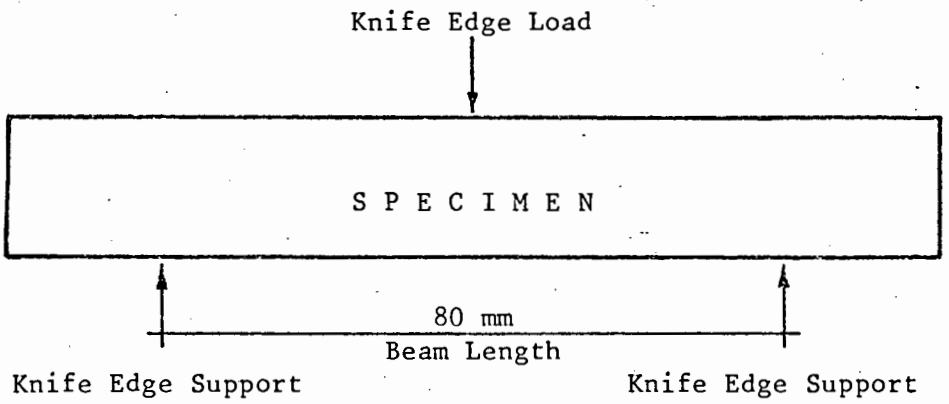
SURFACE STAINED IN INK SOLUTION

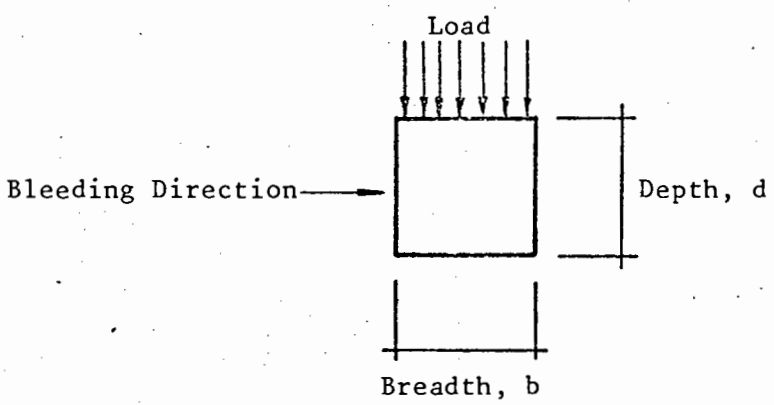
0 5 10 15 20

SCALE IN MILLIMETRES

FIG. 3.10.

DETAILS OF SPECIMEN LOADING IN TENSOMETER





$$\text{Modulus of Rupture} = \frac{3\,P\,l}{2\,b\,d^2}$$

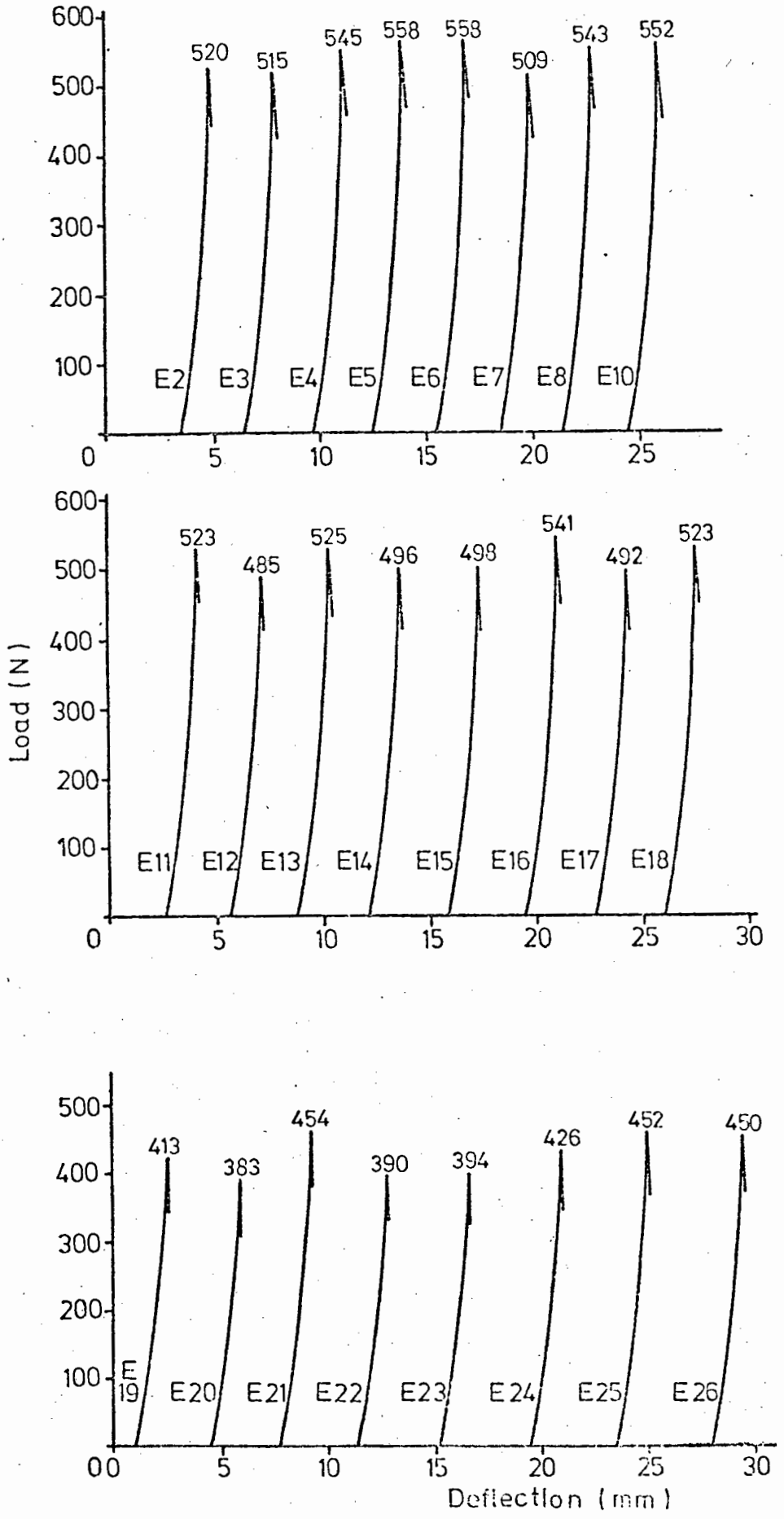
where P = load of failure (Newtons)

l = beam length (80 mm)

d = mean depth

b = mean breadth

FIG. 3.11.



Automatic Recording Results from the Tensometer Showing Failure Loads (in Newtons) for Specimens in Bending, Three Point Loading.

POROSIMETER

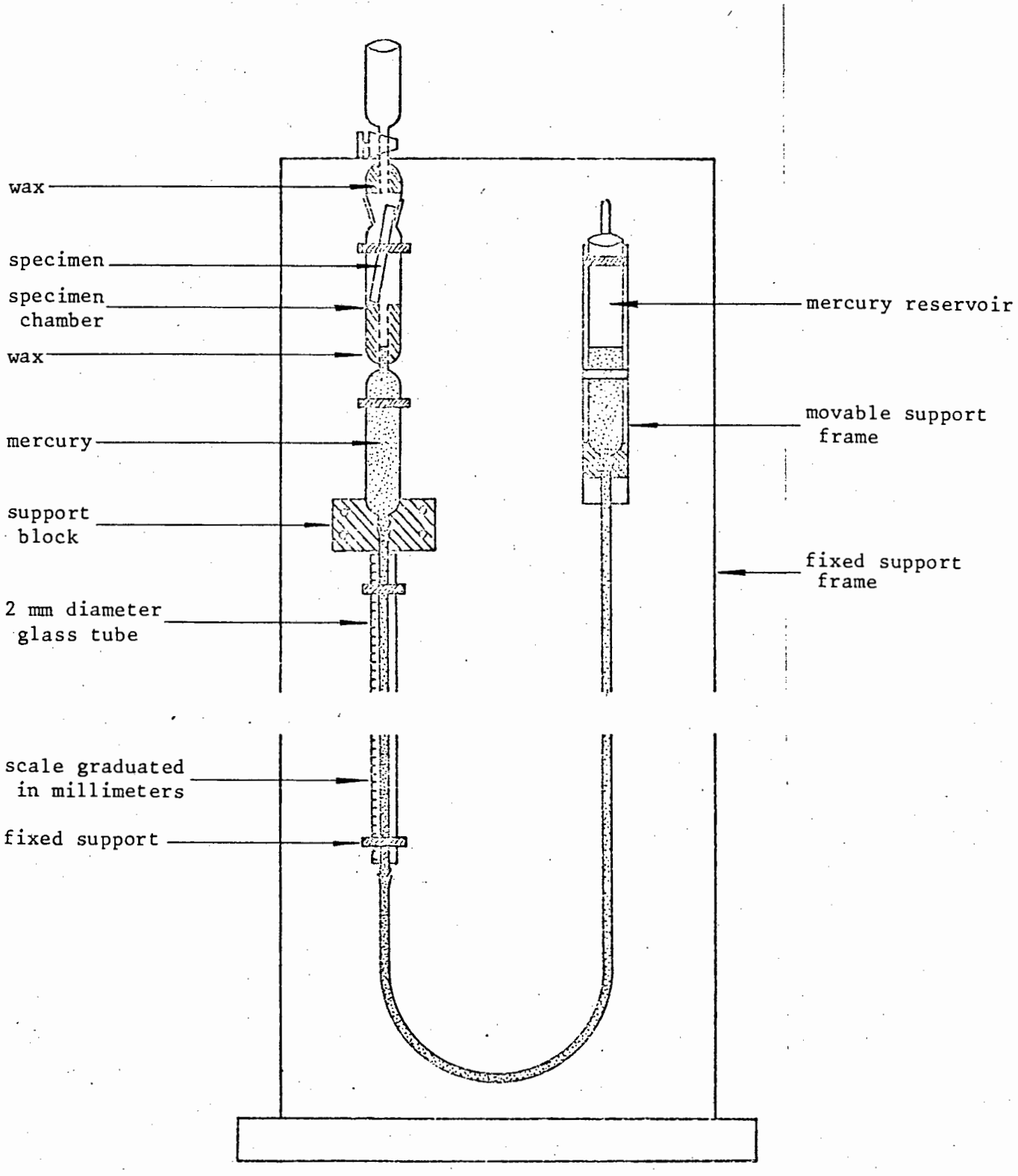


FIG. 3.12.

OPERATION OF POROSIMETER

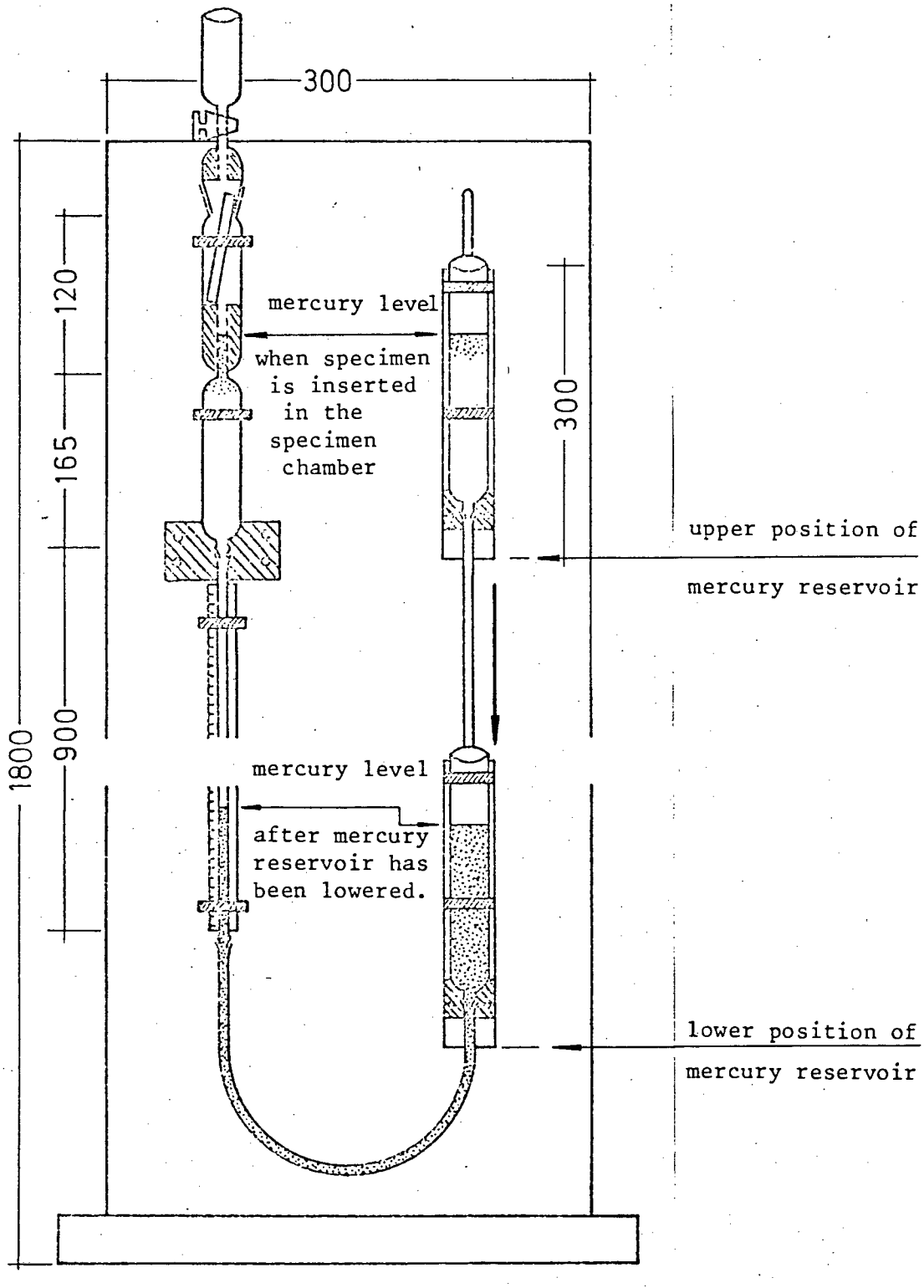


FIG. 3.13.

FIG. 3.14.

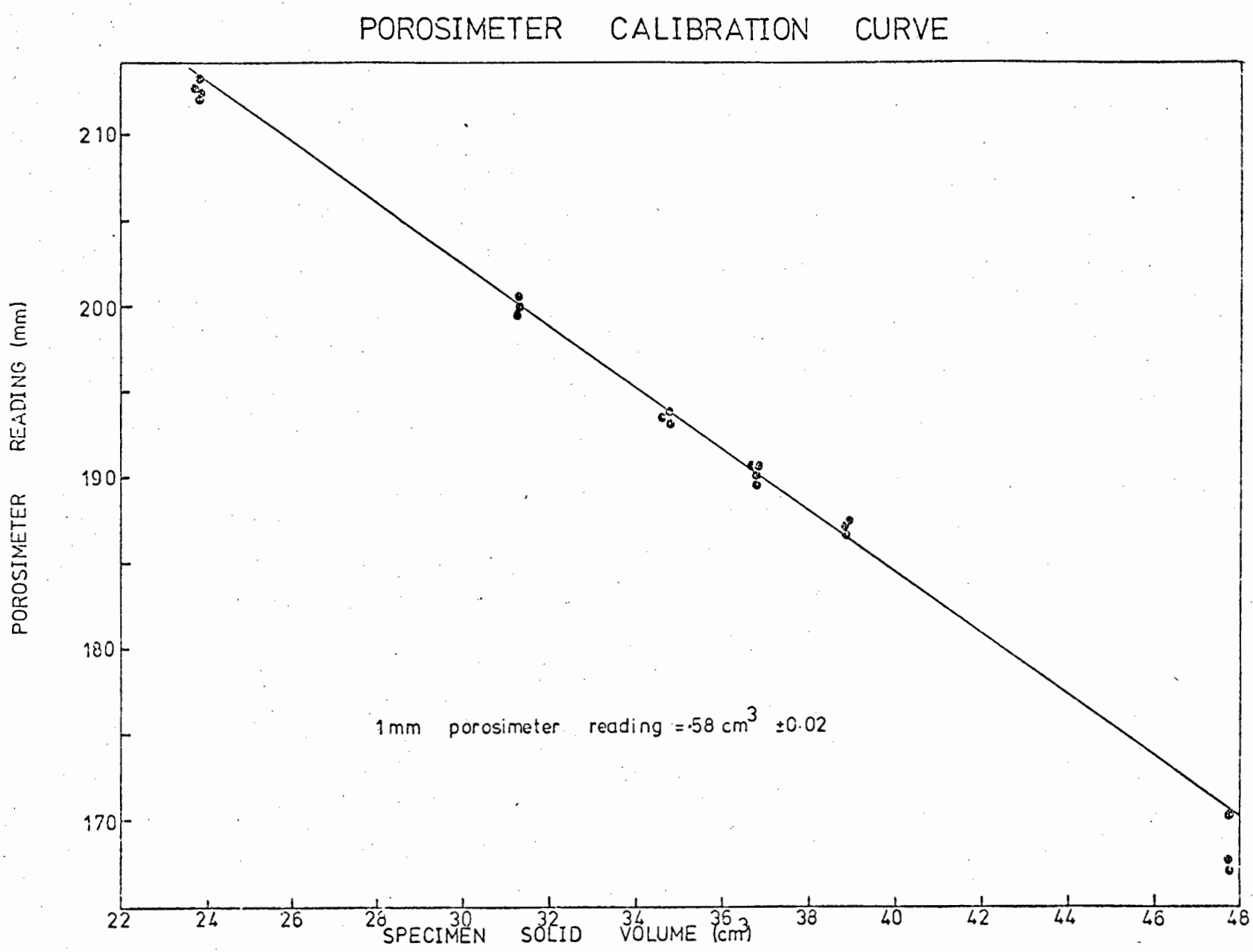

POROSIMETER CALIBRATION CURVE
POROSIMETER READING (mm)
210
200
190
180
170
1 mm porosimeter reading = ·58 cm³ ±0·02
22
24
26
28
30
32
34
36
38
40
42
44
46
48
SPECIMEN SOLID VOLUME (cm³)

PLATE 3.1: Perspex Mould Box

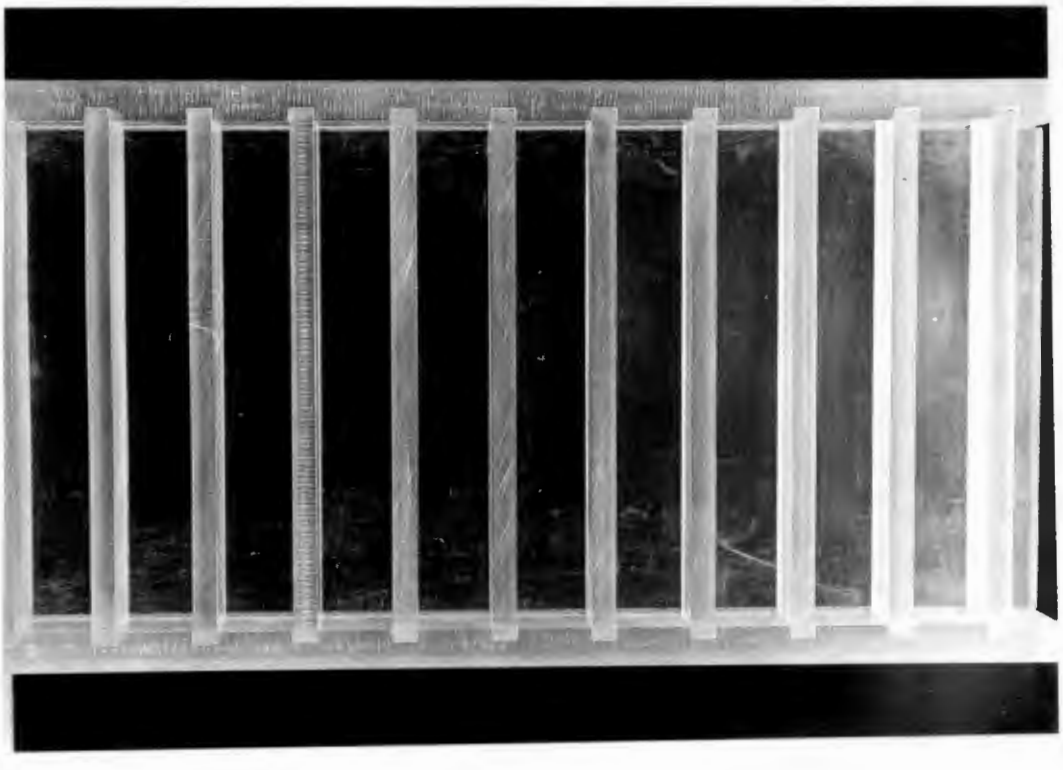
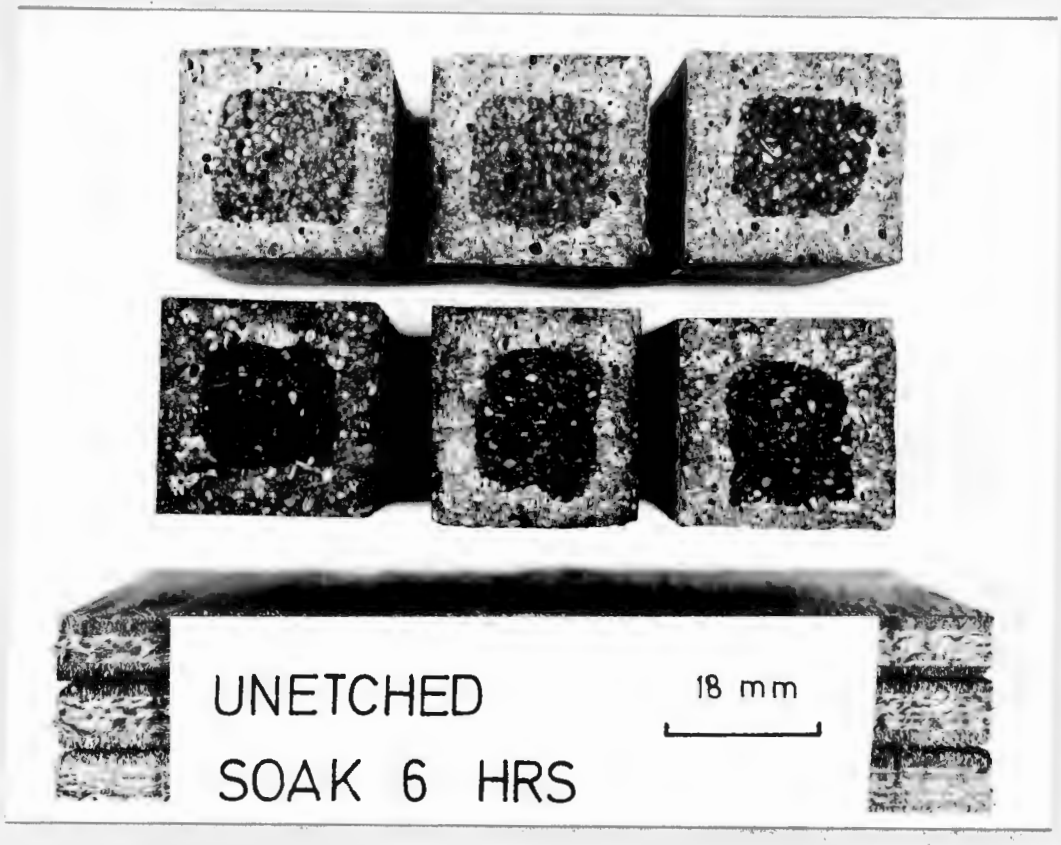


PLATE 3.2: The Standard Ink Staining Technique for Illustrating Impregnation Depth



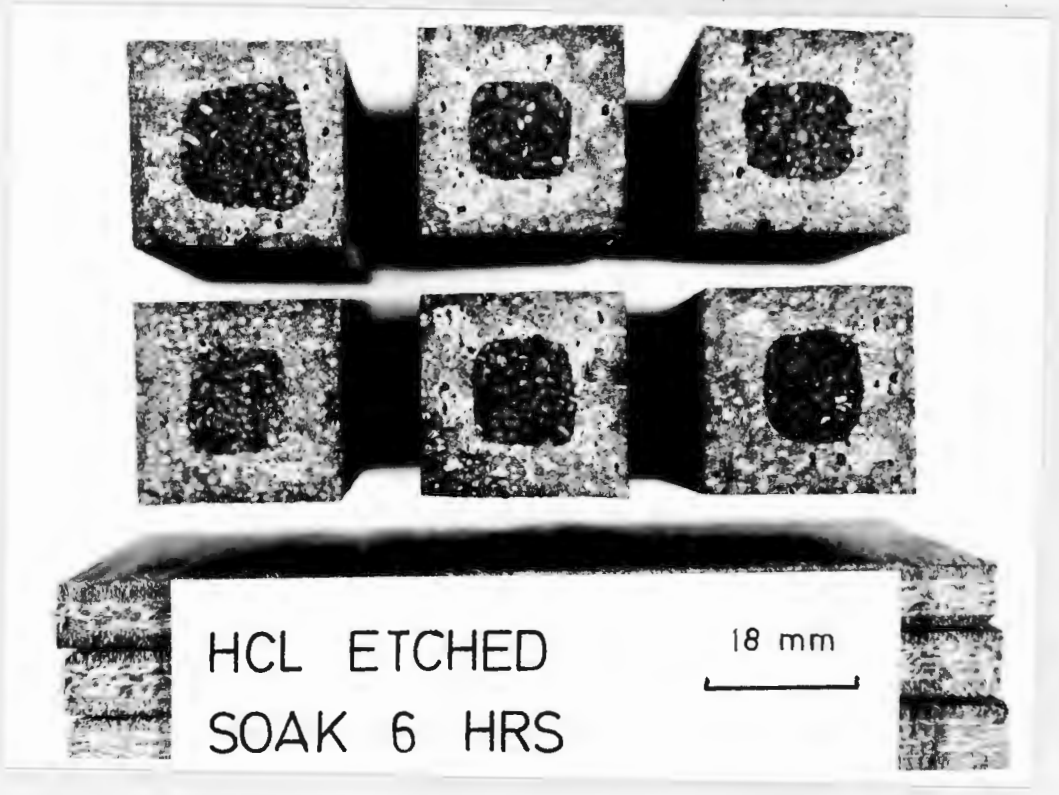


PLATE 3.3: Epidiascope used for Facilitating Impregnation Depth Measurement

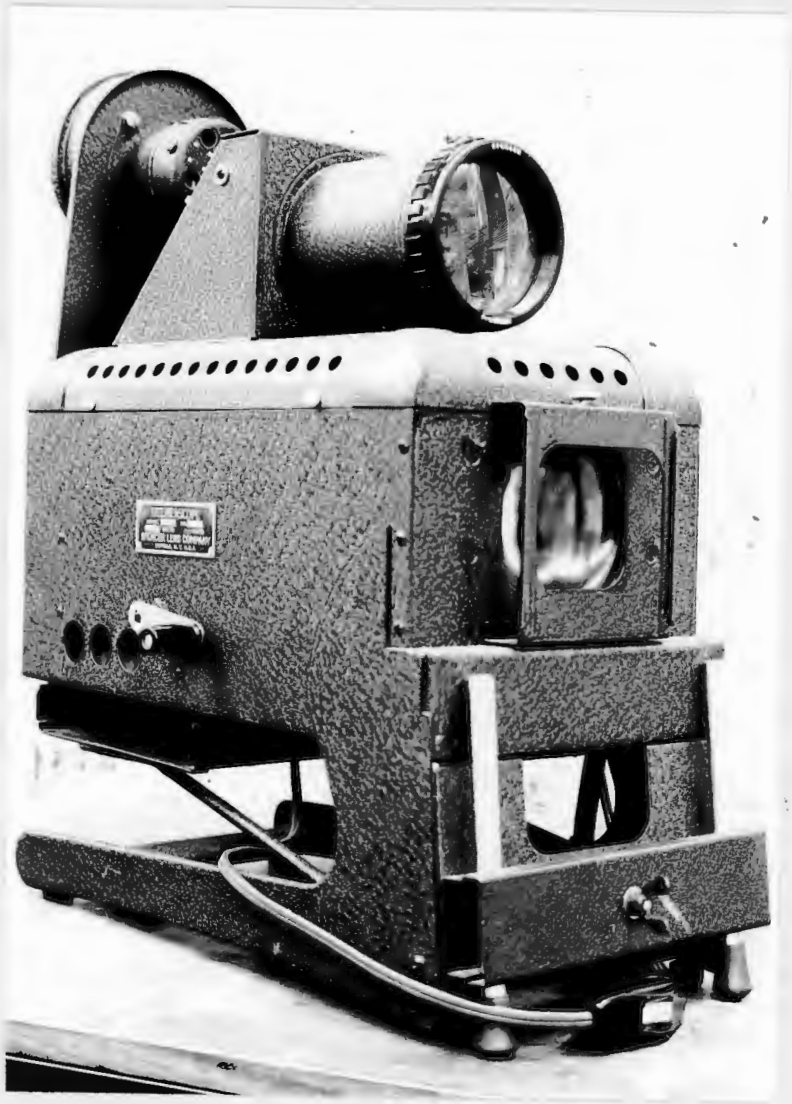


PLATE 3.4: Hounsfield Tensometer

CHAPTER 4

4. SPECIFIC TEST PROCEDURES AND TECHNIQUES

4.1 INTRODUCTION

The previous chapter introduced the basic building blocks, the materials, general impregnation procedure and testing and measurement apparatus that was generally common to all subsequent work. This chapter describes specific test programs that were conducted to investigate the effects of specific parameters on performance. In particular, this includes the very important areas of drying temperature, soaking time and vacuum and pressure effects, as well as the sections on solvent dilution, differential pressure investigations and acid corrosion, the latter two of which were more of a preliminary nature.

4.2 TEMPERATURE EFFECTS AND SPECIMEN DRYING

4.2.1 Introduction

It is reasonable to expect (see section 2.6.2) that temperature affects polymer impregnation of concrete in two principal ways. Firstly, the temperature to which the concrete (or polymer) is subjected before impregnation, affects (i) the strength of the concrete, (ii) the time required to achieve total drying (to constant weight), and (iii) the depth and degree to which concrete can be impregnated. Secondly, the temperature of the concrete or polymer at the time of impregnation would presumably have some effect on the penetrability, or degree of impregnation, that can be achieved. The effect of prior heating (and subsequent cooling) of the polymer before impregnation has yet to be investigated, but it is believed to have a deleterious effect. The experiments conducted were thus chosen accordingly, bearing in mind the discussion above.

The drying process was necessary for various reasons:

(a) The residual moisture content should as closely as possible be identical in all specimens if results of experiments are to be comparative.

(b) Any significant quantity of water left in the pores of the mortar specimens may inhibit the penetration of polymer

into the pores.

(c) Removal of all evaporable water effectively arrests any further curing of the specimen so that the "porosity", for present purposes, remains constant for the duration of subsequent experiments on the particular specimen.

(d) In addition, the removal of water from the specimens ensures repeatability for subsequent testing measurements. For example, spurious readings which could result from moisture contamination in the porosimeter are obviated.

Although the effect of drying temperatures on the strength of concrete has been reported,(8, 12, 16) it was decided to carry out the experiment described below in Section 4.2.2 to determine the effect of various drying temperatures on the strength of the particular concrete mix used in this project. This provided a baseline with which subsequent strength measurements and improvements, arising from impregnation, could be compared.

4.2.2 Determination of the Effect of Drying Temperature on Concrete Strength

Procedure

Twenty five concrete specimens were prepared following the procedure mentioned in sections 3.2.1 - 3.2.5, and using the materials described in sections 3.1.2 - 3.1.4 (Later Series, sand/cement ratio = 2,5 : 1).

After air drying for 24 hours, 5 specimens were placed in an evacuated desiccator and the remaining 20 specimens were placed in an oven and dried for 24 hours at 50°C (see plate 4.1). After drying, a further 5 specimens were removed and placed in the desiccator to cool, the remaining 15 specimens being dried at 90°C for 24 hours. This process was repeated for temperatures of 125°C and 175°C.

A second batch of 25 specimens was similarly prepared and dried in reducing multiples of 5 at temperatures of 110°C, 150°C, 200°C, 250°C and 300°C.

All specimens were then placed in the test rig of the Tensometer (see section 3.5.2) and loaded in flexure to failure. Modulus of Rupture values were calculated (see fig. 3.10),

subsequent to vernier calliper measurements, and plotted (see fig. 5.1 in Chapter 5). The results are given in section 5.2.2, Chapter 5, and as can be seen, there appears to be a plateau in strength in the vicinity of 100 - 150°C.

4.2.3 Determination of the Minimum Period for Drying

The previous section described the effect of drying temperature alone on concrete strength. This section deals with the time required to achieve constant weight at such temperature which can be considered as representative of the approximate maximum of strength. This was undertaken to facilitate speed of testing and to determine the period necessary to dry specimens fully, but at the same time not wasting oven drying time. In addition, tests to determine subsequent re-absorption of moisture were also undertaken simultaneously to examine the seriousness of short periods out of the desiccator.

Procedure

Six specimens were cast following the procedure mentioned in sections 3.2.1 - 3.2.5 and using materials described in sections 3.1.2 - 3.1.4 (Initial Series, sand/cement ratio = 2,75 : 1).

After 9 days of underwater curing and at an age of 10 days, each specimen was removed from the water bath, touch dried with absorbent paper and weighed before placing in an oven operating at a temperature of 115°C ($\pm$ 5°C). After 5 minutes in the oven, specimens were cooled in a desiccator containing silica gel for 10 minutes and weighed again. This process was repeated for varying periods of time the specimens spent in the oven.

The results are shown and plotted (see fig. 5.2, table 5.1, Chapter 5), and are fully discussed in section 5.2.3, Chapter 5.

4.2.4 Variation of Impregnation Depth with Drying Temperature

For this series, five groups from a batch of 25 specimens were variously dried at the same age and for the same time at: room temperature in air, 50°C, 110°C, 180°C and 250°C and then cooled in a desiccator. All the specimens were impregnated and subsequently cured for 7 days before being measured for impregnation depth and strength (M.O.R.) in the standard manner. The results are shown in section 5.2, Chapter 5.

4.2.5 Determination of the Effect of Concrete Impregnation Temperature

In this series of tests, specimens were dried at 110°C in the usual way and then impregnated at this temperature. In addition, specimens which had also been dried to this temperature, but allowed to cool in a desiccator until at approximately 50°C, were also impregnated. Control impregnation tests which had experienced an identical history but allowed to cool to room temperature, were also conducted. The soaking in all cases in this section was of 5 hours' duration. The results are given in section 5.2, Chapter 5.

4.3 THE EFFECT OF SOAKING TIME ON DEGREE OF IMPREGNATION

4.3.1 Introduction

The easiest method of achieving impregnation was simply to allow a concrete specimen to soak totally submerged in polymer. The economic advantages of this method of impregnation are apparent when it is realised that large scale and very costly mechanical vacuum and pressure vessels would be required in a full scale factory pressure impregnation. This is particularly important, for example, where pipes of 1,8 m diameter and larger, often weighing over 6 tonnes, are to be impregnated. An experiment described below was carried out to determine the effect of time of soak of concrete specimens in pure polymer, on depth of impregnation, as this would provide a basis against which other methods using pressure, vacuum, dilution of the polymer etc., could be measured and compared (see sections 4.4 - 4.7). In effect, the rate of impregnation was to be determined and, in addition, the optimum impregnation time to be estimated from the change in this rate. The effect of prior etching was also briefly examined.

4.3.2 Procedure

(a) Two batches of 25 specimens each were prepared, as described in sections 3.1.2 - 3.1.4 and 3.2.1 - 3.2.5 (Initial Series, sand/cement ratio = 2,75 : 1).

(b) The 50 specimens were then divided into 10 groups of 5 which were submerged in the pure polymer (without any addition of catalyst), for periods of ½, 1, 2, 3, 5, 6, 8, 12, 24 and

48 hours. After removal from the polymer, excess polymer was wiped off with absorbent paper and the specimens were placed on the shelf to cure in air for seven days.

(c) Subsequent to flexural strength testing (see section 3.5), the depth of impregnation was determined by the composite procedure involving ink staining, epidiascope and digitiser techniques (see section 3.4), and results plotted graphically (see section 5.3, Chapter 5).

(d) In addition, the effect of etching specimens prior to soaking was examined and compared with non-etched, but identically soaked specimens. The etch consisted of removing the surface film of cement from specimens by submerging them for 15 to 30 seconds in 20% hydrochloric acid and then washing thoroughly with water.

Results are given and fully discussed in section 5.3, Chapter 5.

4.4 PRESSURE IMPREGNATION

4.4.1 Introduction

The success of polymer impregnation of concrete under various conditions of pressure and vacuum has been reported,(12, 16, 17, 23) and it was considered an important aspect which needed further investigation in relation to the impregnation of the particular polymer, used in this project.

Consideration was later given to a possible improvement in the rate of impregnation by subjecting a flat circular disc of concrete to a pressure gradient, as opposed to a simple application of pressure or vacuum, by applying pressure to one side and a vacuum to the other (see section 4.6).

A relatively low cost pressure/vacuum chamber was constructed for this purpose and is described in the following sections.

4.4.2 Apparatus

A steel pressure chamber was constructed in which specimens could be impregnated under various pressures from a vacuum of -85 kPa representing 650 mm of mercury to a pressure of +400 kPa (see fig. 4.1, plates 4.2, 4.3).

The main body of the chamber was constructed from a 10 mm thick, 260 mm internal diameter water pressure pipe welded to a flange in which 8 holes were drilled and a 6 mm deep groove machined for a 300 mm diameter rubber O-ring. The flange was coupled to a circular steel cover plate, which, together with 8 bolts and the O-ring, ensured an air-tight seal. The base plate was a 12 mm thick steel disc welded to the opposite end of the pipe.

The following connections were drilled and tapped in the side of the pipe using 3/8" B.S.P. threads:

(i) Pressure Gauge (0 to +400 kPa).
(ii) Vacuum Gauge (0 to -100 kPa).
(iii) Hand operated pressure release valve.
(iv) Air inlet connection (Pressure connection).
(v) Air exhaust connection (Vacuum connection).

The air inlet and exhaust points were connected with two high pressure flexible plastic pipes, each 1 m long, through two non-return valves to a type GAST 0522-V4-G21DX vacuum/ pressure pump fitted with two 3/8" B.S.P. gate valves, one on each of the pressure and vacuum pipes.

4.4.3 General Procedure

The following procedure was adopted:

(i) Following placement of the specimen and associated impregnation apparatus in the pressure chamber, the cover plate was secured, tightening the bolts in opposing order sufficiently to ensure an airtight seal but still with regard to the integrity of the O-ring.

(ii) Prior to either pressure or vacuum operation, the pressure release valve on the side of the chamber was closed.

(iii) Subsequently for pressure operation the pressure line gate valve and the pump suction valve were opened, and the vacuum line gate valve and pump pressure valve were closed. For the vacuum condition, the operation of the various valves was reversed.

(iv) With the pump running, any desired pressure (or vacuum) within the limits of the apparatus could be achieved and maintained by suitable adjustment of the pump pressure (or vacuum)

valves. A certain amount of the air delivered by the pump could be released to the atmosphere by way of the pump pressure valve, while the remaining portion would be diverted under pressure to the chamber. In this way, a constant pressure could be maintained in the chamber.

During testing of the pressure apparatus, the maximum pressure and vacuum levels achieved and maintained indefinitely were as follows:

Pressure:	+250 kPa	($\pm$ 38 lbs/in^2)
Vacuum:	-85 kPa	($\pm$ 13 lbs/in^2)

Operation of the apparatus is uncomplicated and quick; the average time taken from the insertion of the specimen in the chamber to attaining the maximum pressure or vacuum is typically less than 4 minutes.

In subsequent work, in order to be able to subject the concrete to a pressure gradient, modifications to the pressure chamber consisted of making a new lid with tapped holes for the pressure pipe inlet connection, a pressure gauge and a hole, with a plug, through which the polymer could be introduced. A small second pressure chamber was constructed by welding two flanges to a short length of 100 mm diameter steel pipe; this apparatus being subsequently bolted to the lid of the main pressure chamber and the concrete disc, as shown in fig. 4.2 and plate 4.4. All bolted joints were sealed with flat annular rubber gaskets, and threaded holes with taped screw plugs.

By attaching the pressure inlet line to the lid and sealing the pressure hole in the main pressure vessel, pressure could be built up in the small chamber while a vacuum could be maintained in the main chamber. In this way, a pressure gradient, typically from +250 to -85 kPa, could be set up across the concrete disc. Polymer was normally introduced through the hole in the new lid, which could then be sealed with the plug prior to operation of the air pump.

4.4.4 Pressure Impregnation Tests

At this stage in the project, the effect of pressure on the impregnation of polymer on the mortar specimens was unknown, and to gain an initial understanding of this, the experiments described in the following sections were conducted.

Procedure 1

Twenty-four specimens (designated "D") were chosen from a batch of 26 specimens prepared as described in sections 3.2.1 - 3.2.5 and using the materials as mentioned in sections 3.1.2 - 3.1.4 (Initial Series, sand/cement ratio = 2,75 : 1). These were divided into three groups of 8 specimens each. After drying and cooling, those specimens to be impregnated were weighed and their solid volumes determined in the porosimeter (see section 3.6.2). Catalyst was added to the polymer in amount of 3 ml/litre, and thoroughly mixed.

The impregnation procedure for the three groups of specimens was as follows.

D1 - D8 : Control specimens, not impregnated.

D9 - D16 : Dipped into the polymer, removed and placed on two parallel steel rods, exposed to the atmosphere for 30 minutes, cleaned of excess polymer and placed on the shelf to cure in air.

D17 - D24: Similarly coated with polymer, placed on steel rods inside the pressure chamber, exposed to a pressure of +250 kPa for 30 minutes, cleaned of polymer and stored.

After curing for 7 days, the impregnated specimens were again weighed and their solid volumes determined in the porosimeter.

Subsequent to vernier calliper measurements to determine their dimensions, both control and impregnated specimens were loaded to failure in the Tensometer and the Modulus of Rupture of each determined.

Results and discussion are given in section 5.4, Chapter 5.

Procedure 2

Further work was undertaken to observe the effect of pressure on totally submerged specimens. Procedures and materials for the manufacture and preparation of the specimens were similar to those mentioned in the previous Procedure 1.

A batch of 24 specimens was divided into 4 groups of 6,

submerged in uncatalysed polymer, and impregnated under pressure as follows.

6 specimens: 100 - 150 kPa for 15 minutes

6 specimens: 100 - 150 kPa for 60 minutes

6 specimens: 200 - 250 kPa for 15 minutes

6 specimens: 200 - 250 kPa for 60 minutes

After impregnation, all specimens were cleaned of excess polymer and cured in the air for 7 days. Subsequent to vernier calliper measurements, the impregnated specimens were tested for Modulus of Rupture in the Tensometer (see section 3.5.2) and for depth of impregnation using the standard ink staining technique (see section 3.4.2).

To determine whether the differences in the means of the results of each test of each group of 8 specimens were significant, the Standard Deviation was determined for each group, where:

$$\text{Standard Deviation } S = \frac{(x - \bar{x})^2}{n - 1}^{\frac{1}{2}}$$

where x = each individual result

$\bar{x}$ = mean of all results in one group and one test

n = number of results in one group (i.e. 8)

Results are given and discussed in section 5.4, Chapter 5.

4.5 VACUUM IMPREGNATION

4.5.1 Introduction

The effect of the application of a vacuum during the impregnation process is significant in reducing impregnation time and achieving greater depths and rates of impregnation. This has been reported in several papers and references.(15, 16, 17, 23) It was considered that a greater depth of impregnation would provide a correspondingly increased corrosion protection to concrete sewer pipes, and tests to confirm and evaluate this important aspect of impregnation procedure were therefore carried out as described below.

4.5.2 Vacuum Impregnation - Initial Series

To determine the general effect of vacuum on the impregnation of the specimens in a manner analogous to pressure in

4.4.4, a batch of specimens was prepared in the usual manner, grouped, weighed and measured in the porosimeter and impregnated with catalyst-activated polymer as follows.

E2 - E10 : Totally immersed in polymer, kept under a vacuum of -85 kPa for 30 minutes, and while still immersed, exposed to atmospheric pressure for 30 minutes, removed, cleaned and stored.

E11 - E18 : Also immersed, kept under a vacuum of -85 kPa for 15 minutes, then a pressure of +250 kPa for 15 minutes, and similarly removed, cleaned and stored.

E19 - E26 : Control specimens, not impregnated.

After curing in air for 7 days, the specimens were similarly weighed, measured in the porosimeter and tested in the Tensometer after their dimensions had been measured using vernier callipers. Results are given and discussed in section 5.5, Chapter 5.

4.5.3 Suspended and Submerged Evacuation: Modification of the Pressure Chamber

In order to be able to subject specimens to a vacuum before submerging them in polymer, and to submerge them while still under a vacuum, the lid of the pressure chamber was modified. As shown in fig. 4.3 and plates 4.5 and 4.6, an airtight piston rod was fitted through the lid; the airtightness being maintained by a vacuum seal. A sieve basket was suspended from the piston by means of wire.

With the piston fully withdrawn, the specimens could be subjected to a vacuum while suspending them in the basket above the polymer liquid. By depressing the piston slowly, the specimens could then be submerged into a beaker of polymer while still under vacuum (see fig. 4.3).

Two methods were used for evacuating the specimens. Firstly, the specimens were evacuated while being suspended in the basket above the polymer, and then submerged while still under vacuum. Secondly, specimens were evacuated only after being submerged. A vacuum of -85 kPa was used throughout the test.

Specimens were prepared as previously described (see

sections 3.1.2 - 3.1.4 and 3.2.1 - 3.2.5, Initial Series, sand/cement ratio = 2,75 : 1).

After curing and drying, the batch of 25 specimens was divided into 5 groups of 5 specimens each, and impregnated with uncatalysed polymer as follows.

(a) Evacuated for 15 minutes while suspended, then submerged and soaked for 3 hours.

(b) Evacuated for 15 minutes while submerged, then soaked for 3 hours.

(c) Evacuated for 60 minutes while suspended, then submerged and soaked for 3 hours.

(d) Evacuated for 60 minutes while submerged, then soaked for 3 hours.

(e) Control specimens: soaked for 3 hours.

After cleaning and curing, Modulus of Rupture and depth of impregnation were determined as described in sections 3.5.2 and 3.4.2, subsequent to vernier calliper measurements.

Results are given and discussed in Section 5.5, Chapter 5.

4.5.4 Evacuation and Time

To determine the effect of time of exposure to vacuum on impregnation depth, the following experiment was conducted.

Two batches of 24 specimens each were cast and prepared as previously mentioned (Later Series, sand/cement ratio = 2,5 : 1), and divided into 8 groups of six specimens.

The groups were submerged in uncatalysed polymer and impregnated under a vacuum of -85 kPa for periods of $2\frac{1}{2}$, 5, $7\frac{1}{2}$, 10, $12\frac{1}{2}$, 15, $17\frac{1}{2}$ and 20 minutes, and soaked in the polymer under atmospheric pressure for 3 hours.

After removal and cleaning, specimens were cured in air for 7 days and subsequently broken in the Tensometer and the depths of impregnation determined in the usual manner.

Results are given and discussed in section 5.5.4, Chapter 5.

4.6 DIFFERENTIAL PRESSURE IMPREGNATION

4.6.1 Introduction

As mentioned in section 4.4.1, it was thought that an improved impregnation of concrete might result if the polymer was impregnated into a specimen under the influence of a differential pressure, or pressure gradient. The total pressure difference would then be the numerical sum of the positive pressure and the absolute value of the negative vacuum, e.g. +250 kPa Pressure + -85 kPa Vacuum = +250 + |-85| = +335 kPa. Physically this effect is not the same as applying a pressure of +335 kPa to one side only, as in the first case the polymer is forced into the concrete by the pressure on one side, and also sucked through the specimen from the other side. The removal of the air barrier from the pores of the concrete may prove to be a significant factor in the relative success of this method (as discussed in section 5.5) for achieving optimum impregnation in minimal time.

The main pressure chamber had already been constructed, and it was therefore considered worthwhile to modify the pressure vessel to provide a facility whereby concrete specimens could be impregnated under a pressure gradient. The smaller pressure vessel, described in section 4.4.3, was therefore constructed and used in the following experiment.

4.6.2 Specimen Preparation

200 mm by 150 mm diameter cylinders, and 20 - 40 mm thick by 150 mm diameter discs were cast using the following concrete mix.

Cement:	13,2 kg	
Sand :	27,5 kg	
Stone :	24,3 kg	(Malmesbury shale)
Water :	5,5 kg	(water/cement ratio = 0,42)

Three test cubes were cast simultaneously with the specimens from the same mix, and all concrete was cured under water for 7 days.

After curing, the cubes were crushed and yielded a mean crushing strength of 46,6 MPa, with a standard deviation of 0,5 MPa.

Discs of 25 mm thickness were cut from the cylinders subsequent to air drying for an indefinite period and oven drying for 24 hours at 115°C (± 5°C).

4.6.3 Impregnation Procedure

A disc was bolted into position in the test apparatus as described in section 4.4.3 and the rest of the apparatus assembled. Uncatalysed polymer was poured onto the disc through the polymer inlet to a depth of approximately 20 mm, and the top of the disc was then pressurised to +250 kPa, while the main chamber was evacuated to -85 kPa. A pressure difference of 335 kPa was thus achieved, and this was maintained for 20 minutes.

The impregnated disc was then removed, wiped clean and stored on the shelf to cure in air for 7 days.

The depth of impregnation resulting from this technique was significant and details are more fully discussed in section 5.6, Chapter 5.

4.7 SOLVENT EFFECTS: DILUTION

4.7.1 Introduction

As mentioned in section 2.6.5, the dilution of the polymer greatly affects the rate and depth of impregnation. Initial studies appeared to indicate that small dilution of the polymer with solvent improved impregnation depth and impregnation rate. In such studies, contrary to expectations, the more dilute the polymer was made, the less impregnation depth was achieved, although parallel strength tests were less conclusive than depth measurements. It was felt that relatively small addition of solvent may be sufficient to disrupt the molecular structure of the polymer, resulting in improved impregnation, and to confirm and investigate this aspect further, the following tests were carried out.

4.7.2 Procedure

Several batches of concrete specimens were prepared as described in sections 3.2.1 - 3.2.5 and using the materials mentioned in sections 3.1.2 - 3.1.4 (Later Series, sand/cement ratio = 2,5 : 1).

After drying and cooling as described in section 3.2.5

the specimens were formed into groups of 4 and 5 units each, and impregnated as described below. One group of cast specimens from each batch was not impregnated but simply stored in a desiccator for use as controls; the remaining groups were submerged in various dilutions of Xylene solvent and polymer ranging from 0% to 75% (solvent in polymer). After soaking for 24 hours at atmospheric pressure, specimens were removed, cleaned and cured in air for 7 days.

Subsequent to curing of the polymer, all specimens were loaded in flexure to failure in the Tensometer, and the depth of impregnation of impregnated specimens determined, using the standard staining techniques.

The results are given and discussed fully in section 5.7, Chapter 5.

4.8 SULPHURIC ACID CORROSION TESTS

4.8.1 Introduction

The corrosion of concrete sewers and structures by bacteriologically produced sulphuric acid has been described in detail in Chapter 1. Sulphuric acid concentrations of 5%,(15) 10%(13) and pH of 1,0(4, 5) have been reported in sewers. It was considered that the establishment of a corrosion test system or "cell" using acid concentrations of up to 10% by volume, would constitute an effective accelerated corrosion test. This follows from the large volume of acid available in a litre jar in the laboratory, to the relatively small size of specimen ($\pm$ 39 cm^3), as opposed to a thin film of acid adhering to the large area of a pipe wall in a sewer. Also, the rate of corrosion of concrete in sulphuric acid solutions increases to a maximum at 10% dilution,(15) and falls off with increasing acid concentration. By making use of such a corrosion cell, preliminary accelerated corrosion studies of polymer impregnated specimens were carried out, as described below, on both singly and doubly impregnated specimens. It was thought that a second impregnation, in effect a second polymer layer, might provide superior corrosion resistance over single impregnation.

4.8.2 Procedure: Single Impregnation

Three batches of 24 specimens each, M, N and O, were

prepared using the procedures and materials described in sections 3.2.1 - 3.2.5 and 3.1.2 - 3.1.4 respectively (Later Series, sand/cement ratio = 2,5 : 1).

Twelve specimens from each batch were impregnated by soaking in uncatalysed polymer for 24 hours and curing in air for 7 days; the remaining unimpregnated specimens were stored in the desiccator for use as controls.

Six unimpregnated and six impregnated specimens from each batch were loaded and broken in the Tensometer and the remaining specimens were weighed, measured for volume in the porosimeter (see section 3.6.2) and finally immersed in dilute solutions of sulphuric acid in the following sequence.

Specimens N : 6 unimpregnated control and 6 impregnated specimens immersed in 1%, by volume, sulphuric acid solution.

Specimens M : Similarly immersed in 5%, by volume, sulphuric acid solution.

Specimens O : Similarly immersed in 10%, by volume, sulphuric acid solution.

After immersion in the acid solution for three days, specimens were lightly washed under tap water, air dried for 6 hours, oven dried for 6 hours at 110°C and finally 150°C for 12 hours (see section 3.2.5). After cooling in an evacuated desiccator, mass and volume measurements were recorded and specimens were again immersed in fresh solutions of acid. This process was repeated several times for immersion periods of three days each over a period of three weeks.

The results are presented in graphical form and discussed in section 5.8, Chapter 5.

4.8.3 Procedure: Double Impregnation

The procedure for the preparation, impregnation and corrosion testing of the specimens of three further batches, Q, R and S, was the same as that described in section 4.8.2, with the exception that specimens were impregnated a second time by soaking in uncatalysed polymer for a further period of 24 hours within ½ hour of the first impregnation having been completed.

The results are given and discussed in section 5.8, Chapter 5.

4.9 SUMMARY

The tests described in this chapter form the major part of this study. The apparatus and techniques developed and discussed in Chapter 3 have been used, as described in this chapter, to examine the effect on impregnation capacity of the following parameters:

temperature (including the effect on the concrete itself)

impregnation, or soaking, time

Pressure and Vacuum (coupled with pressurisation time as another variable)

Differential Pressure or pressure gradients, and finally

Corrosion studies, using sulphuric acid on optimally impregnated specimens.

The results and the attendant discussion are given in the next chapter.

FIG. 4.1. PRESSURE CHAMBER

DETAILS AND OPERATION

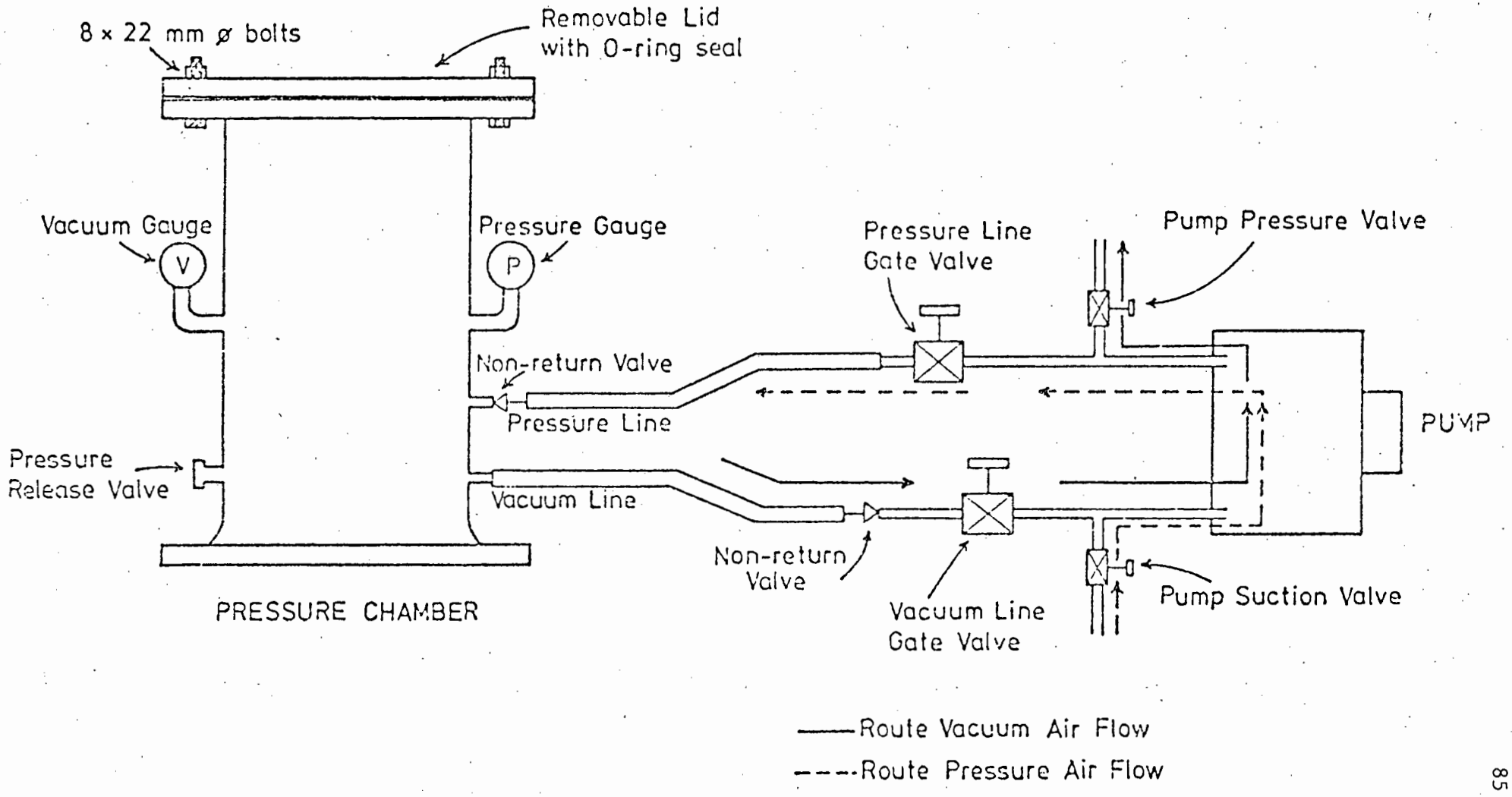


FIG 4.2.

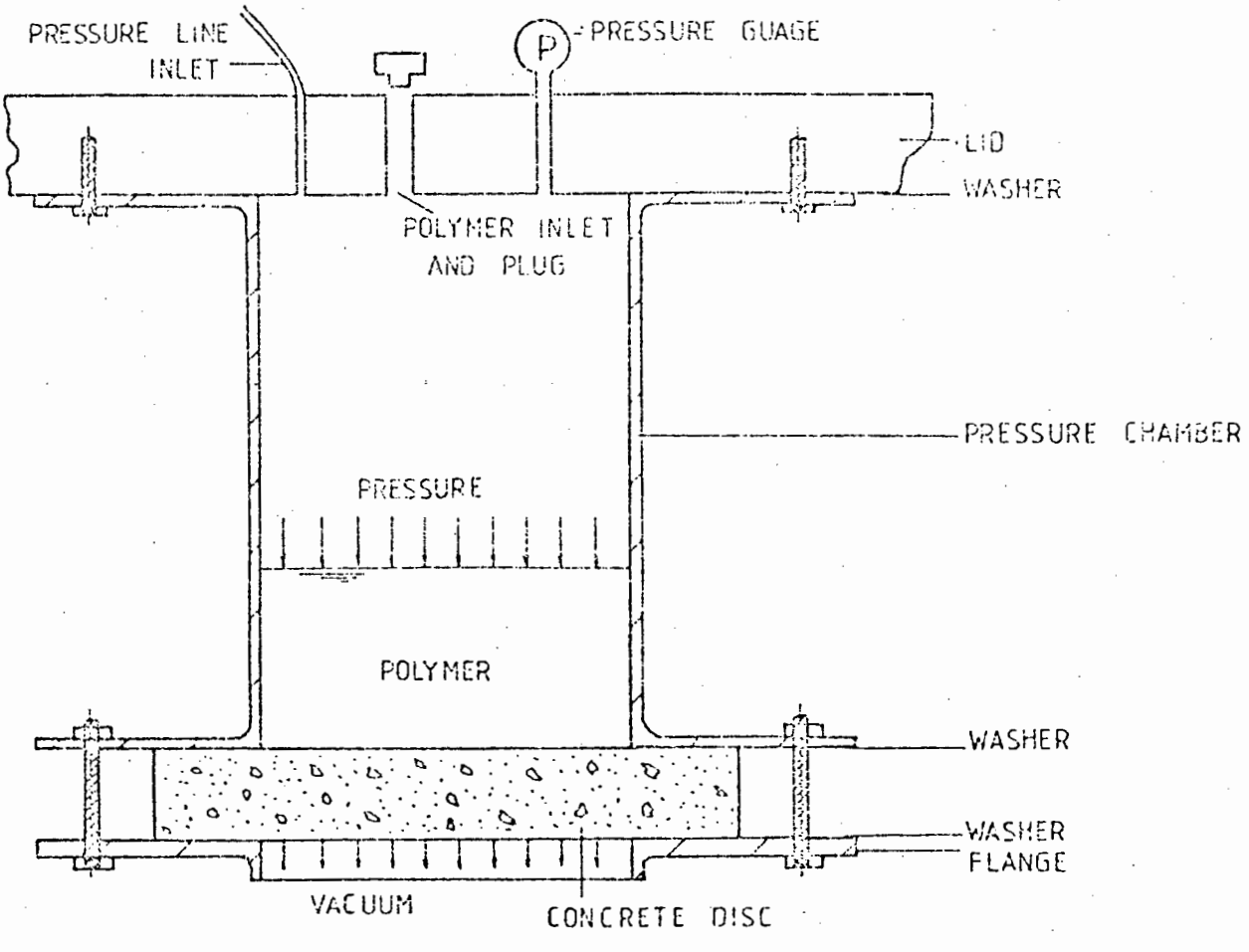
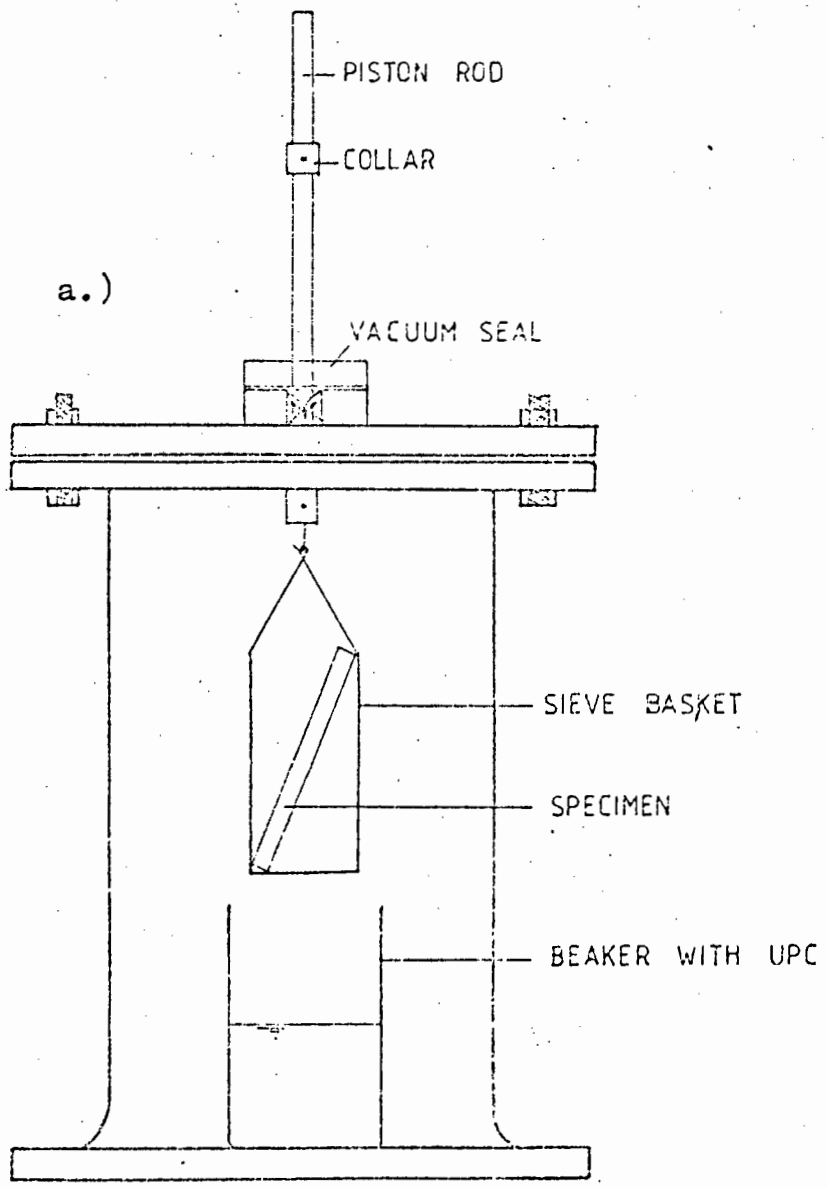
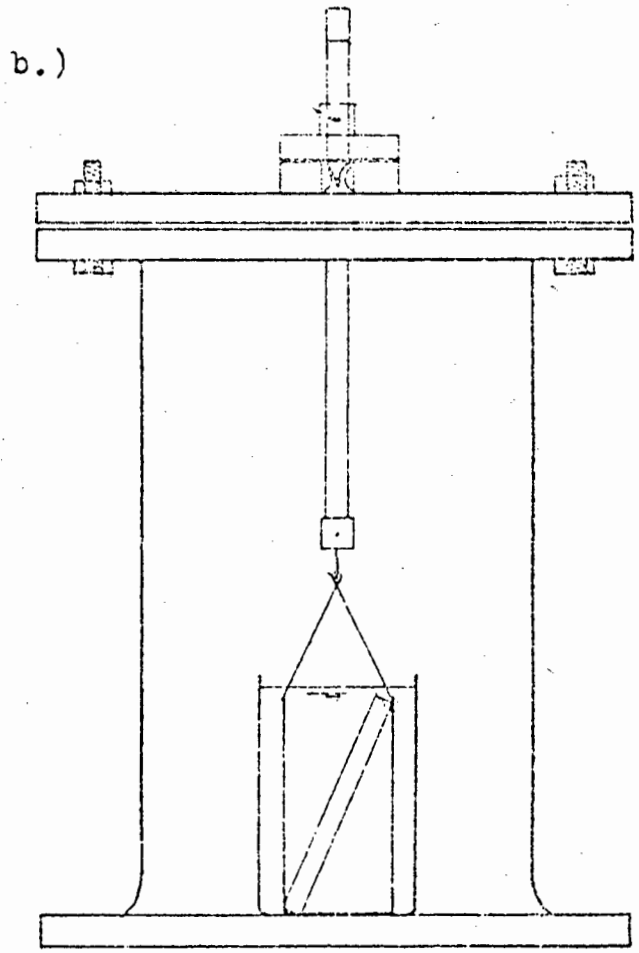

PRESSURE LINE INLET
P
PRESSURE GUAGE
LID
WASHER
POLYMER INLET AND PLUG
PRESSURE CHAMBER
PRESSURE
POLYMER
WASHER
WASHER
FLANGE
VACUUM
CONCRETE DISC

FIG. 4.3

DIAGRAM SHOWING USE OF PISTON AND VACUUM SEAL TO SUBMERGE SPECIMENS WHILE UNDER A VACUUM



SPECIMENS SUSPENDED IN BASKET UNDER VACUUM



SPECIMENS SUBMERGED WHILE STILL UNDER VACUUM

PLATE 4.1: Drying Oven

PLATE 4.2: Pressure and Vacuum Chamber Apparatus (Side View)

PLATE 4.3: Pressure Chamber (Top View) showing Impregnation Specimens

PLATE 4.4: Differential Pressure Apparatus for Concrete Discs

PLATE 4.5: Pressure Vessel Lid with Vacuum Sealed Piston for Submerged and Suspended Impregnation

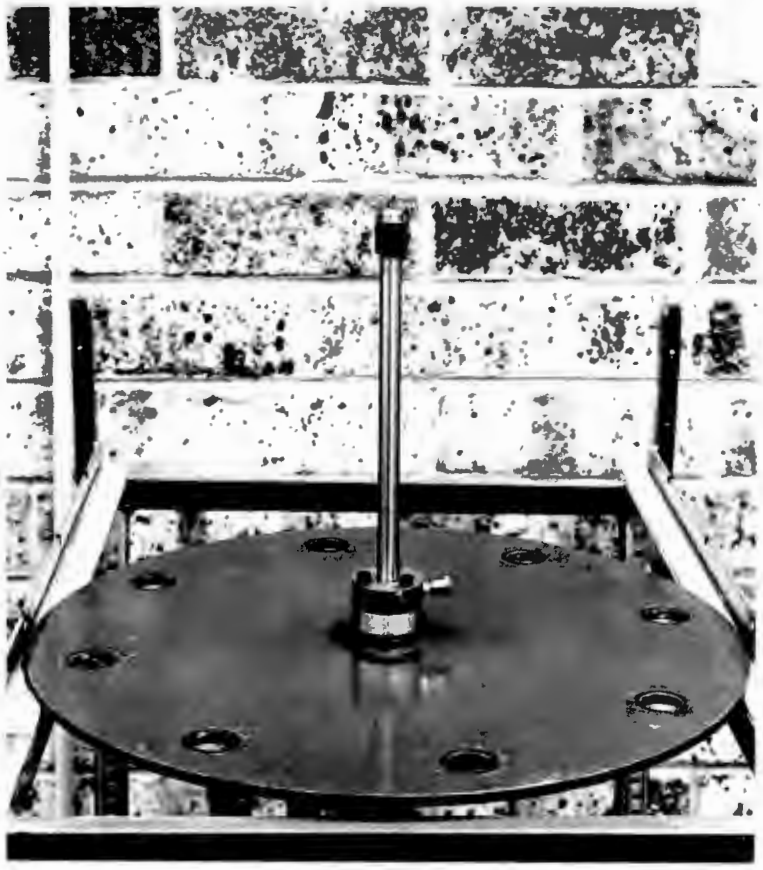
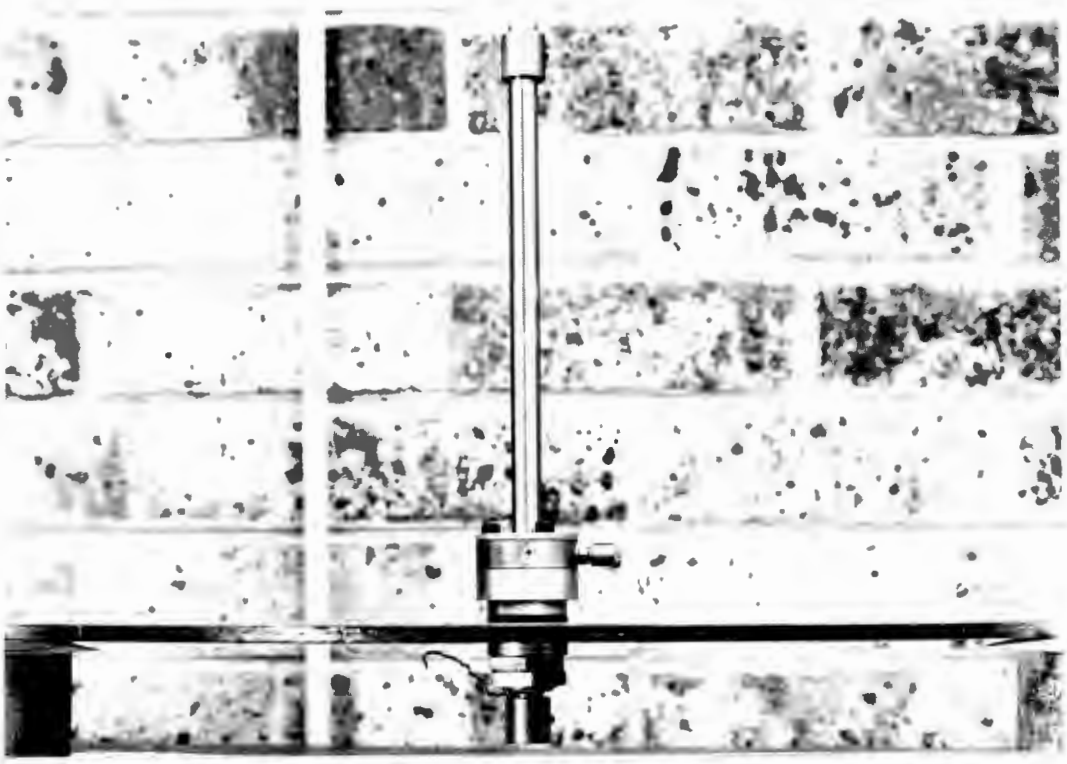


PLATE 4.6 Side View



CHAPTER 5

5. RESULTS AND DISCUSSION

5.1 INTRODUCTION

In this chapter, the results of the experiments conducted as described in Chapter 4 are presented, and observations made during the experimental work, as well as the significance of the results, are discussed. The parameters measured specifically are impregnation depth, breaking strength, i.e. maximum failure load (or, sometimes, Modulus of Rupture), and rate of acid corrosion of impregnated specimens (both by weight, and volume, loss). Impregnation depth was determined from the ratio of impregnated to total concrete cross-sectional areas, as measured by the epidiascope and digitiser process, fully described in section 3.4.2. The Modulus of Rupture, MOR, is derivable from the breaking strength but since the specimens were ostensibly of similar dimensions and tested under the same conditions, it was often thought adequate to describe the concrete strength simply in terms of breaking strength. This assumption was made for all specimens with the exception of the most recent batches concerning corrosion where it was found that wear in the components of the perspex moulds was of such a degree as to make the manufacture of uniformly sized specimens, with special reference to the vibration sequence, very difficult. In these cases each specimen was individually measured after being broken in the Tensometer, and its Modulus of Rupture calculated. Corrosion was measured by monitoring changes in mass, and volume, using the porosimeter (see section 3.6.2). Good correlation was found between the results of both these measuring methods. The recording of volume changes was later discontinued in favour of the more easily performed weight loss recordings, which had the added advantage of giving less scatter.

Some reservation must be placed on some of the results as consistent reproducibility was only partially achieved. Certainly within batches or sets, comparisons of different impregnation variables are perfectly valid but it was difficult to guarantee that results from one batch would be identical to those of another batch under similar conditions. The trends are quite

unmistakable however, and there is a lot of confidence attached to the results mentioned below. For more accurate data, however, further tests would need to be conducted with polymer of a consistent quality. Variation in specimen preparation and curing was reduced to a minimum with presumably the only additional improvement being increased drying time - thereby minimising further dry variation - but the same cannot be said for the polymer, which was extremely variable. Changes in age and storage conditions resulted in viscosity fluctuations and, almost certainly, variations in polymer chain length. This in turn affects the polymer's ability to impregnate concrete. Even polymer very stringently stored in steel containers and of the same viscosity at time of impregnation, showed significant variation in impregnation depth. It would seem, therefore, that besides moisture curing, which increases polymer viscosity, there are further chemical or other reactions which affect the impregnation capabilities, but which are not readily detectable. For full scale development of this work, it would appear essential to have a continuous polymer preparation facility so that the polymer being impregnated is continually fresh.

5.2 TEMPERATURE EFFECTS AND SPECIMEN DRYING

5.2.1 Introduction

Four experiments are described in this section, namely (i) the effect of various drying temperatures on concrete strength, (ii) the length of time required to dry concrete specimens, of the size used in this project, to constant mass, (iii) variation of impregnation depth with drying temperature, and (iv) impregnation of "hot" concrete.

5.2.2 Determination of the Effect of Drying Temperature on Concrete Strength

A graphical plot of the results of experiments described in section 4.2.2 relating to drying temperature and Modulus of Rupture tests is shown in fig. 5.1. These results shown in fig. 5.1 agree reasonably well with previous published work that was, for example, discussed in section 2.6.2, and displayed in fig. 2.3.

Although scatter is relatively large, it appears that the strength of the dried concrete initially increases with rise in drying temperature to a plateau in the temperature range 100°C to 150°C, and subsequently displays rapidly decreasing strengths at higher temperatures. This increase is in the region of 15% to 20%, and may possibly be due to a massive increase in the rate of hydration of the cement for a short period of time, due to the increased rate of chemical activity caused by the higher temperatures, i.e. "accelerated curing".(7, 30) At higher temperatures the free water evaporates and the hydration process is rapidly arrested. At higher temperatures still, breakdown of the hydrates occurs(31) with a consequent significant loss of strength.

This drying temperature plateau of 150°C compares well with the work of Fulton,(8) Troost(12) and others,(16, 31, 23) where it has been reported that a sustained temperature of 150°C has a negligible deleterious effect on concrete strength, and that this temperature is optimum for drying concrete prior to impregnation. This confirmed earlier work(12) which found that maximum flexural strength is achieved with specimens dried at approximately 145°C before impregnation.

5.2.3 Determination of the Minimum Period for Drying

The effect of an adequate drying time, or a lack thereof, is of great importance in the impregnation of concrete, and has been widely reported.(12, 16, 17, 23) Indeed it has been reported that concrete dried at temperatures below 100°C could not be impregnated at all.(12) It appears that both temperature and the time of exposure at that temperature are important parameters.

The results of the drying test described in section 4.2.3 are given in table 5.1, and are plotted in linear/log graphical form in fig. 5.2.

From these curves it appears the minimum period required for adequate drying (i.e. drying to near constant mass) of the specimens is approximately 5 hours, after which subsequent weight decrease through loss of moisture is apparently negligibly small.

The dotted lines on the curves, fig. 5.2, show an interesting effect when the specimens were left out of the desiccator

after cooling. In all cases the specimens appeared to gain weight due to absorption of moisture from the atmosphere (points 1 and 2 on the curves), this moisture being lost on subsequent redrying (points 3 and 4). As can be seen, however, the relative amount of weight increase on exposure to the atmosphere is very small and for the purposes of these tests the effects of the re-absorption of moisture during handling and testing was regarded as negligibly small. To minimise this already small effect, however, the time spent by the specimens out of the desiccator during experimental testing was reduced to a minimum.

The results showed a marked decrease in the weight of specimens as a result of moisture loss from oven-drying, over a period of about 5 hours, and only small subsequent weight gain on re-exposure to the atmosphere, and for the present purposes were regarded as "dry" for the purposes of testing.

In subsequent drying, to minimise the already unlikely probability of cracking wet specimens when placed in the oven, specimens were air-dried by exposure to the atmosphere for 24 hours before being placed in the oven for at least 24 hours.

5.2.4 Variation of Impregnation Depth with Drying Temperature

The series of experiments described in section 4.2.4 effectively parallel those mentioned in section 5.2.3. The results are shown in fig. 5.3, where it can be seen that impregnation depth and consequently strength, increase with temperature, at approximately 150°C After this stage the loss of hydrate strength in the cement itself cannot be overcome by the strength gain due to polymer impregnation and the impregnated strength curve (fig. 5.3) consequently falls, but the drop is relatively gradual. Observations of increasing depths of impregnation with increasing drying temperature are consistent with those of impregnated auto-claved concrete, and is thought to be due to improved shape of the pores of the cured concrete. (17, 23).

It appears, therefore, that a drying temperature of approximately 150°C is the optimum as far as the strength of both unimpregnated and impregnated concrete is concerned.

5.2.5 Determination of the Effect of Concrete Impregnation Temperature

Tests conducted on the effects of temperature of the concrete at time of impregnation on depth and strength have been described in section 4.2.5. The results of these "hot concrete" tests are shown in fig. 5.4. The results are perhaps too sparse to be conclusive, but it appears that the temperature at the time of impregnation has less effect than the actual degree of drying or moisture removal as mentioned earlier. This probably masks any effect due to small variations in viscosity that might be expected at higher temperatures. In addition, the effect of temperature on the polymer itself is still to be determined and this area of study is one which could do with further research. However, the value of this approach is debatable and for time considerations no further tests were conducted.

5.3 THE EFFECT OF SOAKING TIME ON DEGREE OF IMPREGNATION

5.3.1 Introduction

The results of the series of experiments described in section 4.3 to measure the effect of soaking time on impregnation depth are discussed here. Since pressure and vacuum apparatus is expensive, any undertaking to impregnate pipes on a large scale would need to be considered from an economic standpoint, and if time and storage space are sufficient, it may well be preferable simply to soak units rather than pressure (or vacuum) impregnate them.

5.3.2 Results and Discussion

The results of impregnation depth for non-etched and etched specimens, which had been impregnated by soaking for various times, are shown respectively in fig. 5.5(a) and 5.5(b). It can be seen that impregnation depth, D, increases with time, but at an ever decreasing rate. From the results it would also appear that the scatter increases with time, possibly implying a greater dependence on the relative concrete curing characteristics. The above results seem to indicate an exponential kind of behaviour, and indeed if such results are replotted on a log time scale (against impregnation depth) for two different arbitrary temperatures, it can readily be seen that there is a

linear relationship (see fig. 5.6). The impregnation depth is obviously greater for specimens dried at 115°C rather than 60°C but in both cases a linear relationship is obtained between impregnation depth, D, say, and log t,

$$\text{i.e.} \quad D = a + b \log t$$

where t represents time and a and b are impregnation constants. On differentiating,

$$\frac{dD}{dt} = \frac{b}{t}$$

i.e. the rate of increase of impregnation depth varies inversely with time.

This is a very reasonable physical phenomenon; the rate of impregnation being fastest moments after immersion and rapidly decreasing with time. Earlier investigations indicated that there was a certain minimum "response time" of the order of a few minutes for impregnation to occur, which again is physically reasonable and certainly the equation above, implying that as $t \to 0$, $\frac{dD}{dt} \to \infty$, is physically unrealistic in the limit. This work is far from complete, however, and more data is required, although it is an area more of academic, rather than practical, importance at this stage.

It can also be seen that etching would appear to improve the impregnation depths marginally, e.g. approximately 6,8 mm to 7,5 mm at 24 hours (see fig. 5.7). Scatter is, however, large and some reservation must be placed on this conclusion. Such improvement, if substantiated by further testing, is presumably due to the removal of the dense "bleeding" skin on the surface of the specimens which forms during vibration and casting.

5.3.3 Breaking Strength

In an analogous way to impregnation depth, the strength increases with degree of impregnation for both non-etched and etched specimens, figs. 5.8(a), 5.8(b) respectively. However, the etched specimens would appear to be marginally weaker than non-etched for long soaking time and deep impregnation depths. This is possibly because of the action of the acid locally worsening any deep defect in the specimen which is not subsequently filled with polymer and which then may act as a source of weakness

during the strength test. Such shortcomings may be improved by going to larger specimens. The scatter on these results is, however, large and it would perhaps be more circumspect to say, at this stage, that more tests need to be done on the effects of etching, and that it would appear to improve impregnation depth only marginally. It is of interest to note that control (non-impregnated) specimens have a flexural breaking strength of about 400N, hence impregnation to depths of 6 to 8 mm with associated strength in excess of 800N improves the strength by a factor of approximately 2 for these size specimens - a significant improvement. This is of the same order as previous studies (see fig. 2.2 and 2.3) for flexural strength tests, while compressive tests in the literature report a four-fold increase.(17)

5.4 PRESSURE IMPREGNATION

5.4.1 Introduction and Initial Tests

The tests described under Procedure 1, section 4.4.4, were conducted during the earliest stages of the project, and before the standard ink technique for determining impregnation depth had been developed. Specific reference to the actual depth of impregnation in this earlier work cannot, therefore, be made. As mentioned in section 5.1, the effect of age of the polymer is critical in achieving significant impregnation. The importance of this factor was not fully appreciated when the initial experiments (Procedure 1, series D) were carried out, with the result that the limited increases in Modulus of Rupture (and other results) of impregnated specimens were a direct result of using polymer that was not factory fresh and of relatively high viscosity. The results are given in fig. 5.9 and are therefore more of academic interest, but are included because they illustrate the significance of the quality of impregnating polymer.

These earlier studies, undertaken before the use of the ink staining technique, only exhibit a 20% increase in Modulus of Rupture, whereas for fresh polymer and truly deep impregnation, mentioned in section 5.3.3, the MOR increase is approximately twofold.

The volume and weight percentage loading is relatively

small, approximately 2%, and consistent with the thicker nature of the polymer used. Unfortunately, weight percentage loading was not undertaken for subsequent tests, using fresh polymer which impregnates deeply, and this is an area of study which should be resolved.

5.4.2 Later Test Series: Procedure 2

Results of the pressure tests (see fig. 5.10) reveal that impregnation increases for longer pressure duration and also for higher pressures.

It would appear that pressure impregnation improves strength for comparable impregnation depths achieved simply by soaking, possibly as a result of a denser, but not necessarily deeper, impregnation (see fig. 5.11).

5.5 VACUUM IMPREGNATION

5.5.1 Introduction

The almost dramatic effects of vacuum application prior to impregnation of concrete has been reported by several investigators.(15 - 17, 23) It is thought that this is due to the removal of the physical barrier presented by air trapped, in the pores of the concrete, by the incoming polymer; indeed in other tests, prior evacuation is generally applied to obtain maximum polymer loadings.(17)

These observations were generally confirmed by the results of the tests described in section 4.5, presented and discussed below.

5.5.2 Initial Series

The results presented here concerning vacuums, parallel those described in section 5.4.1 for pressure tests and suffer from the same shortcomings as regards polymer quality, but are included for completeness. They were in fact performed with the same polymer batch. The results of Modulus of Rupture tests, after loading with polymer by vacuum impregnation, are shown in fig. 5.12. In addition, one can see the degree of polymer loading both in terms of mass and volume changes which are once again of the order of 2% loading (with this high viscosity polymer).

5.6.2 Results and Discussion

Impregnation of concrete discs under a pressure gradient described in section 4.6 proved highly successful, as impregnation of 15 to 20 mm was achieved after only half an hour (see plates 5.1 to 5.3). It can be seen that polymer flows up to the aggregate particles and, to some extent, around them, e.g. plate 5.1 and 5.2. Whether this is due primarily to the pressure gradient or possibly because of the more porous structure of the coarse aggregate concrete mix, or a combination of both, is not clear. The tests conducted were of a very preliminary nature but appear most promising, and further work is necessary to consolidate this area of the research.

5.7 SOLVENT EFFECTS: DILUTION

5.7.1 Introduction

As mentioned in section 4.7.1, the dilution of the polymer greatly affects the rate and depth of impregnation. If the full benefits of polymer impregnated concrete are to be realised, maximum impregnation is required, if possible within the minimum of time, effort and expense. The significant effects of polymer dilution on impregnation were observed in the experiment described in section 4.7, the results of which are given and discussed below.

5.7.2 Results and Discussion

The effect of diluting the polymer with solvent to varying degrees prior to impregnation has a very marked effect on the depth of impregnation achieved (see fig. 5.14). The relationship for impregnation depth would appear to increase from 0% solvent in polymer, to reach a peak at approximately 25%, and then decrease from there onwards for increasing dilutions. Presumably small amounts of free solvent are beneficial and assist the polymer impregnation process, whereas for large polymer dilutions the impregnation depth decreases markedly. It must also be remembered that so-called "pure polymer" already contains typically 50% of solvent which is incorporated with the polymer as a result of the manufacturing process.

It is interesting to examine the breaking strength of such specimens which is seen to decrease from zero dilution (see fig. 5.15). This may be due to diluted polymer contributing a lower

proportion of strength to the impregnated concrete specimens than pure polymer would, even though impregnated more deeply (see fig. 5.14). This in turn may be as a result of diluted polymer not coating the walls of the pores in the concrete as thickly as could be expected from pure polymer, even though pure polymer does not impregnate as deeply. It should also be borne in mind that fracture in flexural specimens originates where local stresses in the outermost fibres exceed local strengths (in the same vicinity) and hence lead to fast fracture. Thus it can be seen that more effective strengthening of the outermost fibres is more important than a weaker but deeper contribution to composite strength, as is the case for diluted impregnation. This appears to be borne out by the results.

The scatter in the results, however, is large, and further tests are necessary to consolidate these results.

5.8 SULPHURIC ACID CORROSION TESTS

5.8.1 Introduction

The prime purpose of this project was to examine the corrosion resistance of polymer impregnated concrete with a view to prolonging substantially the service life of concrete pipelines operating under adverse corrosive conditions. The results of the tests described in section 4.8 are the culmination of this project, and show that a significant improvement in the corrosion resistance of this polymer impregnated concrete is achieved in accelerated corrosion tests. However, these results represent only an improvement and it is thought that investigations with other polymers, e.g. polyesters, methyl methacrylates, will be even more successful. Another major problem, however, still remains and that is how such results are to be transformed into predictions of life expectancy of actual in-service concrete pipes. This problem can only be solved by more extensive investigation and both short and long term field tests in acidic sewer environments. For the purposes of this project, however, the results of the tests carried out during the present investigation are presented and discussed below.

5.8.2 Single Impregnation: Results and Discussion

Prior to undertaking corrosion tests at different acid concentrations for the M, N and O series which were nominally cast and impregnated identically, the impregnation depths and flexural strengths were determined on parallel control specimens. These results are shown in fig. 5.16 and it can be seen that, for the purposes of corrosion, they were effectively the same.

The extent or rate of corrosion for the M, N and O series was measured in two ways, namely, by mass loss and volume loss. Both these techniques (see figs. 5.17, 5.18) readily indicate the large difference in corrosion between unimpregnated and impregnated specimens, this being more pronounced, as expected, with the higher acid concentrations. Note that each point on the curves of figs. 5.17 and 5.18 actually represents the mean of five results (see figs. 5.19, 5.20). These experiments can certainly be regarded as accelerated tests because of the excessively high losses experienced by the unimpregnated (control) specimens, these being 3% and 50% mass loss after approximately only 18 days in acid, for the 1% and 10% sulphuric acid concentrations respectively. Such high rates of corrosion are not found in sewers operating under even the highest "natural" corrosive conditions, and would take years to achieve.

When considering the role of the polymer in providing corrosion protection, an interesting phenomenon can be seen, for example, on the 10% acid, impregnated specimens corrosion curve (see fig. 5.17). The section of the curve between the points marked (i) and (ii) represents a sudden increase in the corrosion weight loss, and this is attributed to the final breaking down and removal of the relatively thick (0,5 mm) polymer layer on the external surface of the specimen. What is of particular interest, however, is that after the loss of this protective "skin" at point (ii), and simply impregnated but otherwise bare concrete is exposed to the acid, the rate of weight loss from (ii) to 16 days does not take place at as severe a rate as that for pure mortar in 10% acid (the lowest curve). While there is a significant advantage, it is felt that investigations with other polymers more resistant than polyurethanes (to moisture and acid), would be preferable in that the outer skin would not deteriorate at all.

The weight-loss method of measurement shows a relatively even change in mass prior to point (i), whereas the volume recordings appear to exhibit somewhat more scatter. This is due to the large scatter in observations read from the porosimeter, which can be readily seen in figs. 5.19, 5.20. For interest and to exhibit the increased scatter in volume results, the readings recorded from the porosimeter after the first three immersions (i.e. 9 days in acid) for the M and N specimens are shown; and the increased scatter for volume readings against those for mass readings is apparent. It was therefore considered that mass readings alone would be both preferable and more accurate, and the porosimeter was not used for volume change measurements in the subsequent double impregnation test series.

Strength measurements of control specimens indicate a decrease in strength corresponding to the decrease in cross-sectional area, the most pronounced being that for the specimens immersed in a 10% acid solution (see fig. 5.21, plates 5.4 to 5.6). This may possibly be coupled with a general decrease in strength due to the internal chemical reaction caused by absorbed acid. The polymer is not immune to attack by sulphuric acid, and impregnated specimens exhibited a general loss of strength of between 25% and 50%, depending on the acid concentration. The most important consideration is, however, that the rate of corrosion of impregnated specimens was considerably less than that of mortar control specimens, and the relatively high strengths available after impregnation can be attributed to two factors, namely, (i), the cross-sectional areas of impregnated specimens were not reduced by the same degree as that of control specimens due to the presence of the pore-filling polymer, and (ii) the residual polymer which was not corroded, but possibly weakened by the acid, was still able to contribute some additional strength to the specimens.

Plates 5.4 to 5.6 clearly show the difference in the appearance and degree of deterioration between impregnated and unimpregnated (control) specimens, the most marked being that for those specimens immersed in 10% acid solutions. The impregnated specimens retained more or less their original rectangular shape due to the presence of the polymer in pores and on the surfaces which limited the damage to the concrete material. Sharp edges

are usually particularly vulnerable to corrosion under these test circumstances because they are attacked from two sides; the rate of deterioration is thereby effectively doubled on the outer reaches of the corners. This effect is evident from the size and shape of the control specimens which are nearly circular in section after having suffered severe corrosion on the sides and in particular the corners. Volume losses, confirmed by mass loss readings, were up to 50% for control specimens in 10% acid solution, compared with 25% for impregnated specimens.

The "bloated" appearance of some of the corroded impregnated specimens is due to the expanded corrosion products of the outer polymer skin. As mentioned previously, the polymer is not immune to acid attack, although it did appear to provide a significant inhibiting effect to the acid, possibly by serving as a shield; this was, however, only effective while there was still some form of adhesion to the outer surface of the concrete. It is as a result of this deterioration of the polymer skin, admittedly under severe conditions, that further studies are to examine more resistant polymers, particularly PMMA, acrylics, polyesters and resins. The dark colour comes about as a result of heating the specimens for drying purposes in between acid immersions. This process may indeed have damaged the polymer in some way, although further tests are needed to confirm this.

5.8.3 Double Impregnation: Results and Discussion

The results of the experiments described in section 4.8.3 once again highlighted the importance of using fresh polymer for impregnation purposes. At the time when the double impregnation - acid corrosion tests were conducted, fresh polymer could not be obtained from the suppliers, and use had to be made of a relatively old quantity of polymer which, although it had been stored in suitable steel containers, had already begun to show the signs of age by exhibiting a partially gelled consistency.

The results of these tests were inconclusive, and for the purposes of this project, had to be abandoned.

5.9 SUMMARY

In this chapter, the most important aspects of the project have been presented and discussed at some length, namely, the results of the impregnation and corrosion experiments.

Impregnation depth and rates of impregnation have been shown to depend primarily on (i) the adequate drying of the specimens, (ii) vacuums and pressures applied during the impregnation process, and (iii) the time of exposure to these vacuums and pressures. In addition, small advantages were achieved by pre-etching of specimens to remove cement laitance. The age and quality of the polymer is most important and impregnation ability decreases rapidly with age, even under optimum storage conditions.

The techniques for achieving optimum impregnation of laboratory specimens have been well developed, and may be summarised as follows.

(i) Etch (mildly - further research required).

(ii) Pre-dry specimens to maximum temperature of 150^{o}C, and certainly above 110^{o}C.

(iii) Cool to room temperature in a desiccator.

(iv) Impregnate

(a) if time is unimportant, simply soak pre-dried specimens for at least 48 hours in <u>fresh</u> uncatalysed polymer which is diluted with 25% solvent in polymer, or

(b) if time is critical, vacuum impregnate with the polymer suitably diluted, if necessary, for ideally 15 to 30 minutes, but for as long as 3 hours, and complete the process by pressurising for the same time, using the maximum vacuums and pressures available in the laboratory.

(v) Cure in a catalyst vapour environment.

(vi) Repeat for second, third or fourth layers until sufficient coating is achieved. (Success of this aspect should be determined by future work.)

The success of impregnating under a pressure gradient should not be overlooked, and may yet provide the maximum rates and depths of impregnation if confirmed in further experimental work.

On the corrosion side, UPC polymer has been shown to provide concrete with a relatively successful corrosion resistance to dilute sulphuric acid, although it is considered that this particular polymer is by no means the best for corrosion resistance, and that others, such as polyesters and methyl methacrylates, may prove still more successful.

An important aspect which certainly requires further attention is the effect of the drying temperatures on the polymer itself. Polymers are known to deteriorate at higher temperatures, and this may well be the reason for the only partial success of the polymer in the corrosion tests.

FIG. 5.1.

MODULUS OF RUPTURE vs. DRYING TEMPERATURE
PLAIN UNIMPREGNATED MORTAR

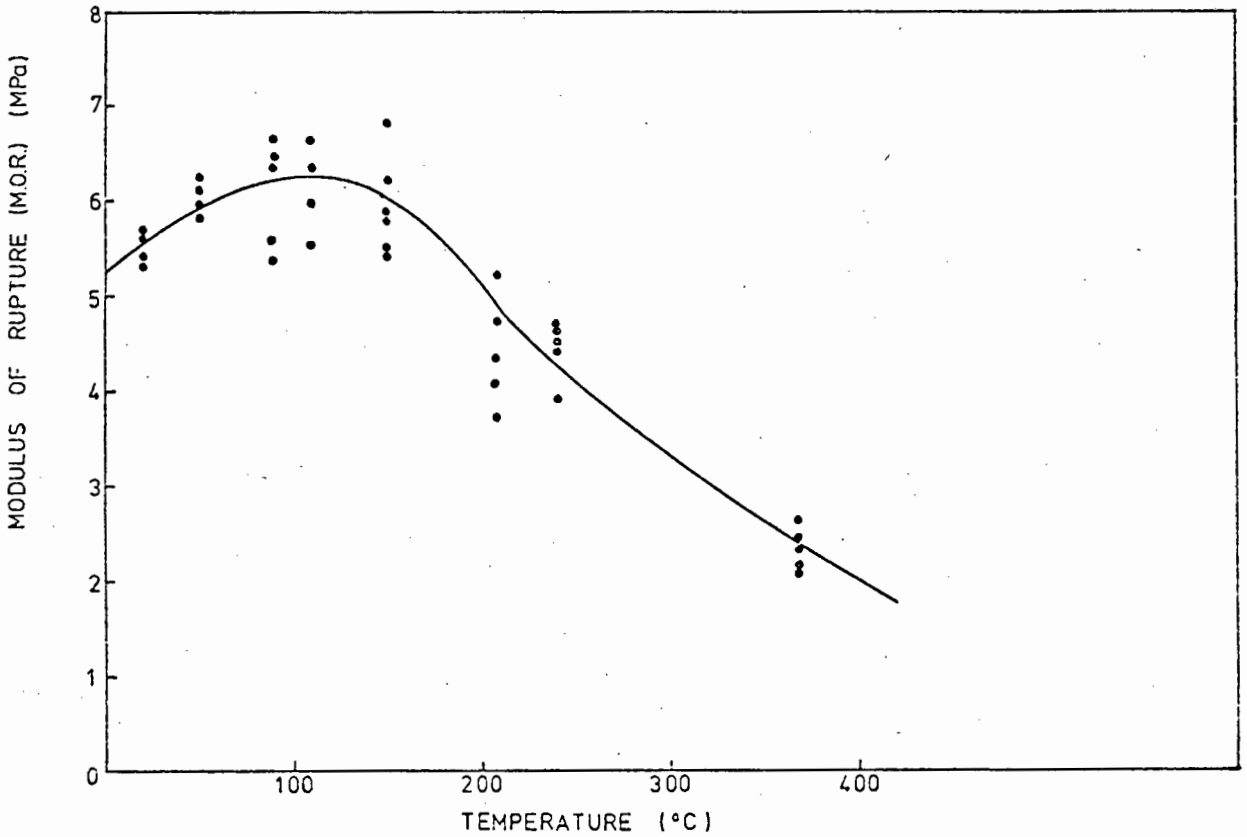


FIG. 5.2.

DRYING OF SPECIMENS

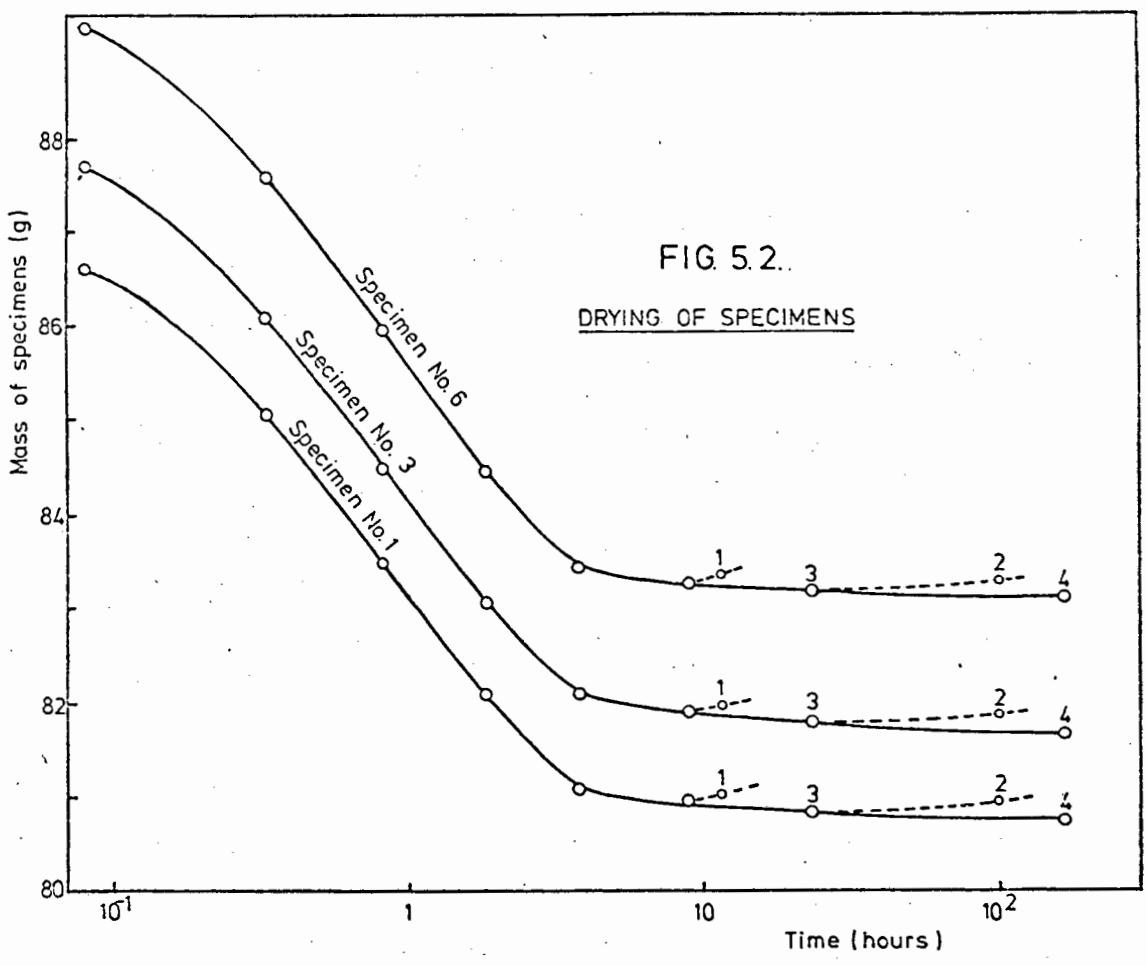


FIG. 5.3.

IMPREGNATION DEPTH AND BREAKING STRENGTH vs. DRYING TEMPERATURE

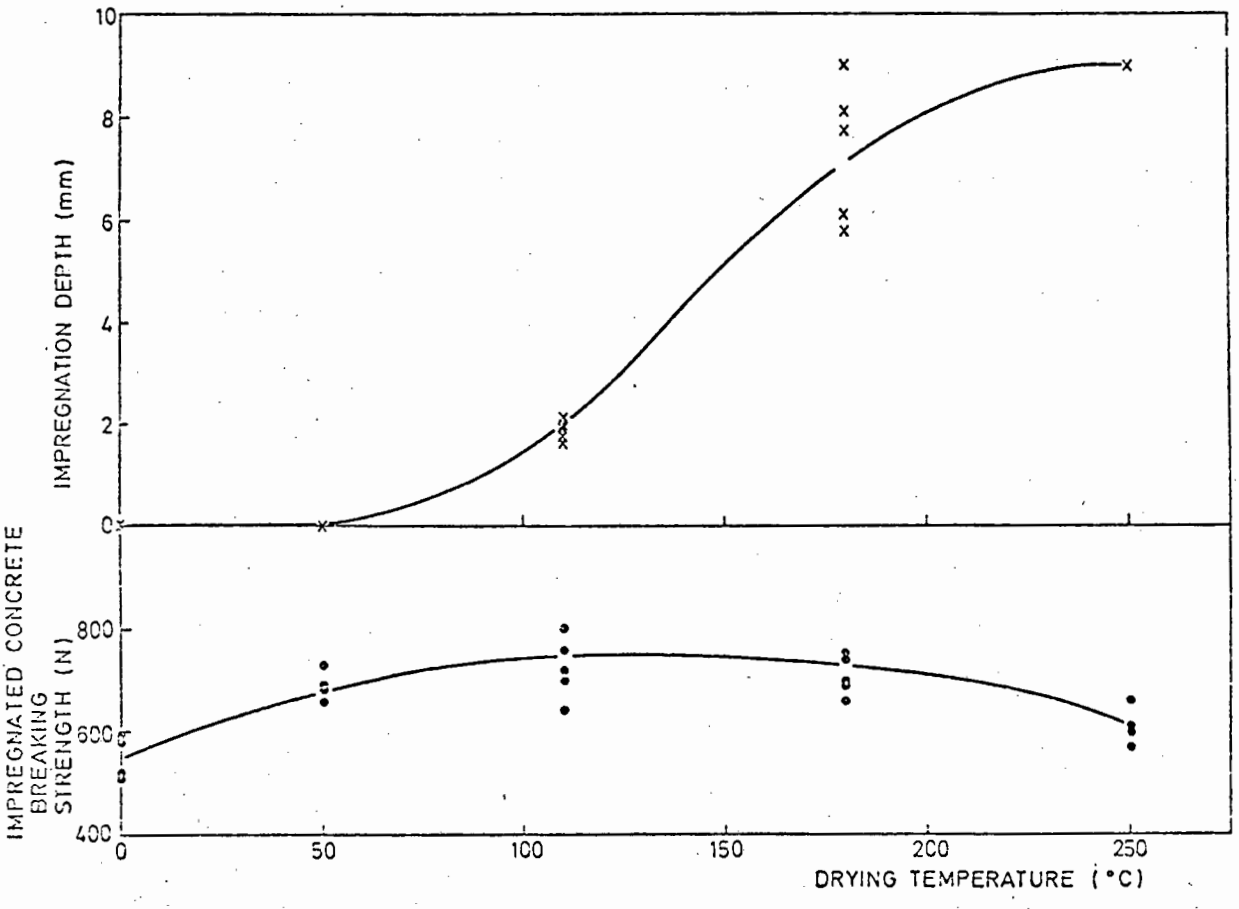


FIG. 5.4.

IMPREGNATION DEPTH AND BREAKING STRENGTH vs. CONCRETE TEMPERATURE AT TIME OF IMPREGNATION

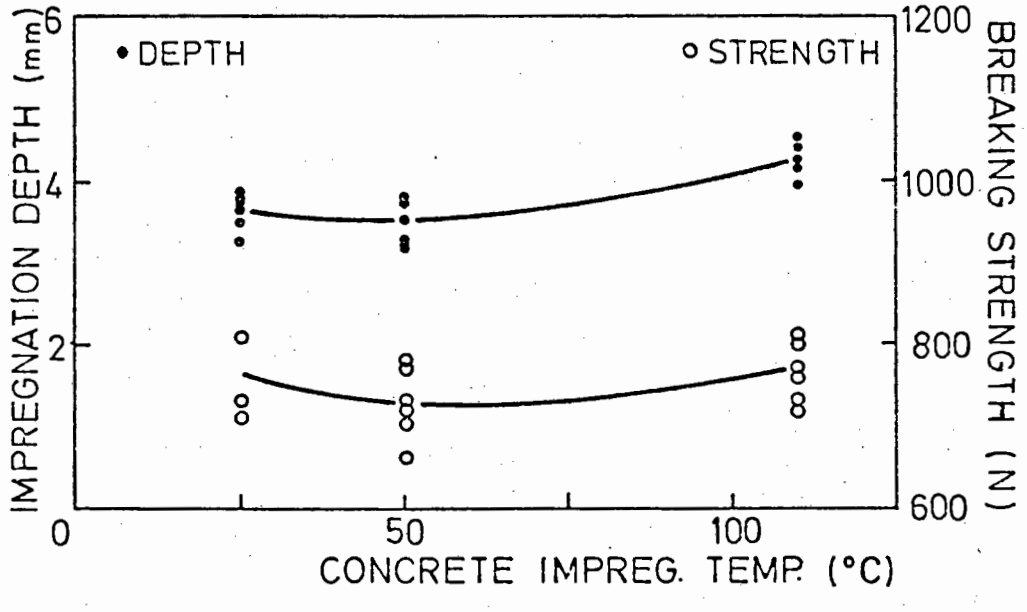


FIG. 5.5a.
IMPREGNATION DEPTH vs. TIME
UNETCHED SOAK

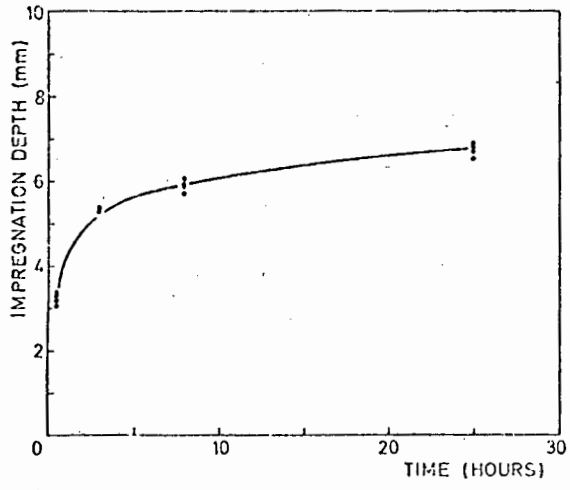


FIG. 5.5b.
IMPREGNATION DEPTH vs. TIME
ETCHED SOAK

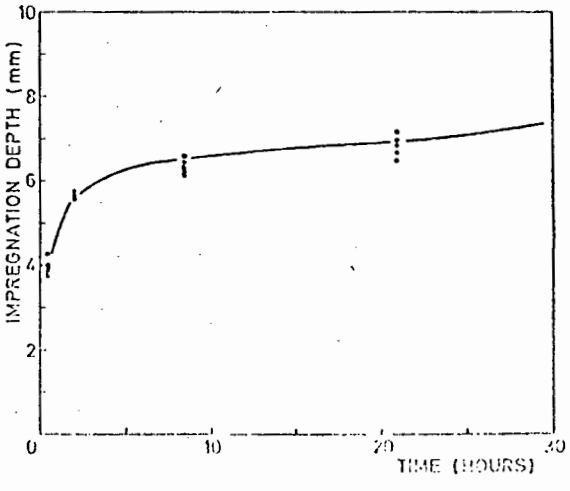


FIG. 5.6.
IMPREGNATION DEPTH vs. TIME (LOG SCALE)

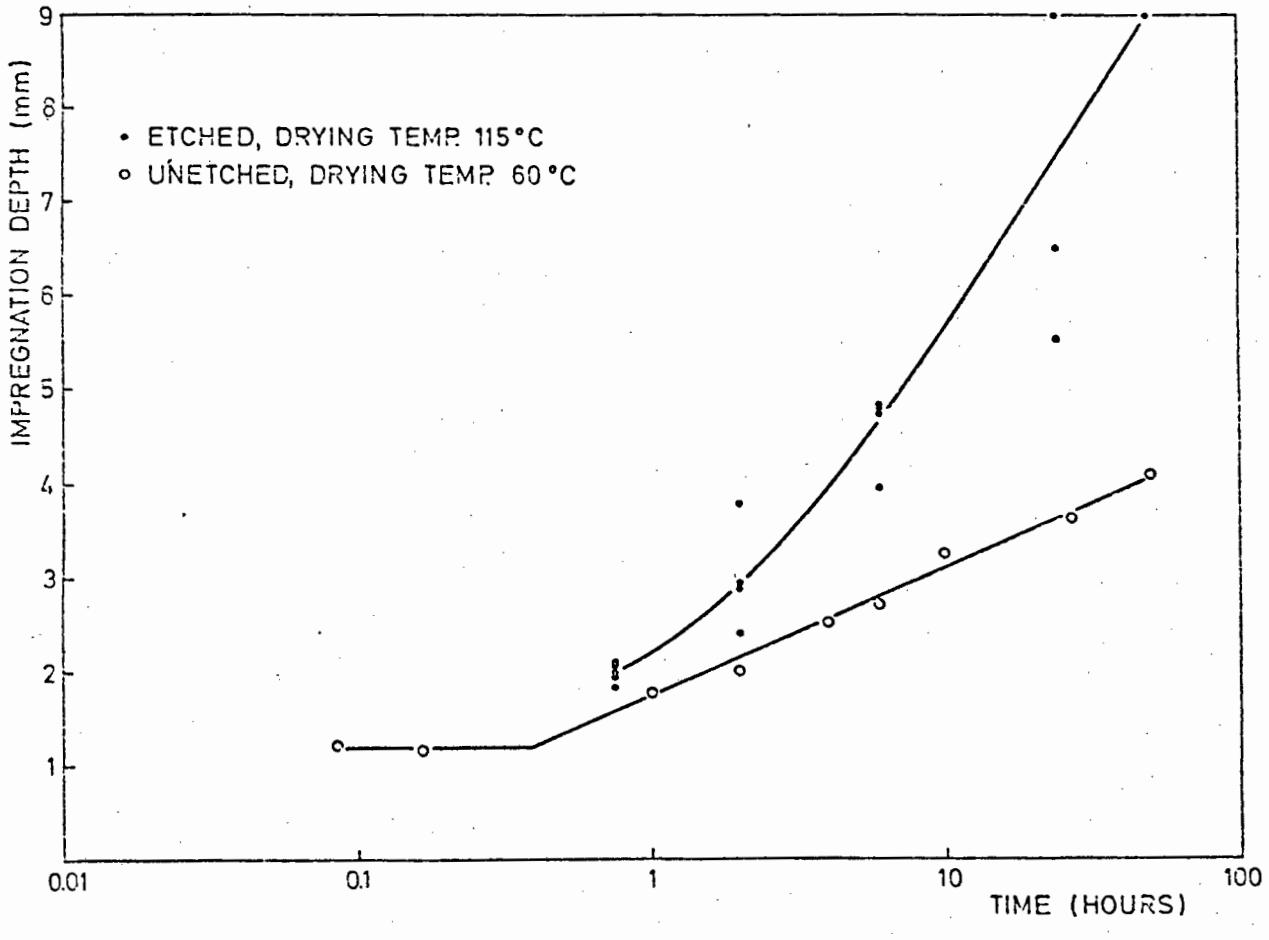


FIG. 5.7.
IMPREGNATION DEPTH vs. TIME
COMPARISON OF ETCHED AND UNETCHED SPECIMENS

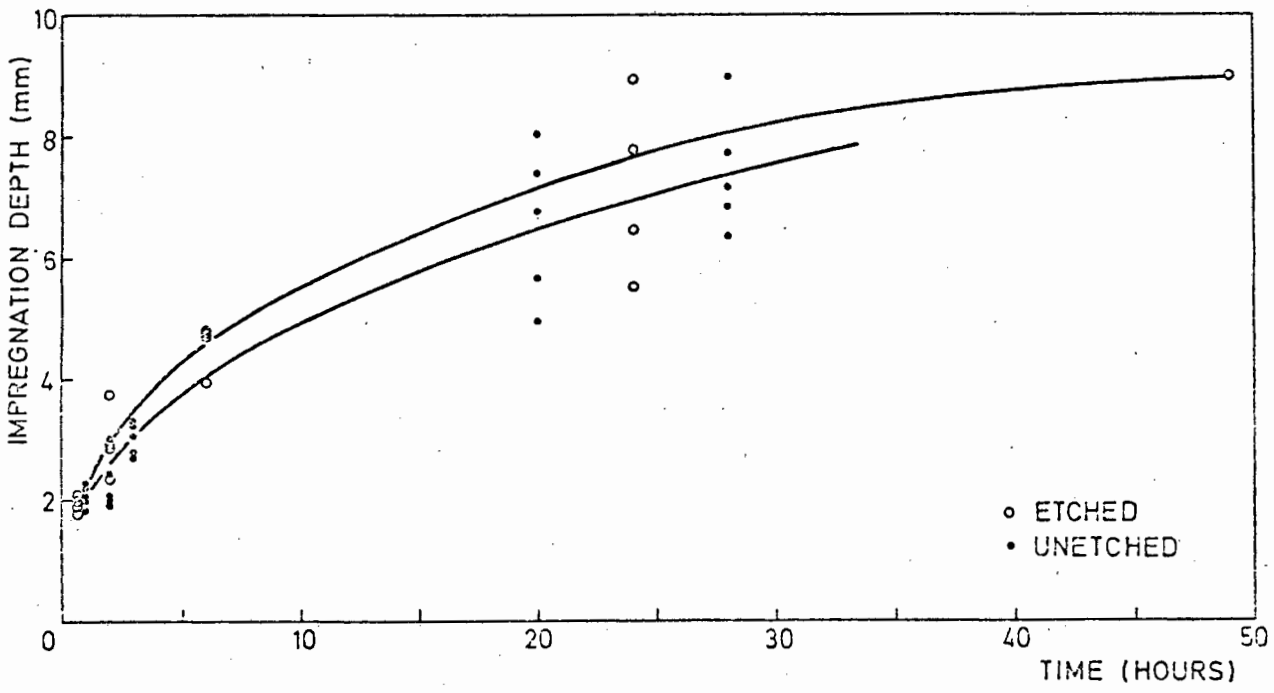


FIG. 5.8a.
BREAKING STRENGTH vs. TIME
UNETCHED SOAK

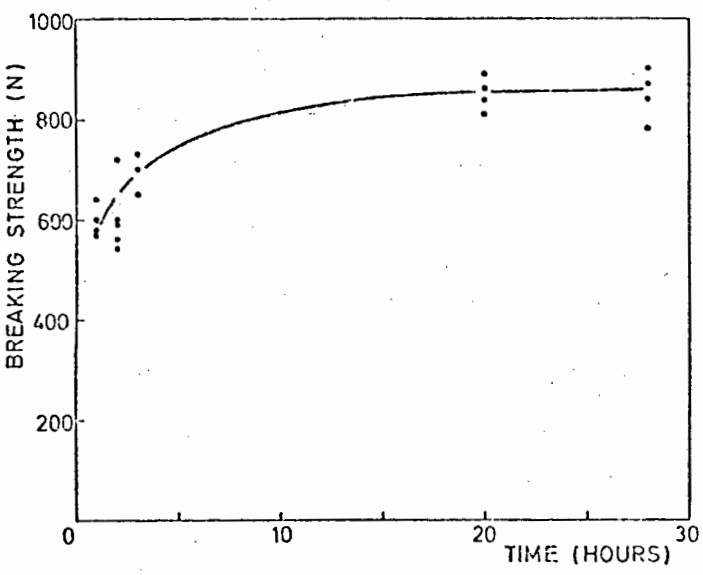
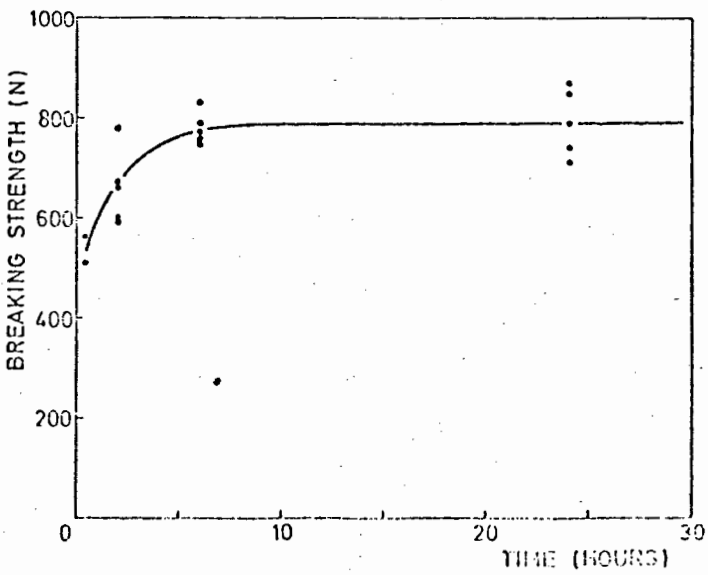
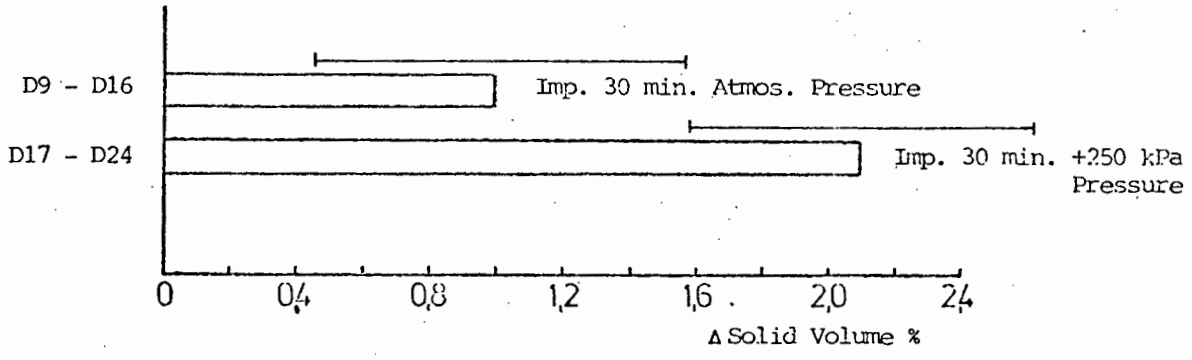
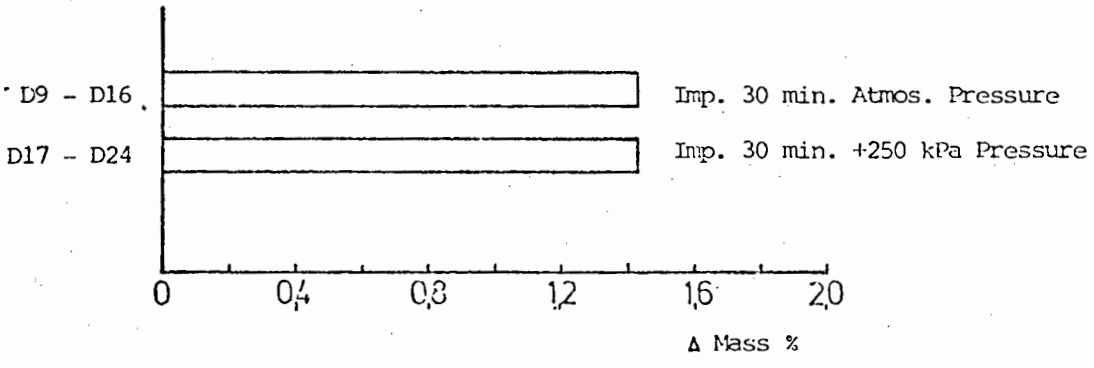
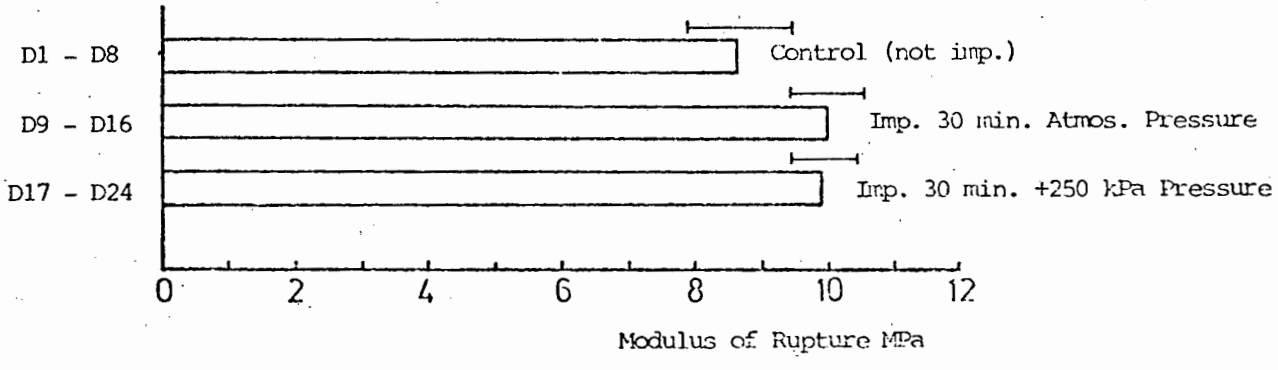


FIG. 5.8b.
BREAKING STRENGTH vs. TIME
ETCHED SOAK









Note: All impregnated specimens were coated with polymer prior and during impregnation

FIG. 5.9.

Results of Specific Impregnation Tests on Mortar Specimens - Series D.

FIG. 5.10.
BAR CHART SHOWING
IMPREGNATION DEPTH FOR BOTH
PRESSURE AND VACUUM

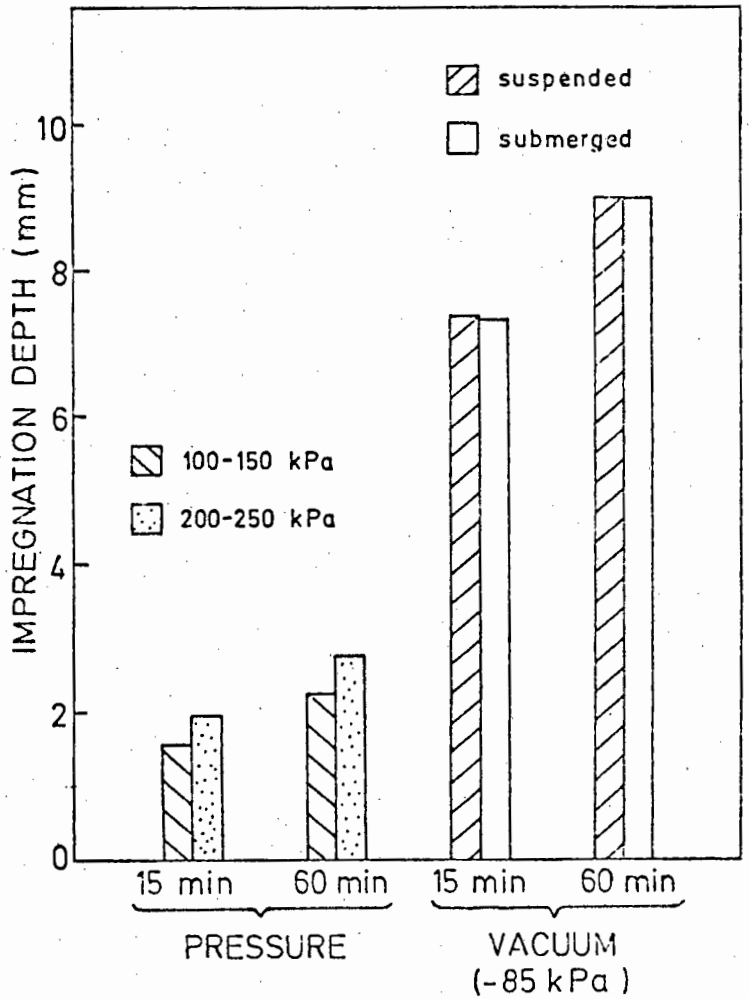
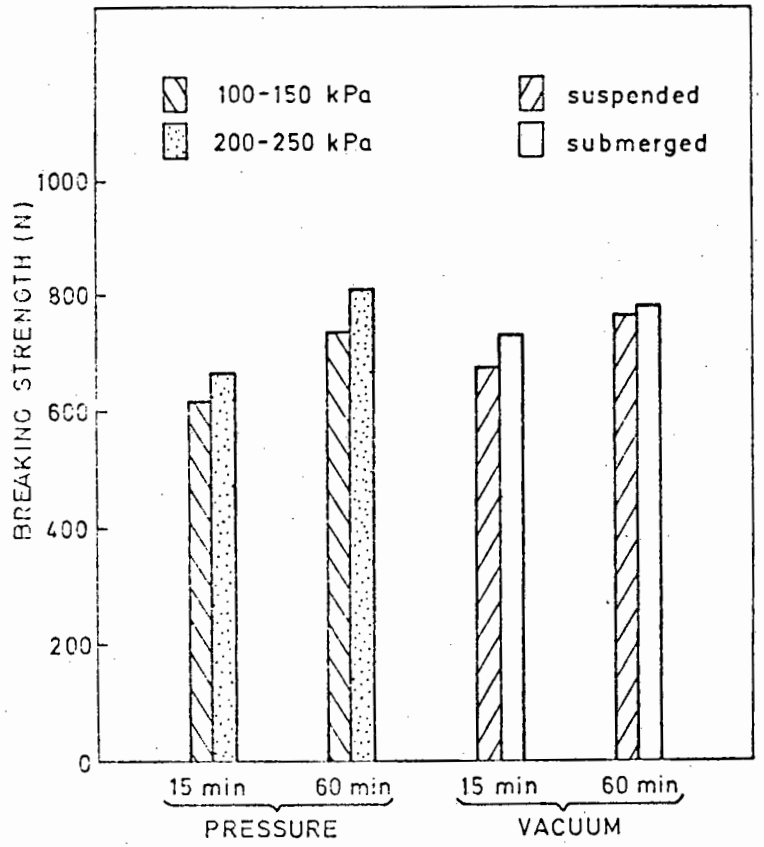
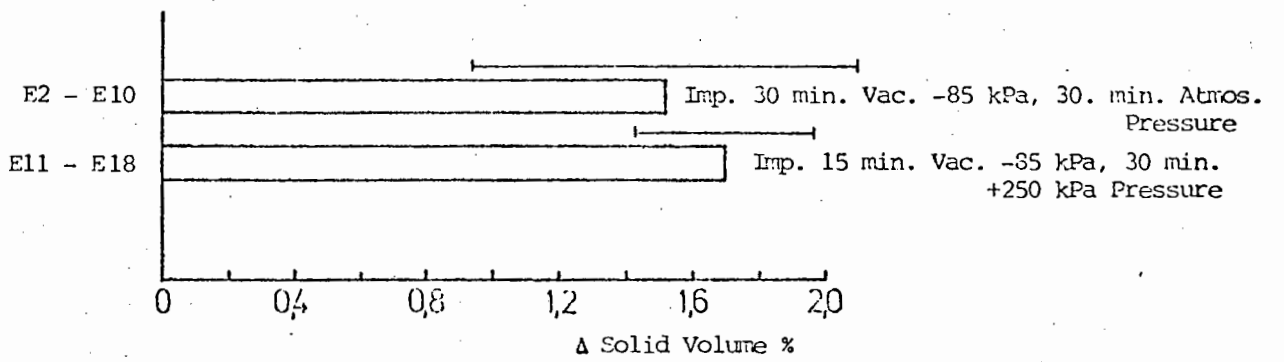
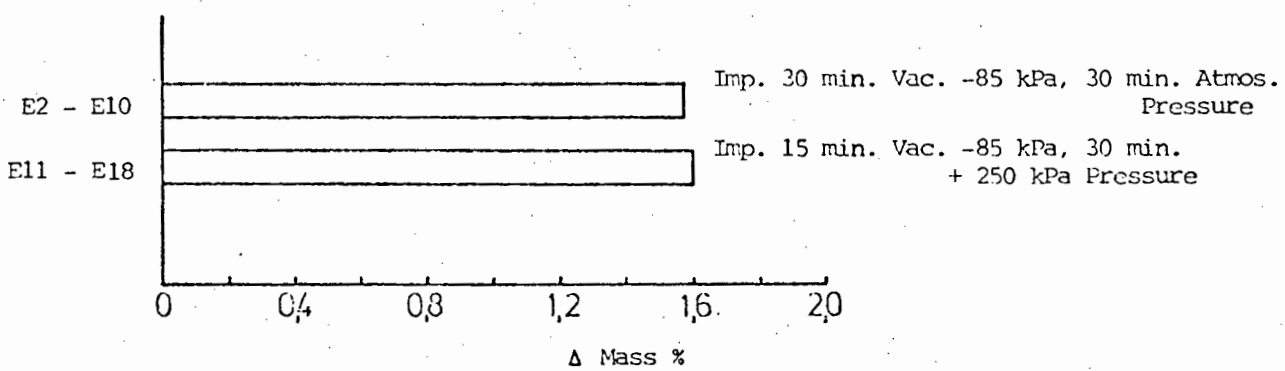
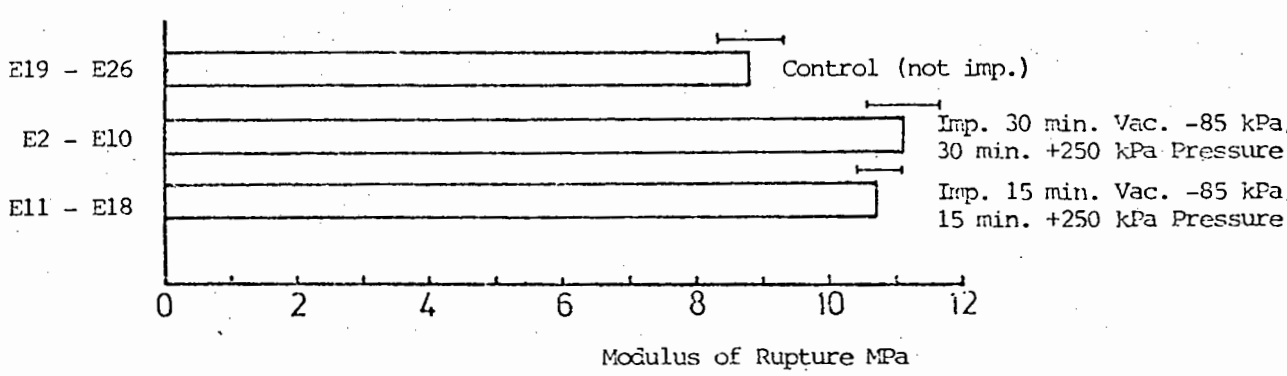


FIG. 5.11.
BAR CHART SHOWING
BREAKING STRENGTH FOR BOTH
PRESSURE AND VACUUM









Note: All impregnated specimens were totally immersed in polymer prior to and during impregnation.

FIG. 5.12.

Results of Specific Impregnation Tests on Mortar Specimens - Series E.

FIG. 5.13.

IMPREGNATION DEPTH vs. EVACUATION TIME

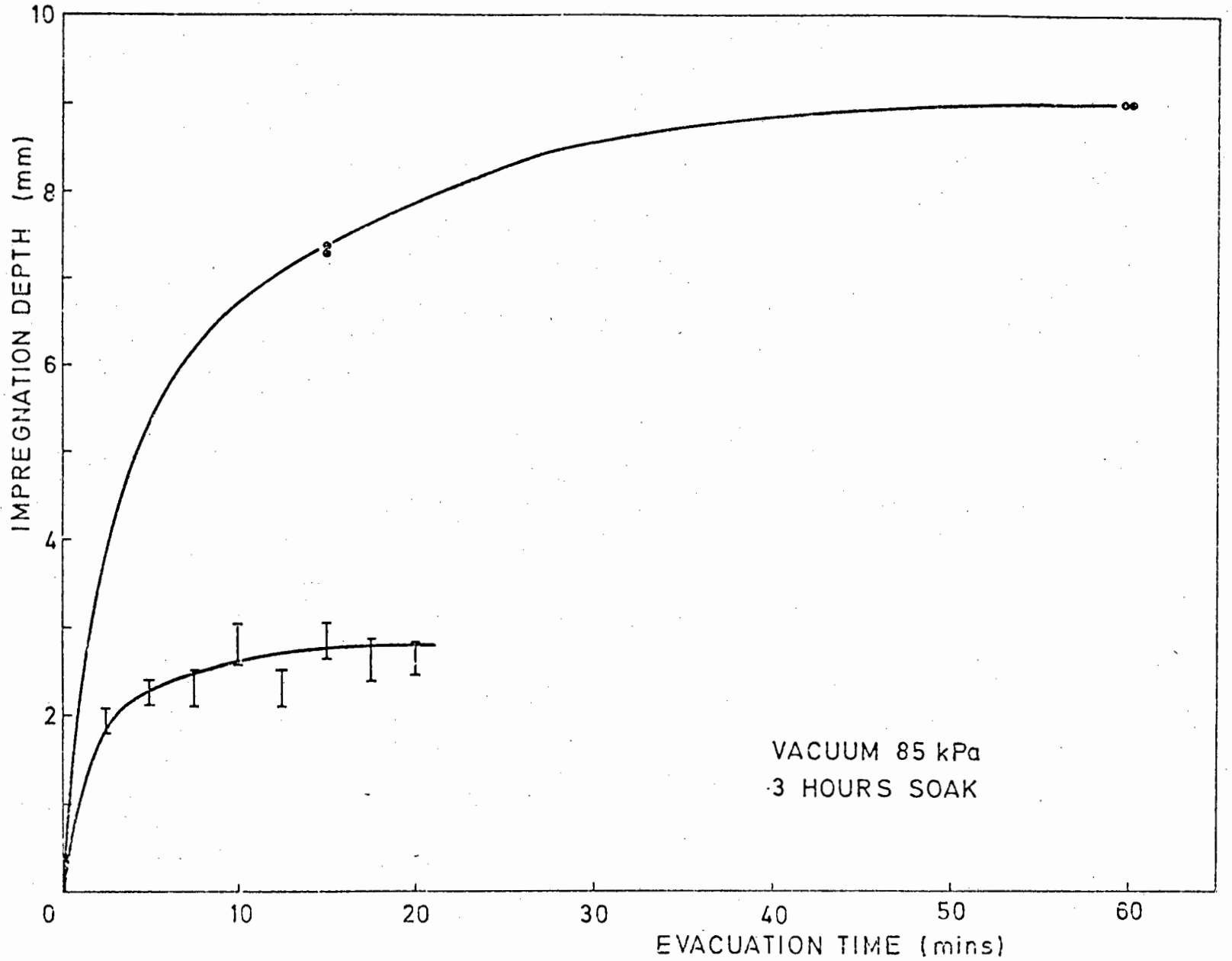


FIG. 5.14.

IMPREGNATION DEPTH vs. POLYMER DILUTION

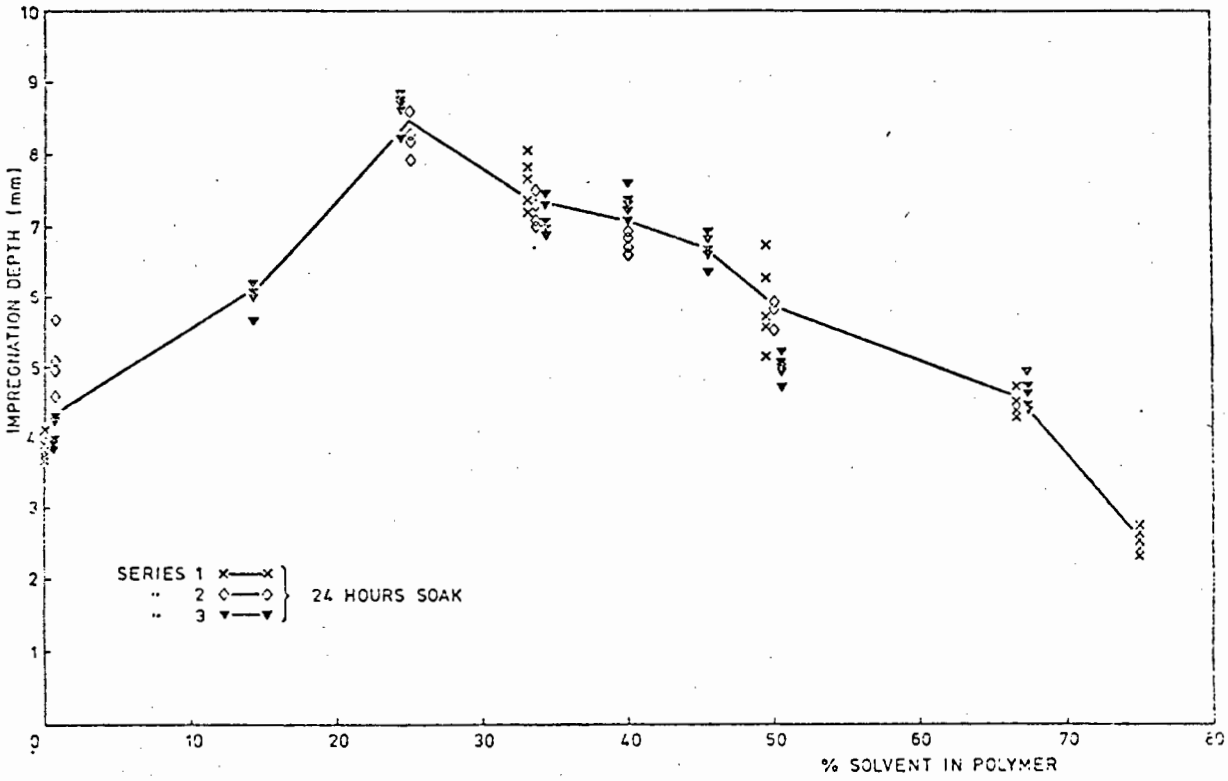


FIG. 5.15.

MODULUS OF RUPTURE (M.O.R. STRENGTH) vs. DILUTION

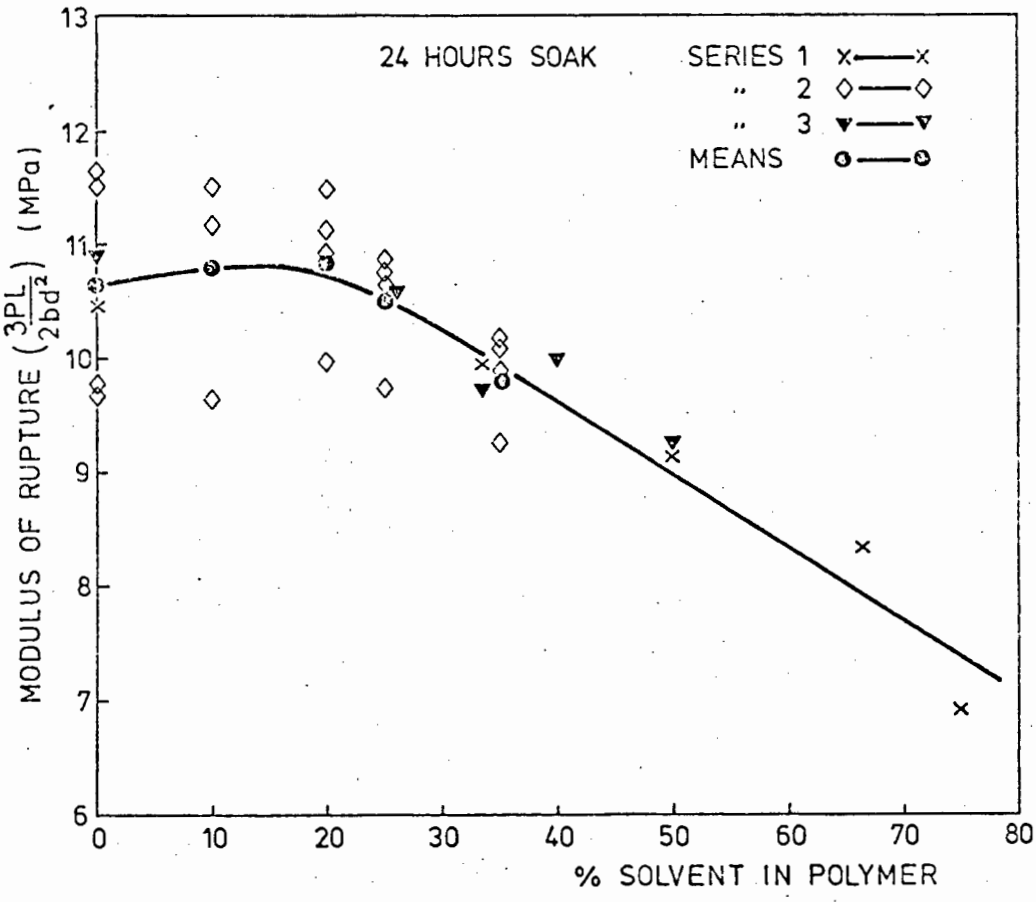


FIG. 5.16.
COMPARABILITY OF BATCHES USED IN CORROSION TESTS

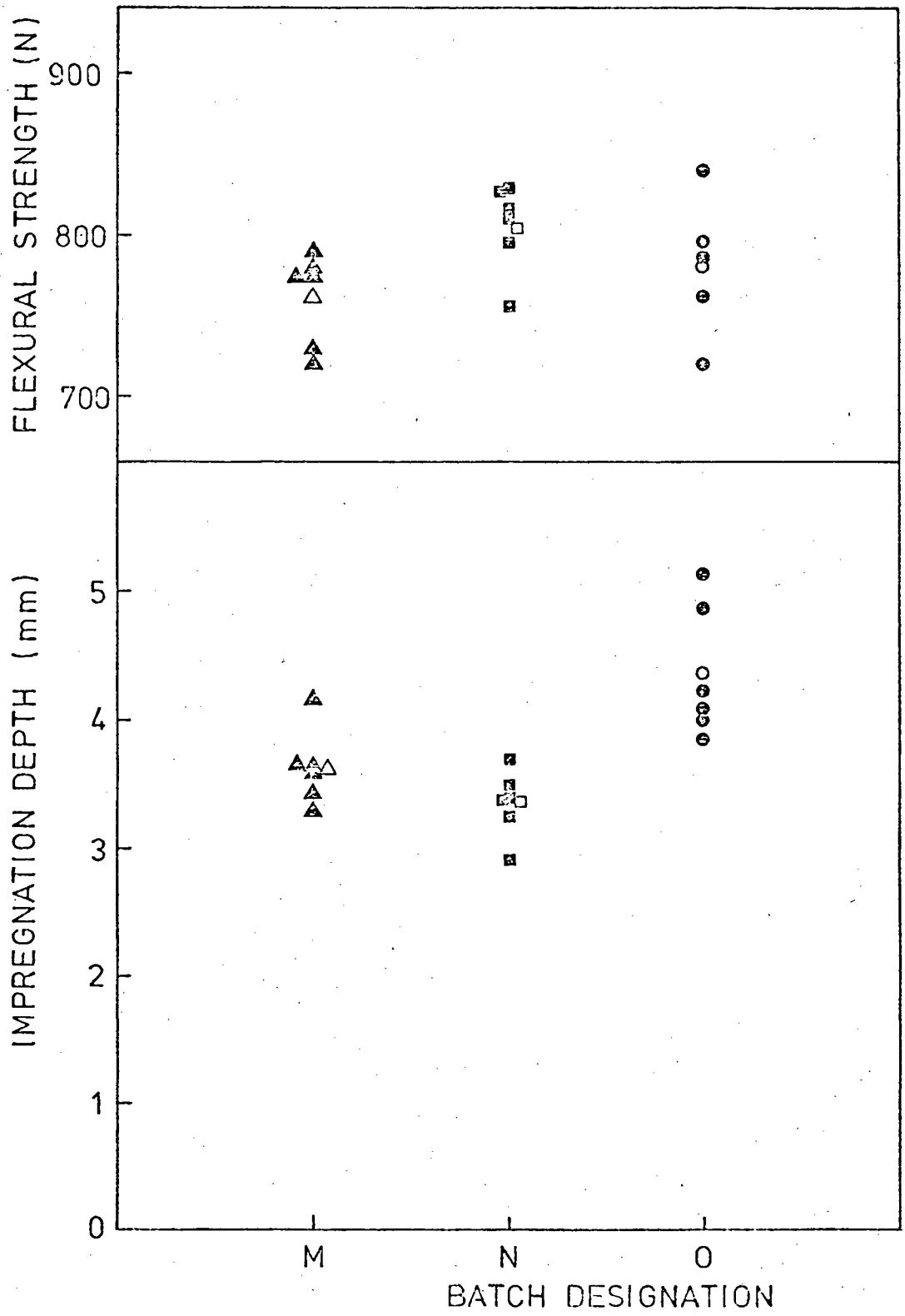


FIG. 5.17

SULPHURIC ACID CORROSION TESTS

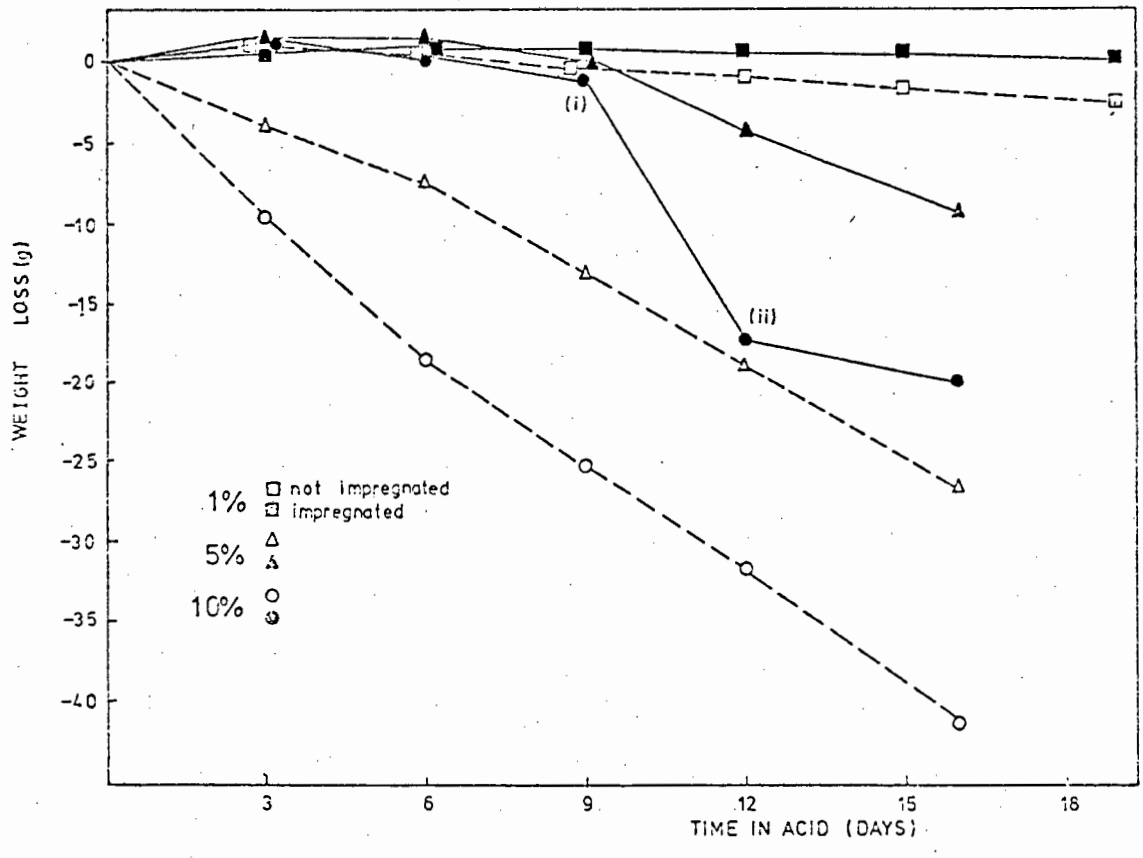


FIG. 5.18.

SULPHURIC ACID CORROSION TESTS

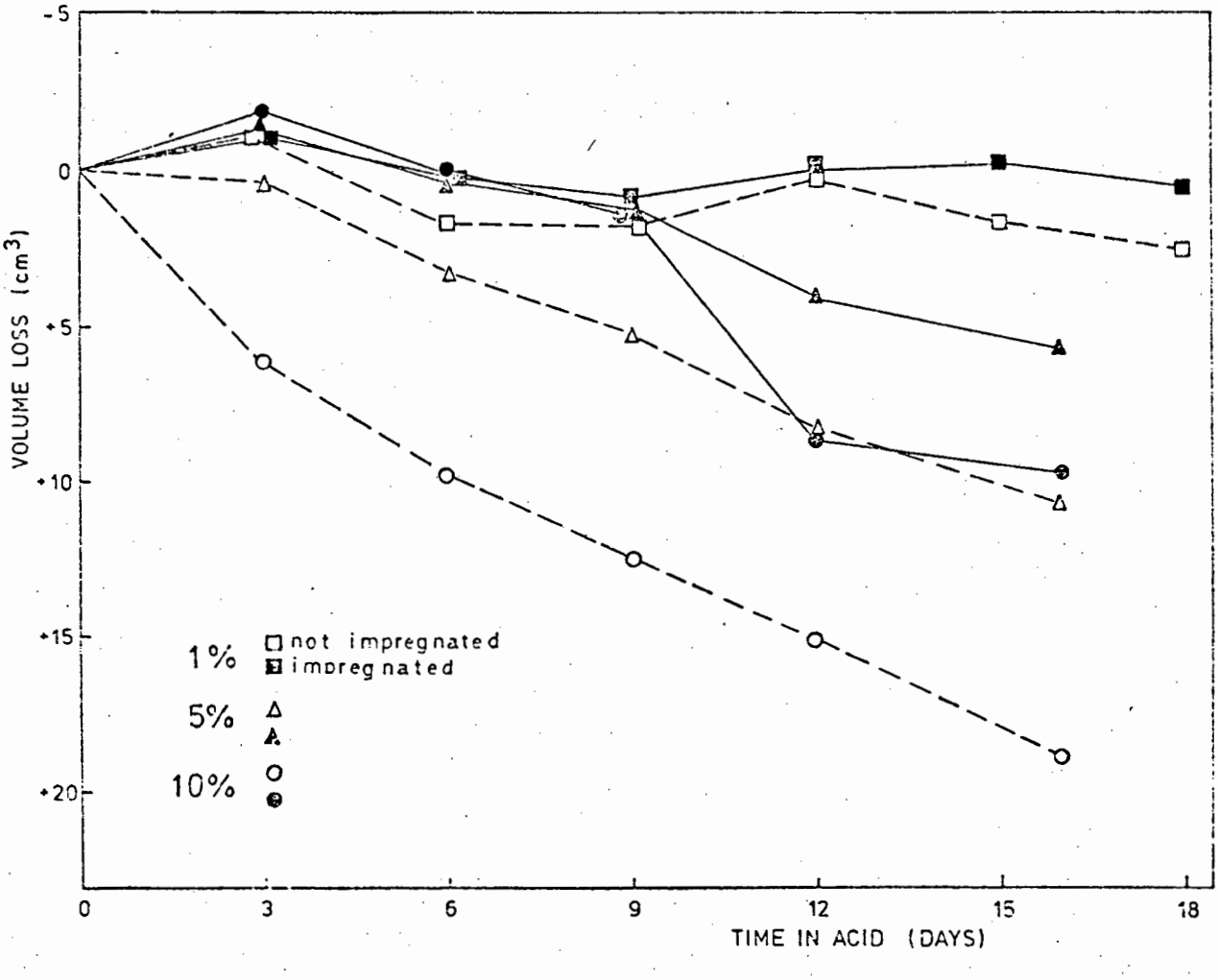


FIG. 5.19.

SERIES N: 1% ACID

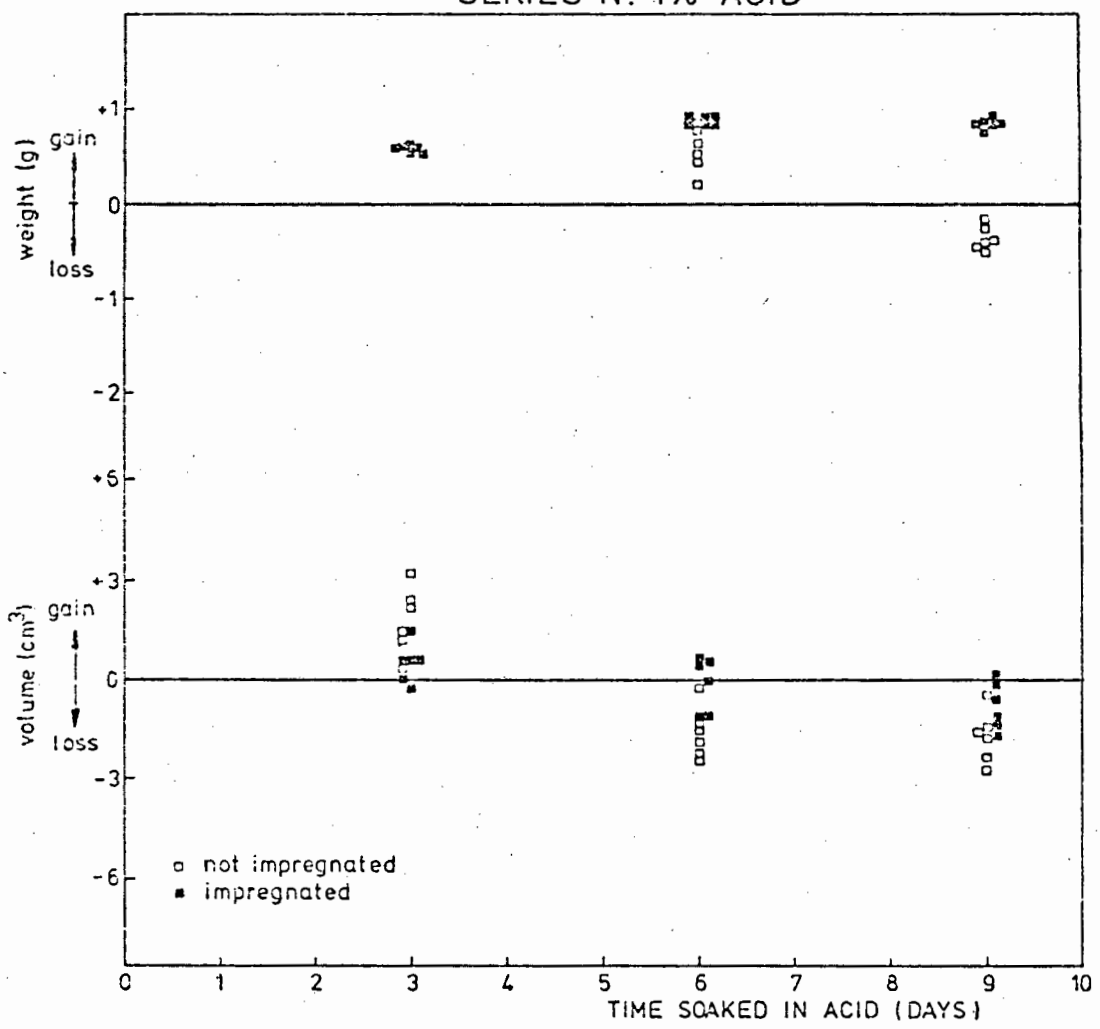


FIG. 5.20.

SERIES M: 5% ACID

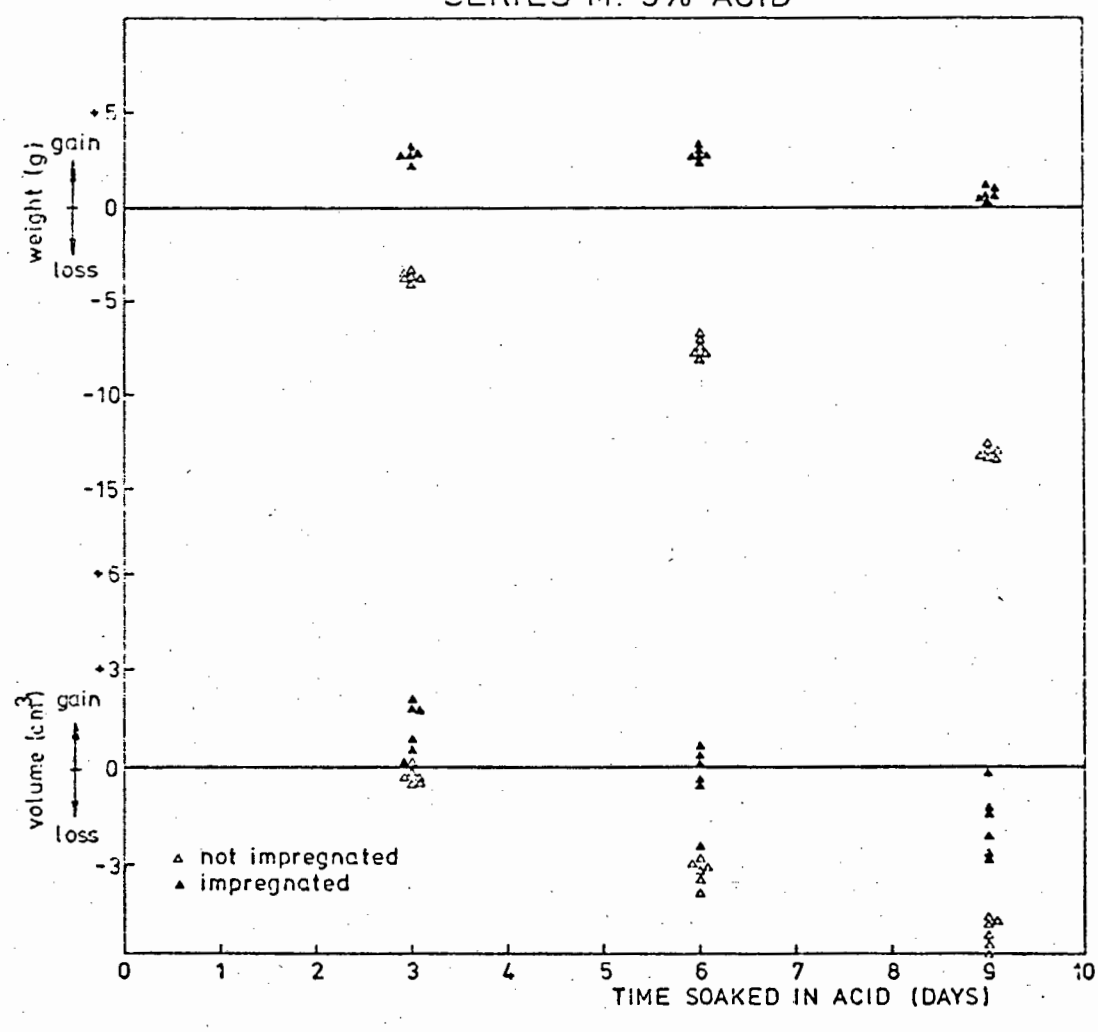


FIG. 5.21.
SINGLE IMPREGNATION:
STRENGTH DETERIORATION WITH CORROSION TIME

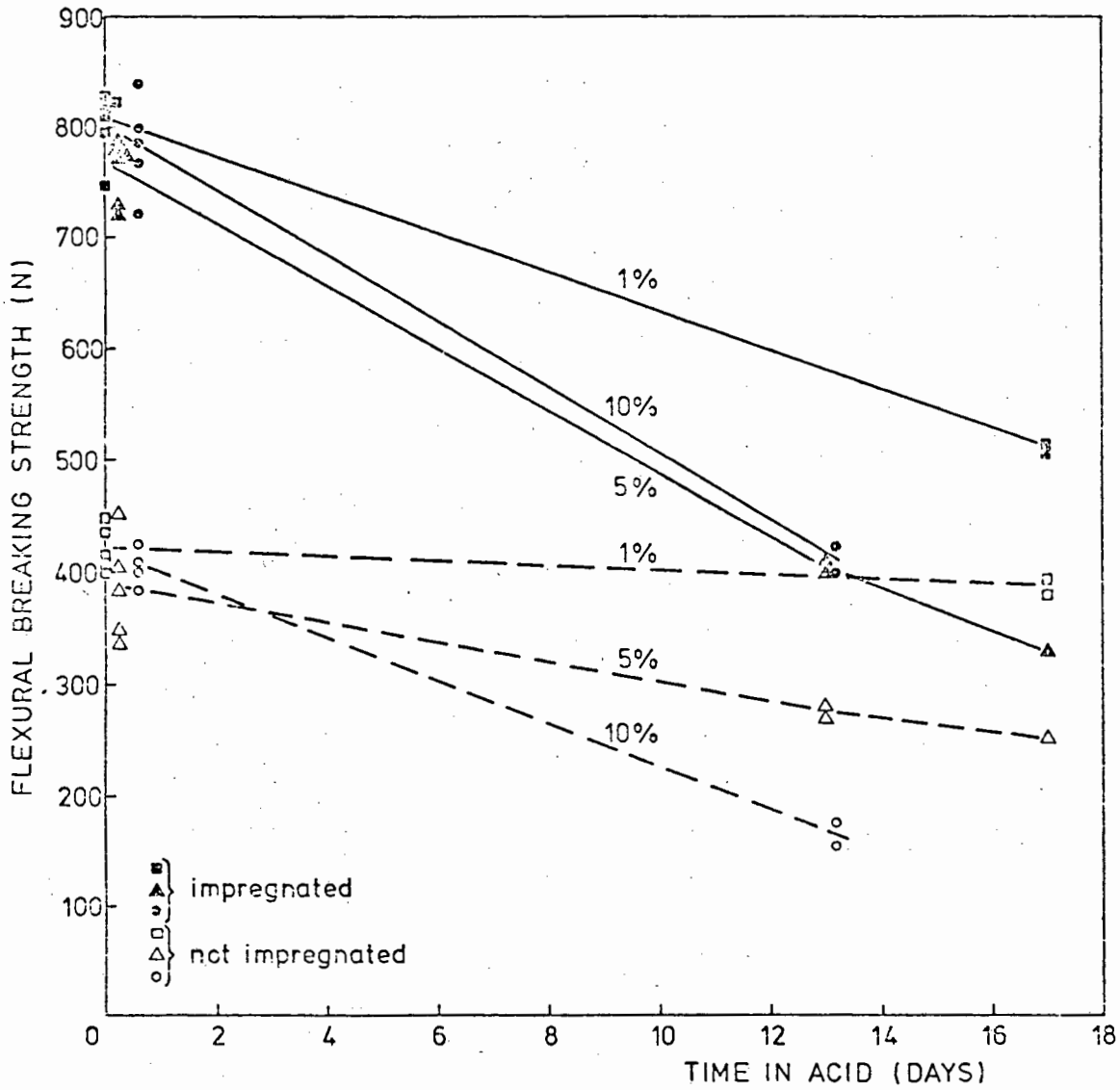


PLATE 5.1: Fractured Concrete Discs that were Impregnated by the Differential Pressure Technique. Impregnation Depth can be seen.

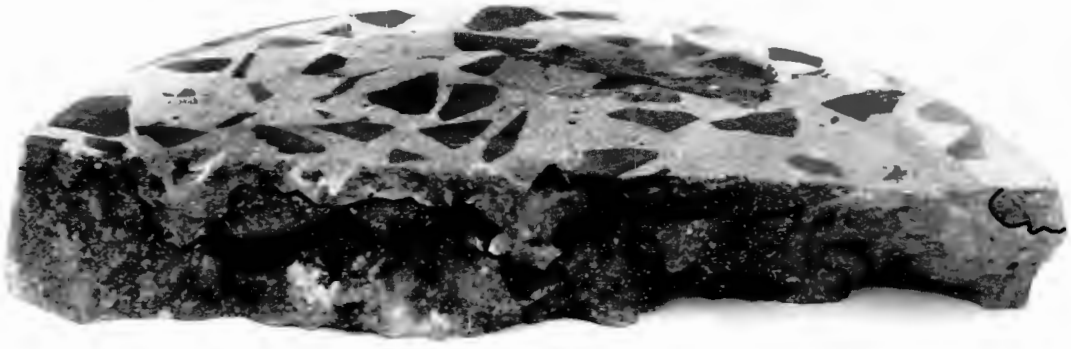


PLATE 5.2

PLATE 5.3

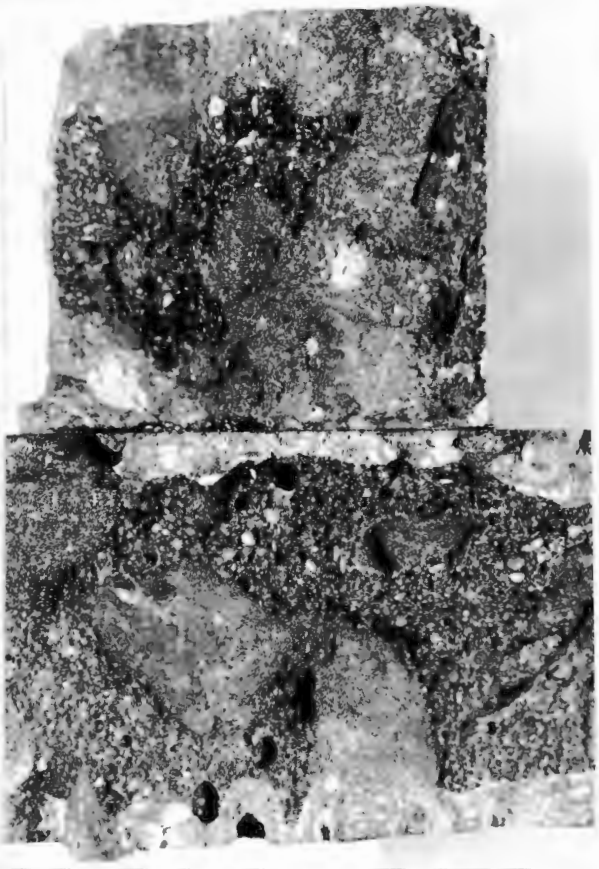
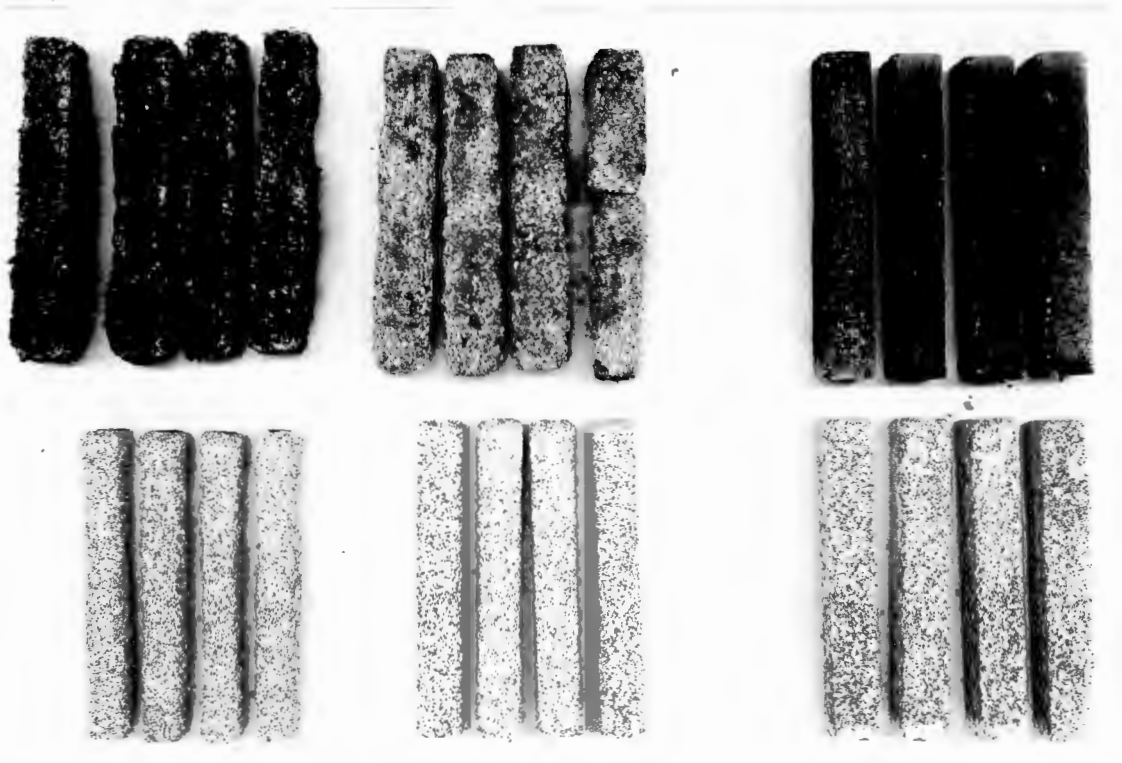


PLATE 5.4: Sulphuric Acid Corroded Specimens (at 2 weeks)
Top Row: Polymer Impregnated
Bottom Row: Unimpregnated Control Specimens



10% acid 5% acid 1% acid

PLATE 5.5: Unimpregnated Corroded Specimens (at 2 weeks)
(top 1% acid; middle 5% acid; bottom 10% acid)

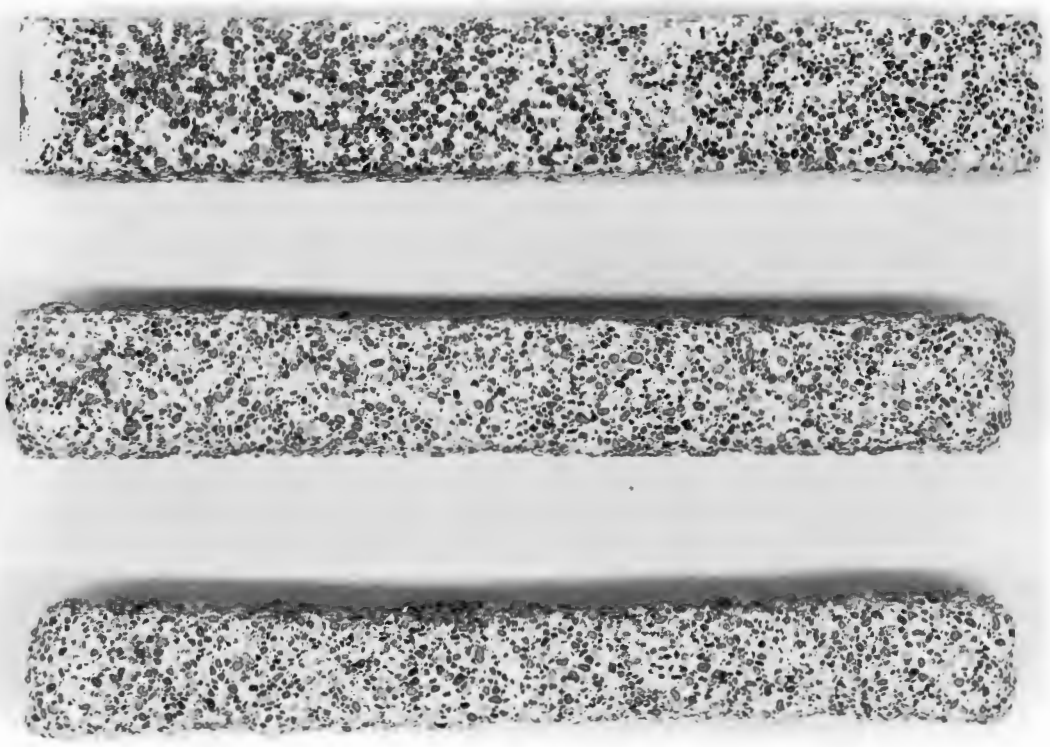
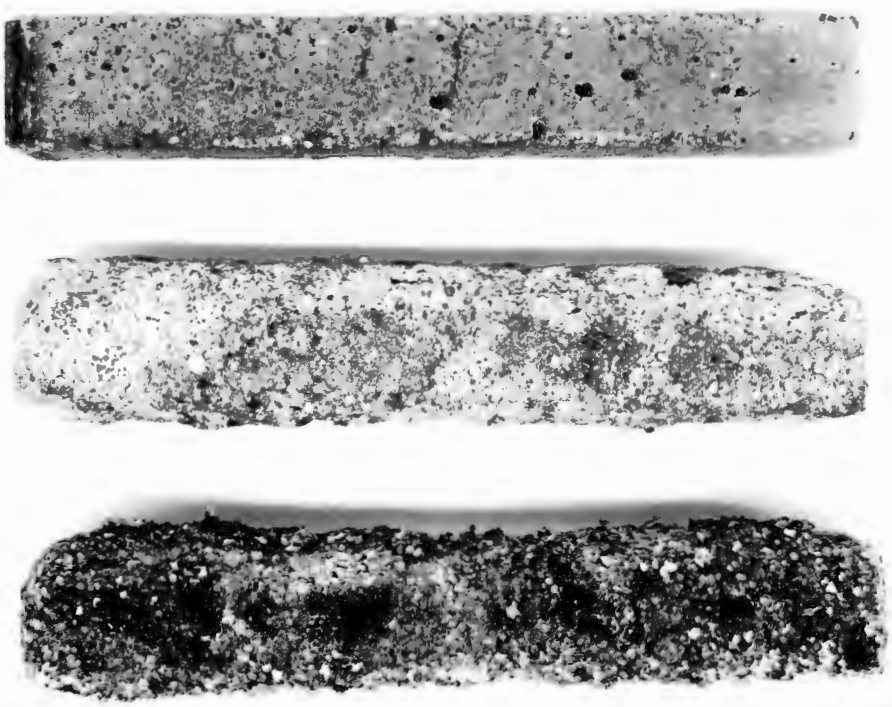


PLATE 5.6: Impregnated Corroded Specimens (at 2 weeks)
(top 1% acid; middle 5% acid; bottom 10% acid)



CHAPTER 6

6. GENERAL CONCLUSIONS

6.1 CONCLUSIONS

The primary aim of this project was to test the effects of sulphuric acid corrosion on polymer impregnated concrete with a view to extending substantially the service life of concrete sewer pipes in aggressive acidic sewer environments. Coupled to this was the need to optimise effective impregnating techniques by determining the optimum requirements of both concrete specimens and the polymer necessary for maximum impregnation within a reasonable time, as well as to develop methods of measuring accurately both the depth of impregnation and material loss in accelerated acid corrosion tests.

It has been shown that significant increases in the impregnation capability of this moisture curing polyurethane polymer into a high strength mortar can be achieved by suitable variation of certain parameters, namely, increases in soaking time, adequate drying of the concrete, impregnation under vacuum and pressure, age and dilution of the polymer, and acid etching of the concrete prior to impregnation.

It has been found that drying of the concrete specimens at a temperature of between 110°C and 150°C for several hours is a major factor in achieving maximum impregnation. In addition, it is important to stress that "fresh" polymer should be used as its impregnation ability rapidly decreases with age due to its apparent self-setting characteristics. A dilution of approximately 25% solvent and 75% polymer solution has been shown to result in the maximum rate of impregnation under atmospheric soaking conditions, and it is possible that a similar relation exists for vacuum and pressure impregnation techniques.

The effect of etching concrete specimens with dilute hydrochloric acid prior to impregnation has been seen to improve impregnation very slightly, although this technique requires further testing and evaluation.

The use of vacuum and pressure, or a combination of these, in the form of a pressure gradient across a specimen, has been

shown to increase dramatically the rate and depth of impregnation. Thus, the objective of deep polymer impregnation to 30 mm in commercial concretes to form an integral composite material, at least up to this depth, has been achieved.

While the application of the techniques described above is relatively easy to impose on small laboratory scale specimens, the same cannot be said for full scale concrete pipes of up to 1,8 m diameter and weighing in the region of 6500 kg, and which may be produced at a rate of fifty per day (in all sizes). Prior to any large scale development of polymer impregnation of full size pipes based on this study, a complete feasibility study would need to be undertaken. The capital cost of such drying ovens, cooling drying areas, vacuum and pressure apparatus would have to be taken into account and pure soaking, as opposed to pressure or vacuum impregnation, may be preferable. However, before efforts are made in this general direction it is felt that further studies should be undertaken in this study of polymer impregnation of concrete using other very corrosion resistant polymers.

The corrosion resistance of the impregnated concrete is improved by a factor of approximately 2, coupled with a similar increase in flexural strength. While this may appear not to be very significant, it must be remembered that accelerated testing may in fact be more harmful to the specimens over a short period of time than actual in-service corrosion over a long period. This consideration requires further short and long term testing.

Accelerated acid corrosion also reduces the strength of the polymer, as well as causing it to degrade chemically. This was shown in flexural strength tests of specimens, after corrosion, when mildly corroded impregnated specimens exhibited a breaking strength approximately equal to that of uncorroded and unimpregnated concrete specimens.

The overall effect of impregnation, however, is a two to three fold improvement in concrete strength and corrosion resistance. This investigation should, however, be continued as there are many factors which still require further testing and evaluation before full scale impregnation of concrete pipes can be put into operation. Prime among these include investigations

with other polymers; since although major improvements were obtained, it is believed even better results, especially with regard to corrosion resistance, can be achieved with more resistant polymer.

6.2 RECOMMENDATIONS FOR FUTURE WORK

During the course of this investigation, several factors which may affect impregnation capability or corrosion resistance were brought to light from the results and from general observations, but could not be investigated more fully because of time considerations. These are listed below and are recommended for further investigation in future studies in this field.

Specimen Preparation

(a) The manufacture and use of concrete specimens incorporating both large and small aggregate.

(b) Variations in the water/cement ratios to change the pore volume of the specimens.

(c) The use of smaller blocks of moulds. It was found that the large 10-specimen mould boxes were difficult to handle on the vibrating table.

(d) Before impregnation, the rough cast surface of the specimens was ground off on the side of a rotating cutting disc. It is considered that this is a relatively rough grinding technique, and future specimens should be ground by a more gentle, if slower, technique.

Impregnation

As has been mentioned before, probably the most important series of tests to be undertaken concern investigations using the techniques, skills and know-how developed during, and reported in, this thesis but with other more corrosion resistant polymers. These would include presumably PMMA, acrylics, polyesters, resins and indeed any polymer material which exhibited high corrosion resistance but which was still capable of being impregnated (e.g. P.V.C., although ideal on the first count, is probably excluded on the second count). It is anticipated that this would imply monomer impregnation with subsequent polymerisation by heat or radiation. This would require some research to optimise and prevent premature drainage or excessively

expensive procedures.

More specific tests to be undertaken on the existing polyurethane polymer are mentioned below.

(a) An investigation of the effect of temperature on the viscosity of the polymer, its impregnation, strength and durability characteristics, as well as the effect of the temperature of the concrete prior to and during impregnation, should be undertaken.

(b) Further etching experiments to determine more precisely the effect on impregnation and concrete strength.

(c) By recording the relative increases in mass of specimens before and after impregnation, a better understanding of the density and quality of impregnation can be achieved as well as a measure of the polymer loading. The present impregnation depth method is quite adequate but is not normalised.

(d) More tests are required to determine the precise time of impregnation under vacuum to optimise this important impregnation technique.

(e) Impregnation under a pressure gradient has been shown to be very effective and should be considered as a significant impregnation technique to be investigated more extensively.

(f) A more detailed determination of the part played by the outer skin of polymer on the flexural strength of the specimens should be undertaken to assess its importance.

(g) Toughness and adhesion properties of the polymer after impregnation and curing should be investigated, probably using the triangular notched flexural beam test.

(h) The addition of a catalyst to the polymer or curing of the polymer in a catalyst vapour atmosphere may improve curing and hence strength and durability characteristics and should be further investigated.

Corrosion

(a) Impregnated specimens should be lightly ground to remove the polymer coating on the external surfaces to determine the effects of the presence or absence of this outer skin in corrosion tests.

(b) The effect of temperature, after curing, on polymer must be determined as it appears this may have a very deleterious effect on its properties.

(c) The sulphate corrosion of concrete is second only to acid corrosion in importance in sewers, and must be investigated further.

(d) Impregnated and control specimens should be placed in actual corrosive sewer environments, or alternatively, a newly laid concrete pipe should be impregnated to investigate the performance of polymer impregnated concrete under "natural" in-situ service conditions. This is a long term investigation and may possibly form part of an on-going research project.

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APPENDIX

DEPARTMENT OF METALLURGY AND MATERIALS SCIENCE

AREA MEASUREMENT : OPERATING INSTRUCTIONS FOR USE WITH THE SURVEY DEPT. DIGITIZER

Designed for measuring U.P.C. impregnation areas of concrete.

By R.B. Tait and J. Troost

1. Switch on (K3 modules)
2. Punch tape in.
3. FIN 2
4. R
5. OLD
6. R
7. RUN
8. R
9. Scale of original 1 : ?
10. 1 R
11. Do you want screen image ?
12. YES R
13. Do you want plot ?
14. NO R
15. Do you want data on tape ?
16. NO R
17. What are the experiment details ?
18. Type in the heading of your experiment e.g. "IMPREGNATION; 24 HRS." then press then press R.
19. Switch to Point Mode
20. Digitize outside bottom left and top right corners
21. Switch to stream switch
22. Digitize area 1
23. Press flag 1
24. Digitize area 2
25. Press flag 1 (at this stage the program will print out the ratio of the shaded area to the total area, viz.

26. More contours ?
27. YES

28 a) HOME PAGE key, R

or 28 b) R

29. Digitize the next area.

Turn off procedure:

30. Eject tape
31. Turn off power (3 modules).

NOTES: 1. *In case of an error –*
a) punch CLEAR and program will return to statement 9,
or b) punch BREAK BREAK and then RUN and program will also return to statement 9.

2. *To clear the screen press home page.*

3. *R ≡ Return key*

4. *Upper case instructions are to be typed in, lower case to be followed.*

```
 60 RUN 400
 70 IF S<>7 THEN 1090
100 INIT
110 DIM X2(2,2),A4(2)
120 A1=0
130 A2=0
140 A3=0
150 PAGE
160 PRINT "SCALE OF ORIGINAL  1 :  "
170 INPUT Z
180 PRINT "DO YOU WANT SCREEN IMAGE"
190 INPUT A$
200 IF A$="NO" THEN 220
210 A1=1
220 PRINT "DO YOU WANT PLOT"
230 INPUT A$
240 IF A$="NO" THEN 260
250 A2=2
260 PRINT "DO YOU WANT DATA ON TAPE"
270 INPUT A$
280 IF A$="NO" THEN 350
290 A3=3
300 GO TO 340
310 PRINT "WHICH FILE #  "
320 INPUT F
330 FIND F
340 FIND 18
350 S=A1+A2+A3
360 S=S+(S=3)+2*(S=6)-(A3=3)+3*(S=4)
370 IF S>0 THEN 400
380 PRINT "SO WHAT DO YOU WANT ??????"
390 STOP
400 PAGE
410 A=0
420 PRINT "WHAT ARE THE EXPERIMENT DETAILS ?"
430 INPUT N$
440 PRINT @3: USING 450:"EXPERIMENTAL DETAILS :",N$
450 IMAGE FAZXFA
460 PRINT "SET DIGITIZER TO POINT MODE AND DIGITIZE LEFT BOTTOM CORNER"
470 PRINT "AND RIGHT TOP CORNER OF THE AREA TO BE DIGITIZEDG_G_G_G_G_G_G_"
480 INPUT @2:C,X2(1,1),X2(1,2),D
490 INPUT @2:C,X2(2,1),X2(2,2),D
500 X1=(X2(2,1)+X2(1,1))/2
510 Y1=(X2(2,2)+X2(1,2))/2
520 X3=(X2(2,1)-X2(1,1))/2
530 Y3=(X2(2,2)-X2(1,2))/2
540 R8=2*X3/130
550 R9=2*Y3/100
560 IF R8<R9 THEN 590
570 WINDOW X2(1,1)-X1,X2(1,1)-X1+2*X3,X2(1,2)-Y1,X2(1,2)-Y1+2*Y3*R8/R9
580 GO TO 600
590 WINDOW X2(1,1)-X1,X2(1,1)-X1+2*X3*R9/R8,X2(1,2)-Y1,X2(1,2)-Y1+2*Y3
600 PRINT " SET STREAM MODE AND DIGITIZE FEATUREG_G_G_G_G_G_"
610 PRINT " PRESS FLAG 1 IF DIGITIZING IS COMPLETED"
620 REM  DIGITIZING INTERVAL
630 DZ=1
640 PAGE
650 A4(1)=0
660 A4(2)=0
670 K=0
680 REM DIGITIZE
690 A=0
700 K=K+1
710 PRINT " STARTING TO DIGITIZE AREA :",K
720 INPUT @2:C,X,Y,D
730 INPUT @2:C,X,Y,D
740 P=X
750 P1=Y
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760 Q=Y
770 Q1=Y
780 GOSUB 1220
790 INPUT @2:C,X,Y,D
800 IF D=8 THEN 880
810 D1=SQR((P-X)↑2+(Q-Y)↑2)
820 IF D1<D2 THEN 790
830 A=A+(X-P)*(Y+Q-2*Y1)/2
840 P=X
850 Q=Y
860 GOSUB 1100
870 GO TO 790
880 PRINT "G_G_G_G_G_G_G_G_"
890 A=A+(X-P1)*(Y+Q1-2*Y1)/2
900 A4(K)=A
910 HOME
920 PRINT
930 PRINT @3: USING 940:"THE DIGITIZED AREA IS :",A,"MM↑2"
940 IMAGEFA2X6D2XFA
970 IF S=4 THEN 1090
980 IF S=7 THEN 1090
990 IF K=1 THEN 680
1000 A5=(A4(1)-A4(2))/A4(1)
1001 PRINT
1010 PRINT USING 1030:"THE RATIO OF IMPREGNATED TO TOTAL AREAS IS:",A5
1020 PRI @3: USI 1030:"THE RATIO OF IMPREGNATED TO TOTAL AREAS IS:",A5
1030 IMAGE FA2X1D.3D
1040 PRINT "MORE CONTOURS  "
1050 INPUT A$
1060 IF A$="NO" THEN 1080
1070 GO TO 640
1080 GOSUB 1330
1090 END
1100 REM SUBROUTINE
1110 IF S=2 THEN 1170
1120 IF S=5 THEN 1170
1130 IF S=3 THEN 1200
1140 DRAW @32:X-X1,Y-Y1
1150 IF S=1 THEN 1210
1160 IF S=6 THEN 1200
1170 DRAW @1:X-X1,Y-Y1
1180 IF S=2 THEN 1210
1190 IF S=4 THEN 1210
1200 PRINT @33:X-X1,Y-Y1,0
1210 RETURN
1220 REM SUBROUTINE
1230 IF S=2 THEN 1290
1240 IF S=5 THEN 1290
1250 IF S=3 THEN 1320
1260 MOVE @32:X-X1,Y-Y1
1270 IF S=1 THEN 1320
1280 IF S=6 THEN 1320
1290 MOVE @1:X-X1,Y-Y1
1300 IF S=2 THEN 1320
1310 IF S=4 THEN 1320
1320 RETURN
1330 PRINT "DO YOU WANT TO INSPECT THE TAPE CONTEXT  "
1340 INPUT A$
1350 IF A$="NO" THEN 1410
1360 FIND 18
1370 FOR I=1 TO 50
1380 INPUT @33:X,Y
1390 PRINT D;X;Y
1400 NEXT I
1410 RETURN
1420 INPUT @2:A,S,D,F
1430 PRINT A,S,D,F
1440 GO TO 1420
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