

THE UNIVERSITY OF CALGARY

RELATIONSHIPS BETWEEN STRENGTH, PERMEABILITY AND
MICROSTRUCTURAL CHARACTERISTICS OF BLENDED MORTARS

by

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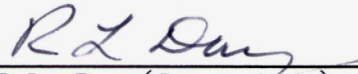
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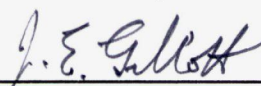
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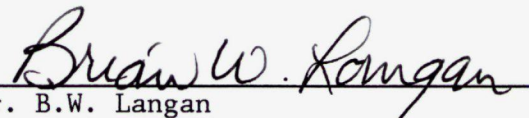
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ABSTRACT

This thesis describes experiments performed to evaluate engineering properties of fly-ash mortars and mortars with latex modifier. The following engineering properties were examined: compressive strength, water permeability, oxygen permeability and permeability of mortars to chloride ions.

Since these properties are closely related to the durability of mortar or concrete, the examination is of prime interest.

The use of fly ash as a partial replacement of cement on engineering properties and microstructure of hardened mortars was investigated. Particular emphasis was placed on the examination of four Canadian ashes. The replacement levels of cement by fly ash were 35 and 50 percent by volume and 50 percent by weight. Three water-cement ratios of 0.35, 0.47 and 0.65 were employed. Latex modifier was utilized in two mixes. The dry latex-cement ratio was 0.15 by weight.

Mercury porosimetry, thermogravimetry, X-ray diffraction and scanning-electron microscopy were performed to explain or support the findings from a fundamental level.

Some mortars with partial cement replacement by fly ash (in this work denoted as blended mortars) displayed superior engineering properties to those of plain mortar. For example, blended mortar #5 with water-cement ratio of 0.47 and replacement level of 35 percent by volume displayed higher compressive strength and lower water, oxygen and chloride permeabilities than control mortar at the age of 160 days.

Relationships with high correlation coefficients were found between water, oxygen and chloride permeabilities.

Good correlation was also observed between engineering properties and microstructural characteristics. It was concluded that permeability relates mainly to the porosity in the large pores, while strength relates to the total porosity (in this work volume of pores down to pore radius of 1.8 nm).

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CHAPTER ONE

INTRODUCTION

1.1 General

The service life of a concrete structure is affected by various chemical and physical attack processes. Chemical attack comprises leaching and efflorescence, sulphate attack, corrosion of steel reinforcement, crystallization of salts in concrete and attack by acids. Physical attack includes freezing and thawing and abrasion. Permeability is the most important parameter which controls the ingress of various aggressive solutions or gases into the concrete or mortar.

From numerous studies it has been shown that partial replacement of cement by a pozzolan can aid durability. R.H. Mills (1983) observed that permeability of concrete was significantly decreased by partial substitution of Portland cement by fly ash. Manmohan and Mehta (1981) studied the microstructural changes in fly ash-cement pastes. They reported that fly ash-cement pastes display finer pore size distribution than plain ones at later ages (see Section 2.4.3, Figure 2.2) which in turn means lower permeability of fly ash-cement systems.

It is not certain whether the partial replacement of cement by fly ash can help to prevent corrosion of steel reinforcement in concrete. In mortar or concrete calcium hydroxide creates a high-alkaline environment (a pH of about 12.0 to 12.5) which prevents the corrosion of reinforcement. In fly ash mortars the Ca(OH)_2 is absent, or present in reduced quantity. On the other hand, corrosion also depends on permeabilities of mortar to water and oxygen; blended

mortars often show superior performance in this regard. Also, chloride ions, if present, have the ability to initiate corrosion of steel reinforcement in mortars even at high alkalinities.

An impermeable concrete is generally more desirable than a concrete with high content of Ca(OH)_2 which may be eventually leached out in the aggressive environment. Since the pozzolanic reaction in the fly ash-cement system can aid to the impermeability, while reducing the Ca(OH)_2 content in the concrete, the utilization of fly ash as a partial replacement of cement may lead to the development of highly durable concrete.

Extensive research on the utilization of fly ash in concrete has been conducted during the past few years. The results indicate that although concrete with fly ash shows low early strength, the ultimate strength may be higher than that of concrete without fly ash. Jawed and Skalny (1984) stated that with proper mix proportioning it is possible to design blended concrete to give any specified compressive strength. Berry and Malhotra (1979) reported that properly proportioned and placed fly ash concrete generally shows improved workability, pumpability, cohesiveness, ultimate strength and durability.

1.2 Scope of Research

The objective of this research was to evaluate the effects of various levels of cement replacement by fly ash on compressive strength and water, oxygen and chloride permeabilities of blended mortars.

Also, very little is known about the changes in the structure of hardened concrete brought about by pozzolanic reaction. To explain

the effect of this reaction on the properties which most affect durability, an extensive examination of microstructure was done.

Porosity and pore size distribution were investigated to show how changes in the structure occur as the hydration and pozzolanic reactions proceed. With the high pressure porosimetry employed in this work, a pore size distribution to pore radii down to 1.8 nm (18 Å) was examined. The progress of pozzolanic reaction was easily determined by monitoring the Ca(OH)_2 content. Thermogravimetry was employed for the quantitative determination of Ca(OH)_2 . Scanning electron microscopy (S.E.M.) and X-ray diffraction were also used to acquire a more complete view of microstructural changes.

CHAPTER TWO

THE USE OF FLY ASH AS A PARTIAL CEMENT REPLACEMENT

2.1 General

Pozzolanic materials, such as volcanic ash and diatomaceous earth, occur naturally and were successfully used in construction by the ancient Romans. Pulverized furnace ash, known as a fly ash, calcined clays and shales are artificial pozzolans. A pozzolan is defined as:

"Siliceous or aluminosiliceous material that in itself possesses little or no cementitious value, but that in finely divided form and in presence of moisture will chemically react with alkali and alkaline earth hydroxides at ordinary temperatures to form or to assist in forming compounds possessing cementitious properties."
(ASTM C618-80)

There is an indication that engineering properties of hardened concrete with pozzolans may be superior to those of concrete without pozzolans (Berry & Malhotra, 1982). Thus, a great deal of effort has been focused on the utilization of pozzolans in concrete.

In recent years, fly ash has been extensively employed as a partial cement replacement because of its availability and low cost. Since fly ash is a waste product, environmental problems may arise in the near future with the disposal of this by-product. In Alberta especially, fly ash is an abundant material because coal is the primary fuel for generating electricity. Therefore, the utilization of fly ash is desirable not only because of improvement of engineering properties of concrete, but also for environmental and economical reasons.

2.2 Composition and Classification of Fly Ashes

Fly ash is composed of tiny spheres of glasses and crystalline compounds formed mainly from SiO_2 , Al_2O_3 , Fe_2O_3 , CaO and MgO . Combustible matter is always present but is often below 3 percent in well burnt materials (Lea, 1970). Ashes containing silica in amorphous form react faster with lime than those containing silica in the crystalline form. Generally, fly ashes from subbituminous and lignite coals contain more CaO and less Fe_2O_3 than those from bituminous coals (see Chapter 3, Table 3.1).

According to ASTM standard C618-84, fly ashes are classified into two categories depending on their chemical composition. If $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content is higher than 70%, the fly ash belongs to Class F; if $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content is in the range from 50% to 70%, it is said to be Class C. Class C fly ash is normally produced from lignite or subbituminous coal; while Class F is produced from burning anthracite or bituminous coal. Table 2.1 shows several different fly ash specifications. Unlike ASTM, Canada has no specification on $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content. Nevertheless, for both ASTM and Canadian specifications the loss on ignition for Class C and F is the same. There is some controversy about this classification system. Manz (1983) showed that in practise many lignite and subbituminous fly ashes can meet the requirements for Class F. Aitcin et al (1986) examined three Class F fly ashes and four Class C fly ashes. They observed that fly ashes from one particular class can behave very differently, whereas fly ashes from different classes can behave similarly. Idorn (1982) divided fly ashes for use in concrete into two groups: the lime rich, which are cementitious as well as

U. S. A.												
	Canada					ASTM						
	Australia	Type C	Type F	India	Japan	U.K.	Class C	Class F	Federal	N.D. Hgw. Dept.	U.S.S.R.	W. Germany
SiO ₂ , min. %				35.0	45.0						40.0	
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ min. %				70.0	70.0		50.0	70.0	70.0	45.0		
CaO, max. %					6.0					35.0		
MgO, max. %				5.0	5.0	4.0	5.0*	5.0*	5.0			
SO ₃ , max. %	2.5	5.0	5.0	3.0	5.0	2.5	5.0	5.0	4.0	12.0	3.0	4.0
Available Alkalies as Na ₂ O, max. %				1.5			1.5*	1.5*	1.5*	7.5		
Loss on ignition max. %	8.0	6.0	12.0	12.0	10.0	7.0	6.0	12.0	6.0	6.0	10.0	5.0
Moisture, max. %	1.5	3.0*	3.0*		3.0	0.5	3.0	3.0	3.0	3.0		

* Optional Requirement

Table 2.1 Fly ash specifications in various countries (from Manz, 1983)

pozzolanic and the lime poor which are only pozzolanic. According to Idorn's classification, fly ashes from Alberta belong to the lime rich group. Probably characterizing and classifying fly ashes according to their physical and chemical properties would be more appropriate than by simple chemical composition. According to Diamond (1982) aspects of importance for proper classification of fly ashes are:

- a) overall percentage of glass present;
- b) type of glass present;
- c) nature of crystalline compound.

2.3 Sources of Variation between Different Fly Ashes

Differences in physical and chemical properties of various fly ashes are closely related to the geological history of the coal from which they come. The details of the combustion process are also important. Diamond (1982) summarized important effects on the nature of fly ashes:

1) Origin of the Mineral Fraction of the Coal

Since fly ashes are formed from inorganic residues of coal, the chemistry of the mineral component of coal has a substantial influence on the chemistry of fly ashes.

2) Formation Process

Details of the grinding and combustion of the coal are of prime importance. In most plants, coals are ground to a fineness of approximately the same order as that of Portland cement. The ground coal is then injected by means of a stream of air into a burning zone. The temperature should be high enough to melt the inorganic components. Also, a sufficient amount of oxygen should be present to combust the organic part of the coal.

The particles which undergo rapid cooling are the most desirable. They remain glassy, retain spherical shape and constitute the reactive portion of fly ash.

3. Details of the Design and Operation of the Recovery System

Fly ash is recovered with mechanical collectors or electrostatic precipitators. The latter are more common because of their higher efficiency. Coarser particles from the recovery system contain higher proportions of quartz and iron oxides, which are both inert under ordinary conditions. Thus, the coarser particles act more as a fine aggregate than as a pozzolan.

The properties of a particular fly ash depend on many factors. Some of the factors are difficult to control during the production of fly ash or are not controlled at all. Better quality control could lead to a more uniform product and thus intensify the utilization of fly ash.

2.4 The Use of Fly Ash in Concrete

In 1948 the U.S. Bureau of Reclamation published the first report dealing with the performance of fly ash concrete used at Hungry Horse Dam (Manz, 1983). In Australia, the first reported use of fly ash in concrete dates back to 1940.

Samarin et al. (1983) reported three different methods of proportioning of fly ash concrete:

- 1) Replacement method: i.e. replacing a portion of Portland cement with fly ash;
- 2) Addition method: i.e. addition of fly ash to cement by replacing part of the aggregate;
- 3) Replacement-addition method: a combination of the two

previous methods.

Throughout this project the replacement method was employed. It is the best one when economic and engineering aspects are considered. When the addition method is employed, more calcium silicate hydrate will be present in concrete. This may lead to undesirable effects such as large shrinkage and creep deformations.

The use of fly ash as a replacement of cement is advantageous partly on economic grounds and partly because of its influence on workability and heat evolution. Nevertheless, the evidence that pozzolanic reaction may aid durability of the structure is the most pronounced effect of the use of fly ash in concrete.

2.4.1 Hydration Products of Mixes with Fly Ash

The pozzolanic reaction can be expressed in a simple form as:



If reactive alumina is present also this reaction occurs:



where:

C-S-H is calcium silicate hydrate, C-A-H is calcium aluminate hydrate. Ca(OH)_2 is liberated during the hydration of Portland cement, SiO_2 and Al_2O_3 are constituents of the fly ash.

The hydration products of Portland cement with fly ash are basically the same as those of Portland cement. The calcium silicate hydrate C-S-H in fly ash cement, formed by the pozzolanic reaction, displays lower Ca/Si ratio of 1.43 compared to that of C-S-H in pure paste which is 1.51 (Mohan & Taylor, 1981). Rayment (1982) reports that the fly ash decreased the Ca/Si ratio of the cement paste from 1.71 to 1.55. The C-S-H in a cement paste with fly ash is formed by

pozzolanic reaction of the silicates in fly ash with the Ca(OH)_2 liberated during the hydration of Portland cement; thus, it can be expected to be of different Ca/Si ratio from that of cement.

The hydration products of the cement compounds have lower specific gravities than the cement compounds themselves. Mindess and Young (1981) stated that the volume of cement gel is approximately 2.3 times the volume of the cement. It is evident that the formation of C-S-H is accompanied by a decrease in porosity.

2.4.2 Compressive Strength

It is widely accepted that the use of fly ash in concrete decreases early strength; however, there is evidence that the ultimate strength of fly ash concrete can be higher than that of the control mix at later ages (see Figure 2.1).

The higher strength of concrete with fly ash at later ages is the

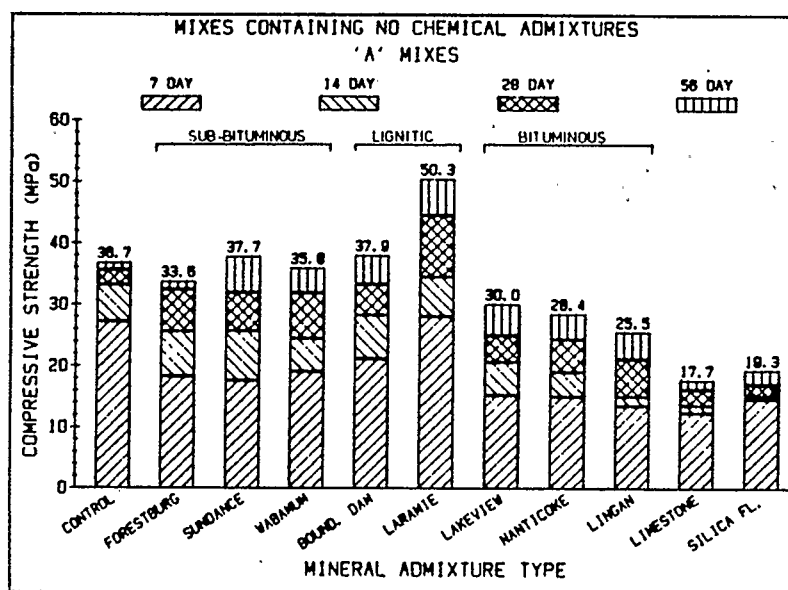


Fig. 2.1 Effect of substituting pozzolan for Portland cement on the strength (Joshi et al. 1985)

result of pozzolanic reaction producing increasing amount of C-S-H while diminishing the amount of Ca(OH)_2 .

Another possible explanation of lower ultimate strength of concrete without any fly ash may be its higher Ca(OH)_2 content. It has been suggested that the increased content of Ca(OH)_2 may be strength limiting because of its tendency to cleave under shear (Mindess & Young, 1981).

As with other porous materials, strength of concrete is closely related to the capillary porosity (see Table 2.2). The different strength values between plain and fly ash concrete result from changes in microstructural characteristics. Mehta (1985) examined the influence of fly ash characteristics on the strength of cement-fly ash mixtures. Mehta observed that variations in chemical constituents other than calcium content have apparently no effect on fly ash reactivity and that particle size distribution is an important parameter controlling the reactivity of fly ash with normal carbon and glass contents. The reactivity of low calcium fly ashes was found to be directly proportional to the amount of particles $< 10 \mu\text{m}$ and inversely proportional to particles $> 45 \mu\text{m}$. It was observed that the pore size distribution did not affect the reactivity of high calcium fly ashes to such an extent as in the case of low calcium ashes.

2.4.3 Permeability - General

Permeability is the most important property of concrete with respect to durability. It determines the rate of entry of aggressive agents into the porous material.

Permeability of concrete is affected by many factors such as proportion of cement, water cement ratio, method of placement, age,

curing, etc. Generally, permeability decreases as the cement content increases and water-cement ratio decreases (Lea, 1970). Properly placed and cured concrete displays a decrease in permeability with time. The coefficient of permeability will be lower for moist cured concrete than for concrete cured in air.

The coefficient of permeability K is closely related to porosity. Nevertheless, it is the capillary porosity and not total porosity which governs the permeability (Manmohan and Mehta, 1981 - see Section 2.4.4). Obviously, gel pores display higher resistance to flow than capillary pores because of their small size. Adsorbed water on the gel pore walls also impedes the flow through the pore. Capillary porosity and permeability decrease as hydration proceeds and the volume of gel increases.

2.4.4 Permeability and Porosity of Blended Pastes

A classification of pore sizes in hydrated cement paste is given in Table 2.2. The boundary between capillary pores and gel pores is, to a large extent, arbitrary. Verbeck (1966) considers gel pores to vary from 1 to 8 nm and capillary pores from 8 nm to 13 μm . According to Mindess & Young (1981), capillary porosity is that which can be seen in the scanning electron microscope; gel porosity cannot be resolved by the SEM.

Powers (1958) was the first who determined the importance of pore-structure parameters other than total porosity in relation to permeability. He found that permeability of a concrete is not a simple function of its porosity but depends also on the size, distribution and continuity of pores. Powers showed that the water in gel pores takes part in flow but only to a limited degree due to its high

Table 2.2
Classification of Pore Sizes in Hydrated Cement Paste
(From Mindess & Young 1981)

Designation	Diameter	Description	Role of Water	Paste Properties Affected
Capillary Pores	10-0.05 μm (10 000-50 nm)	Large capillaries	Behaves as bulk water	Strength; permeability
	50 ~ 10 nm	Medium capillaries	Moderate surface tension forces generated	Strength; permeability; shrinkage at high humidities
Gel Pores	10-2.5 nm	Small (gel) capillaries	Strong surface tension forces generated	Shrinkage to 50% RH
	2.5 ~ 0.5 nm	Micropores	Strongly adsorbed water; no menisci form	Shrinkage; creep
	< ~ 0.5 nm	Micropores "interlayer"	Structural water involved in bonding	Shrinkage; creep

viscosity. The coefficient of permeability of paste containing only gel pores was about 7×10^{-16} m/s. Pastes containing capillary porosity were 20 to 100 times more permeable, depending on actual capillary pore volume. Since only a small amount of flow occurs through gel pores, it is obvious that the main parameter which controls the permeability is capillary porosity.

Recently, Powers' work was repeated and expanded by others (Nyame, 1979; Mehta & Manmohan, 1980; Manmohan & Mehta, 1981; Mansoor, 1983

and Marsh, 1984).

Manmohan & Mehta (1981) studied the relationship between pore structure and permeability of pastes containing fly ash as a partial cement replacement. They reported that when pores greater than 50 nm (500 Å) radius were absent, the coefficients of permeability were too low to give meaningful trends among various specimens. The changes in pore size distribution of cement pastes resulting from the replacement of cement by fly ash are presented in Figure 2.2. At 28 days all blended cements exhibited coarser pore structure than control Portland cement paste. This shows that the pozzolanic lime-silica and lime-alumina reactions had not contributed to significant changes in microstructure. After one year, the situation was reversed; the blended mortars contained less large pores than the control cement paste, thereby indicating substantial progress in the pozzolanic reaction. From the permeability and pore size analysis data, the authors concluded that the pozzolanic action became

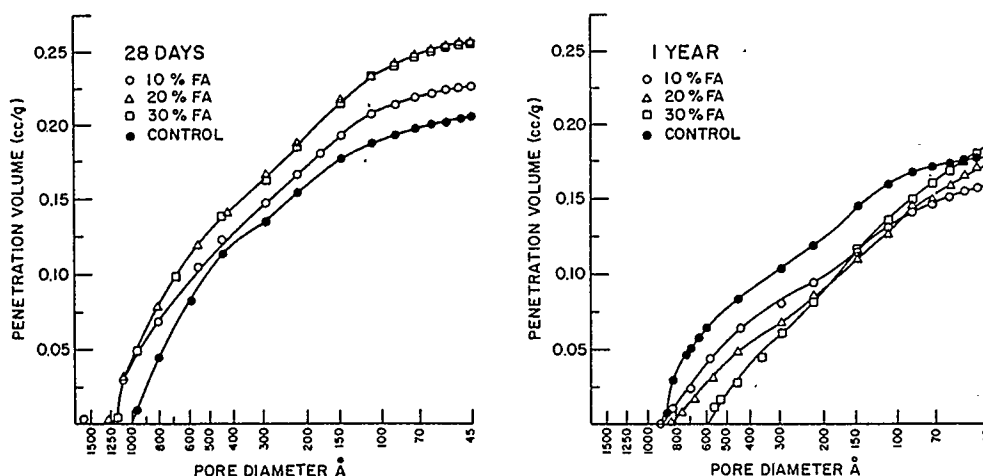


Fig. 2.2 Effect of various proportions of fly ash on pore size distribution of cement pastes. (From Manmohan & Mehta, 1980)

significant during the hydration period between 28 and 90 days. In the present work, the pozzolanic reaction was detected as early as between 7 and 28 days since more reactive fly ashes were employed (see Chapter 6).

Mansoor (1983) looked at the effect of fly ash replacement levels between 0 and 80 percent for pastes with water-solids ratio 0.4 and 0.5. Pastes were cured at room temperature and were examined at 28 and 270 days. A replacement level of cement by fly ash up to 40 percent reduced permeability; higher replacement levels than 40 percent resulted in a large increase of permeability.

Feldman (1981) reported that fly ash cement pastes cured for six months at 21°C and 35°C displayed higher total porosities and finer pore size distribution, measured by mercury porosimetry, than plain cement paste.

Mehta and Manmohan (1980) examined the effect of porosity on the permeability of pastes with water-cement ratios from 0.3 to 0.9. The permeability coefficients increased exponentially with increase in water-cement ratio or total porosity. They also reported that the increase in water-cement ratio manifests itself in increased porosity in the pore size region greater than 132 nm ($1320 \text{ \AA}$) diameter.

2.4.5 Corrosion

Corrosion of reinforcing steel is a serious problem in the construction industry. The corrosion of steel promotes the formation of corrosion products which produce large tensile forces which cause delamination and spalling. There are four requirements for active corrosion to take place in concrete:

- 1) flow of electric current;

- 2) two dissimilar metals;
- 3) oxygen;
- 4) moisture.

Even if these four requirements are met in the concrete, the steel reinforcement will still not corrode due to a passive oxide film which is formed on the steel. This layer is stable in the highly alkaline environment; the passive oxide layer is destroyed when the pH of concrete is reduced below 11.0 (Mindess & Young, 1981).

Ingress of CO_2 reduces the pH of the environment in concrete since it converts calcium hydroxide to calcium carbonate. It is important to note that in fully carbonated concrete the steel still does not corrode unless water and oxygen are also present.

The chloride ion has the unique ability to destroy the passive layer on steel in concrete even when the pH is higher than 11.0. The chlorides can enter the concrete:

- 1) from calcium chloride addition;
- 2) from de-icing salts;
- 3) from seawater.

From the foregoing, it is clear that water, oxygen and chloride permeabilities are of prime importance with respect to corrosion of steel reinforcement and thus the durability of concrete structures.

2.4.6 Permeability Test Methods

2.4.6.1 Water Permeability

Powers et al. (1954) studied the permeability of cement paste to water. For hardened, mature, pastes with water-cement ratios ranging from 0.3 to 0.7, the coefficients of permeability were in the range from 1×10^{-15} to 1×10^{-11} m/s. Decrease of permeability during

hydration was noted; for cement paste with a water cement ratio of 0.70 permeability ranged from 4×10^{-10} m/s at 5 days to 6×10^{-12} m/s as an ultimate value.

The permeability of concrete is generally much higher than that of its equivalent cement paste matrix because the presence of aggregate may result in internal cracking at the paste-aggregate interface. Typical permeabilities of concrete are about 100 times higher than those of cement pastes (see Figure 2.3).

Questions may arise whether the permeability test under high hydrostatic heads simulates practical conditions. Whiting (1981) stated that in many areas of the construction industry, water vapour transmission (WVT) of concrete rather than the permeability of concrete is more applicable. Konecny (1980) measured WVT of concrete made with lightweight aggregate by a "wet cup" technique:

disc specimen of a diameter of 160 mm and thickness of 30 mm is sealed into the shallow pan containing desiccant. Specimens are

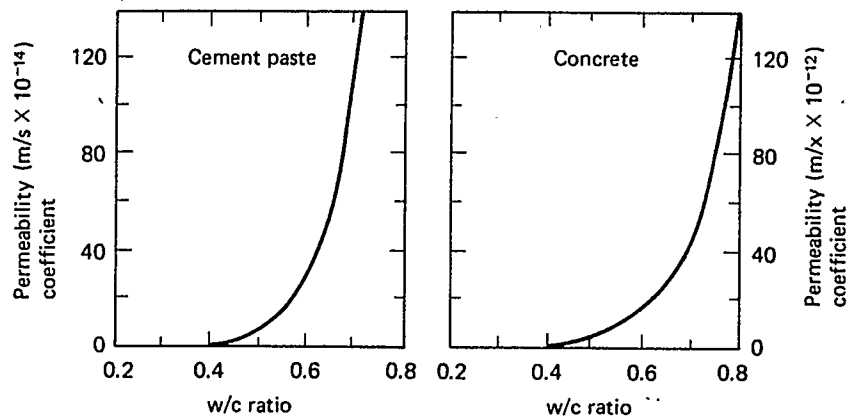


Fig. 2.3 Effect of water-cement ratio on the permeability of cement paste and concrete (from Mindess & Young, 1981)

then exposed to a saturated atmosphere. Flow rate is measured by weighing the entire apparatus. This method is similar in principle to ASTM standard C355-64 (Standard Test Method for Water-Vapour Transmission of Thick Materials). The WVT is calculated as

$$\text{WVT} = \frac{W}{t} \cdot \frac{1}{A}$$

where

WVT = water vapour transmission [$\text{kgs}^{-1}\text{m}^{-2}$]

W/t = rate of water gain [kgs^{-1}]

A = cross-section area of the specimen [m^2]

From work of Wiley and Coulson (1938) it follows that the capillary forces can move water through concrete at a higher rate than can pressures of up to about 3 MPa. Nevertheless, low priority was given to the WVT method in the present project where mortars with relatively low permeabilities are examined; the test is too slow.

The Initial Surface Absorption test (ISAT, BS 1881, 1970, Part 5) is based on the recognition that high pressure permeability test does not simulate practical conditions and may alter the pore structure if sufficiently high pressure is used. The test apparatus is strapped to a specimen. Water is poured into a reservoir to give a 200 mm head and the tap is opened (see Figure 2.4). Water rises into the capillary tube which is held at the same head level. Subsequently, the tap is closed and the drop of water level in the capillary tube indicates the amount of water absorption by the concrete. It is important to note that the main purpose of the ISAT test is to predict the durability of a surface layer of concrete. Thus, this test gives no information on the quality of the interior material.

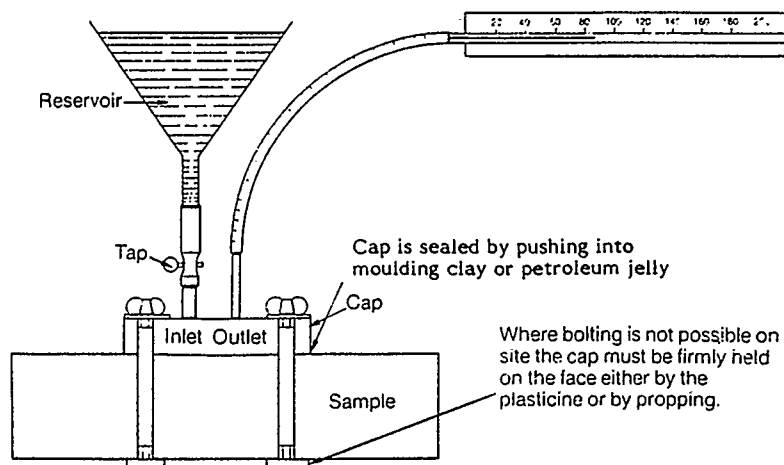


Fig. 2.4 ISAT apparatus for determination of the water permeability of concrete (from BS 1881, Part 5, 1970)

Since the values from the ISAT test are highly dependent on the permeability of a surface layer, Figg (1973) developed the "water injection" technique. With this method, it is possible to evaluate the permeability of concrete at any depth from the surface. The procedure requires a small hole 300 mm deep and 5.5 mm in diameter to be drilled in the specimen. The hole is sealed with a silicone rubber plug (see Fig. 2.5). Subsequently, the syringe is filled with distilled water and the water is forced into the small cavity in the concrete. The stopcock is closed when the water meniscus is brought to a convenient position in the capillary tube. The rate of fall of water in a capillary tube is taken as a measure of the water permeability of concrete. The main drawback of this method is that the moisture content of the concrete has a significant effect on the results -- especially at higher water-cement ratios ($w/c \geq 0.6$).

From the various permeability methods just mentioned, it was

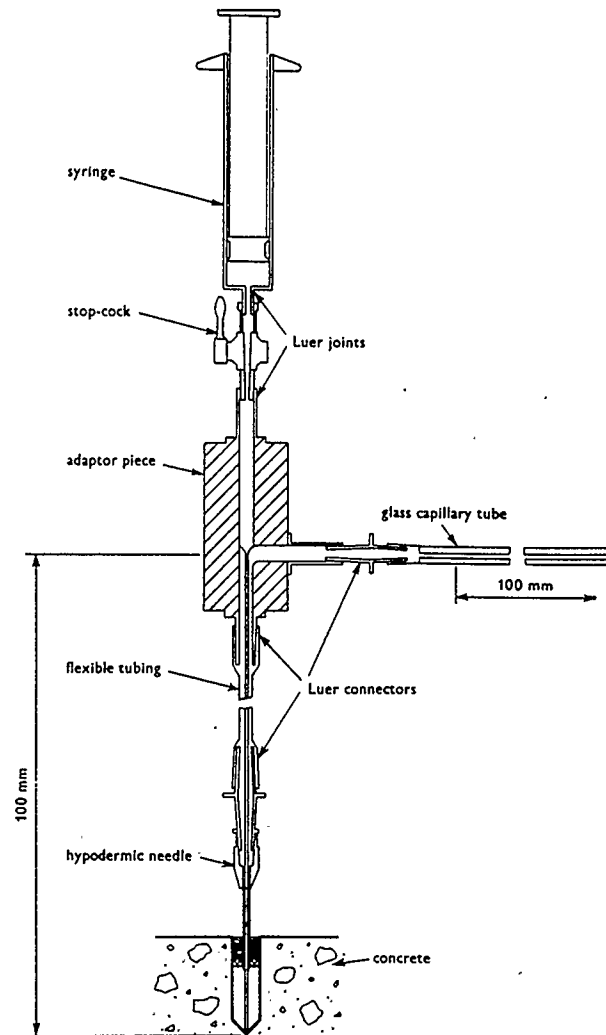


Fig. 2.5 Diagram of the apparatus for determining the water permeability of concrete (from Figg, 1973)

concluded by the present author that the best method for laboratory examination of water permeability is that which uses large pressure heads. This conclusion was based on results of initial pilot tests which follow.

- 1) By vacuum saturation, all specimens have the same initial moisture conditions, thus eliminating the effect of moisture content on permeability measurements.
- 2) Permeability measurements can be taken after reaching a steady-state flow through the specimen. Therefore, each specimen is

tested at the same condition. Pilot tests showed that the period of time to reach this state varies from specimen to specimen depending on mix proportion but generally does not exceed 6 hours (see Figure 2.6)¹.

- 3) It was found that the coefficient of permeability did not vary greatly over wide ranges of pressures (see Figure 2.8). Thus, low permeability specimens showing insignificant flow under a water pressure of 7 MPa could be examined in a much shorter time under an increased pressure of 14 MPa.

As mentioned before, there are objections that the high pressure tests do not simulate the real action of deleterious agents. Nevertheless, in many cases, it is not important to measure exact amounts

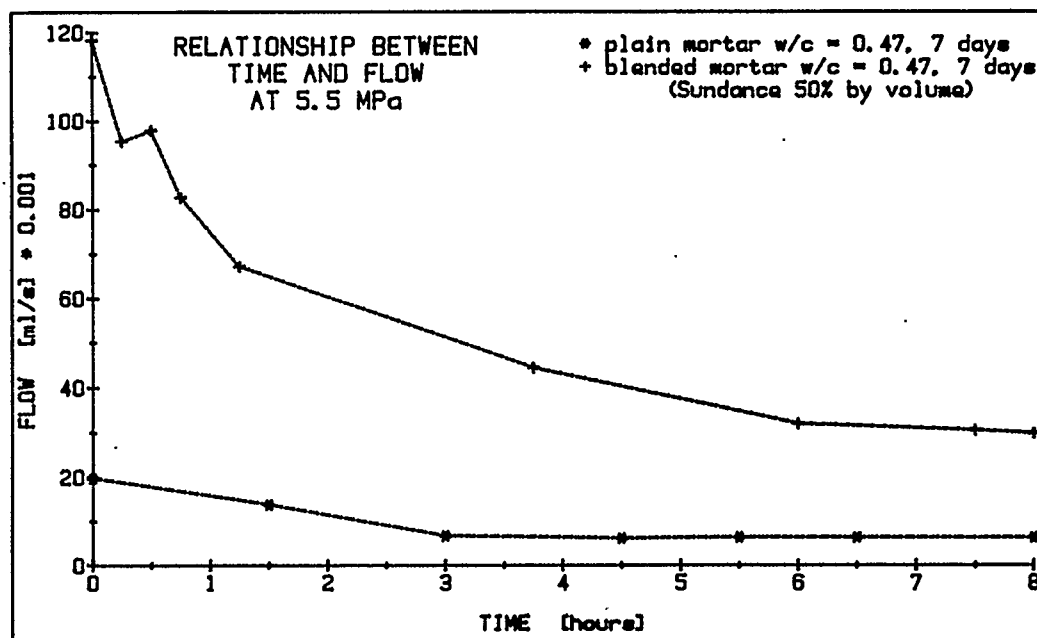


Fig. 2.6 Relationship between time and flow (up to 8 hours)

1. In one case the specimen was left in the permeability cell under pressure for the period of 20 days. A further decrease in flow was recorded (see Figure 2.7). This development was attributed to progress in hydration.

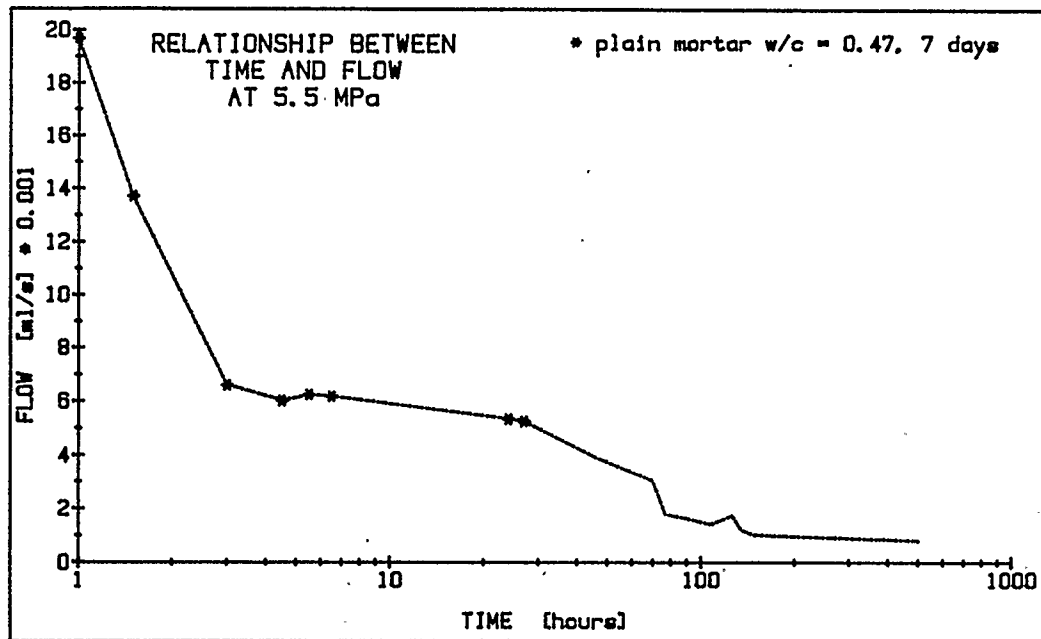


Fig. 2.7 Relationship between time and flow (up to 20 days)

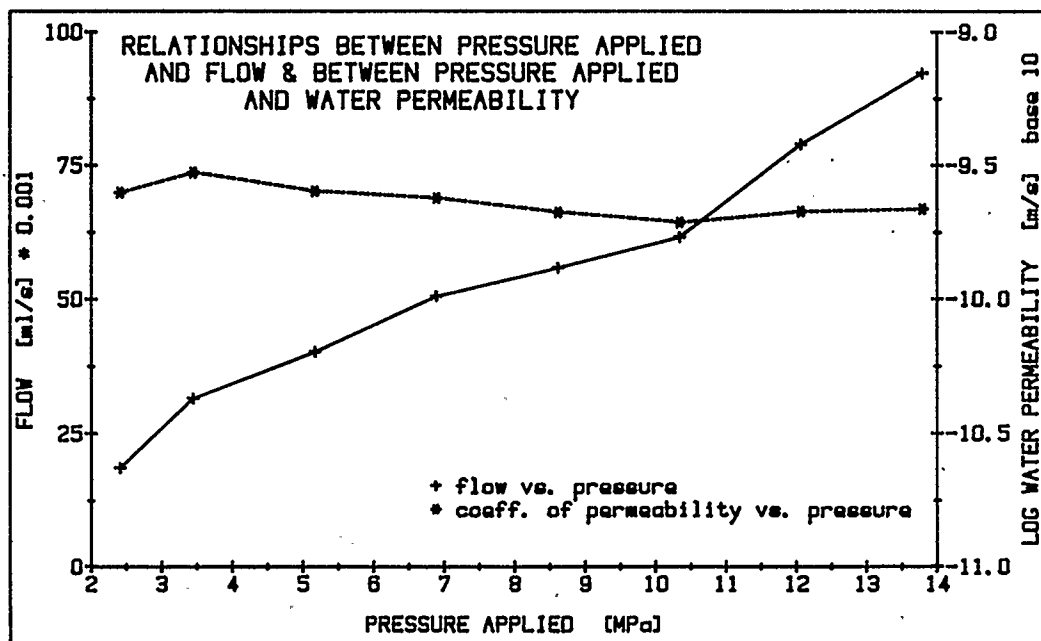


Fig. 2.8 Relationship between pressure applied and coefficient of water permeability

of penetrating agent (be it water, oxygen or chloride ions) through the specimen but all that is desired is a relative comparison of the permeabilities of individual concretes.

The permeability apparatus used throughout this project was designed by Marsh (1985) and is similar in principle to those of Powers et al. (1954) and Nyame (1979). The apparatus, shape of specimens and the procedures are described in detail in Chapter 3.

2.4.6.2 Chloride Permeability

The most detrimental effect on steel in concrete is initiated by the presence of the chloride ion near the steel surface. Chlorides can destroy the passive oxide layer which is formed on the steel in an alkaline environment (see Section 2.4.5) and thus, promote corrosion.

This problem may be solved by using an impermeable concrete cover which can retard or stop the migration of chloride ions to the surface of steel. This might be achieved by the use of an impermeable overlay or by applying a protective coating to the reinforcing bars. This work focused on the first approach so that various low-permeability mortars which included fly ash and latex-modifier were examined.

Much of the work on the chloride permeability of concrete has used the time-consuming ponding test. Chloride migration into concrete is a very slow process; however, chloride ions can migrate rapidly through concrete under an application of an external electric field. A recently developed technique by Whiting (1981) is based on the principle that the resistivity of concrete decreases as the concentration of chloride ions in concrete increases, so that the increase in current with time can be correlated with the amount of chloride entering the concrete. Whiting reports a good relationship

between charge passed in the resistivity technique and the total integral chloride in the 90-day ponding test. A correlation coefficient of 0.92 was calculated. Monfore (1968) stated that the electrical resistivity is a strong function of moisture and electrolyte concentration of concrete. Thus, by bringing the specimens to identical initial moisture conditions (in this project by vacuum saturation) an estimate of chloride permeability from charge passed through the sample can be obtained. Details of apparatus and testing procedures are given in Section 3.6.5.

2.4.6.3 Oxygen Permeability

Availability of oxygen to steel reinforcement in concrete is one of four conditions required for corrosion to occur. Various test procedures have been devised for assessing the oxygen, or air permeability. These procedures can be divided into three categories:

- a) pressure decline;
- b) vacuum method.
- c) high pressure;

Davies & Booth (1961) developed a technique where air permeability is evaluated by timing the pressure drop in a vessel glued to the surface of the specimen.

Whiteway (1960) used a vacuum method for examination of air permeability. Three 100 cm³ bulbs were connected through the specimen to a vacuum pump. By timing the drop in pressure between any two arbitrary pressure values, air permeability was assessed.

Figg (1973) developed an apparatus for the determination of air permeability in-situ. The apparatus illustrated in Figure 2.9 consists of a manometer and hand vacuum pump connected to a hypodermic

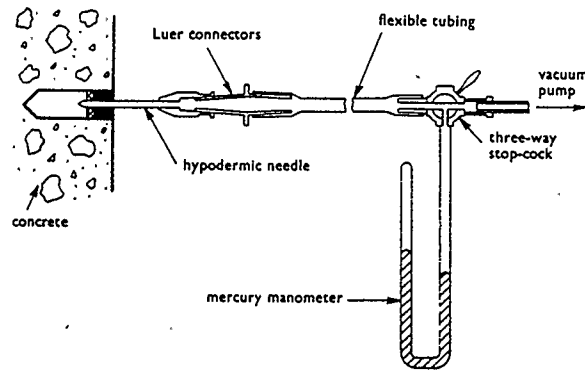


Fig. 2.9 Diagram of the apparatus for determining the oxygen permeability of concrete (Figg, 1973)

needle by a three-way stopcock. The procedure of drilling and sealing the hole is the same as for water permeability measurement (see Section 2.4.6.1). At the beginning of the test, the air is withdrawn from the concrete until a vacuum of 15 kPa is reached. A measure of air permeability in this case is the time required for the pressure to rise from a vacuum of 15 kPa to 20 kPa.

Air permeability of concrete may also be examined under a high pressure head. The apparatus is similar to that used for the determination of water permeability under high pressure. The flow rate of gas through a porous medium increases with time until a steady-state flow is reached. The period of time before steady-state flow is reached, called time-lag, can be used for the calculation of the diffusion coefficient of concrete to gas (Darr and Ludwig, 1973). Once steady-state flow is reached, the coefficient of permeability is calculated from Darcy's Law. Darr and Ludwig stated that Darcy's equation, in order to be valid for gases, has to be corrected because of the compression of gases. Nevertheless, Zagar (1955) reported that the effect of compressibility can be neglected since only a small

deviation from the true specific permeation-coefficient was recorded (less than 3 percent). Thus, the coefficient of permeability to oxygen can be calculated from the same equation as coefficient of water permeability (see Section 3.6.2.1).

In the present project, a high pressure method was chosen for the laboratory examination of oxygen permeabilities of mortars for the following reasons:

1. With a small modification, the same apparatus can be used as for the examination of water permeability. Modification details are described in Section 3.6.3.
2. Specimens can be easily brought to the reproducible initial condition, i.e. by oven drying of each specimen to the constant weight (constant moisture content) and by taking measurements after reaching steady-state flow through the specimen.

It is important to point out that the steady-state flow of oxygen through a specimen is reached in a much shorter period of time than is in the case for water permeability tests.

2.5 Conclusion

The purpose of the literature review in this chapter was to gather available data about production, specifications and properties of fly ashes.

Some effects of a partial cement replacement on engineering properties and microstructural characteristics of pastes, mortars and concretes, as observed by other workers, are presented.

A literature survey was conducted to find suitable and accurate techniques for laboratory examination of water, chloride and oxygen permeabilities.

Pilot tests were conducted in the early stage of the project utilizing the knowledge gained from the literature search.

CHAPTER THREE

MATERIALS, MANUFACTURE OF SPECIMENS AND DETERMINATION OF ENGINEERING PROPERTIES

3.1 Introduction

This chapter describes mixing and preparation procedures of specimens and the method employed to determine strength and permeability.

The basic long-term requirements for a quality concrete are strength, durability and volume stability (Mindess & Young, 1981). It is incorrect to assess concrete quality only in terms of compressive strength. For example, higher cement content added to concrete in order to increase strength may result in increased shrinkage and creep. Durable concrete should generally be dense and impermeable. It will then, naturally, have acceptable strength.

For this reason, water, oxygen, and chloride permeabilities together with compressive strength were examined. Water and oxygen permeabilities were determined using relatively short-term tests (8 hours at most).

Until recently, only a long-term ponding method was available for the determination of chloride permeability. A new technique based on forcing the chloride ions into the mortar by an electrical field was employed in this work. By this technique developed by Whiting (1981), the chloride permeability is assessed within a period of 6 hours.

3.2 Materials

Cement:

Ordinary Portland cement type 10 (ASTM Type I) was used throughout the project. Cement was from a single batch and was stored in a

tightly closed container. The chemical analysis of the cement is presented in Table 3.1

Sand:

Standard-graded Ottawa sand (ASTM C-109) was used for all mortars in this work. Results of the sieve analysis of Ottawa sand is given in Table 3.2.

Fly Ash:

Four fly ashes from different Canadian power plants were employed. Sources, coal type and relevant chemical and physical properties of fly ashes are given in Table 3.1.

Latex-Modifier Emulsion:

Dow Latex-Modifier A was used in two mixes. Specification of latex is presented in Table 3.3.

3.3 Mix Proportions

Fourteen different mixes were cast. A water-cementitious ratio of 0.47 was employed in six mixes, six mixes had a w/c ratio of 0.65. The remaining two mixes contained latex modifier and were cast with a w/c ratio of 0.35, as specified by the latex manufacturer. The sand-cement ratio was 2.75 for all mixes. In the blended mixes part of the cement was replaced by fly ash. The replacement levels were 35 and 50%. In all blended mortars except one, replacement was by volume, so that the actual w/c ratio by weight changed slightly. No correlation for water content were made so that w/c ratio by volume could remain constant. In one case the replacement of cement by fly ash was by weight. Since fly ash has lower specific gravity than cement (see Table 3.1), there is an increased volume of cementitious materials for this mix only. Mix proportions are given in Table 3.4.

Table 3.1
Chemical and Physical Properties of Cement and Mineral Admixtures

Sample	Source	Coal Type	Silica SiO_2 (%)	Alumina Al_2O_3 (%)	Iron Oxide Fe_2O_3 (%)	Lime CaO (%)	Mag- nesia MgO (%)	Pot. Oxide K_2O (%)	Sodium Oxide Na_2O (%)	Sulph- ate SO_3 (%)	Loss on Ign. (%)	Spec. Grav. g/cm^{-3}	Pozz. Activity Index
Control Type 10 Cement	Alberta Canada	N/A	2.09	4.3	2.6	2.9	4.3	0.8	0.1	2.7	1.3	3.14	N/A
Forestburg Class. Ash	Alberta Canada	Sub- Bituminous	55.2	20.7	6.2	8.9	1.2	1.0	4.2	0.4	0.2	2.01	93.0
Sundance Class. Ash	Alberta Canada	Sub- Bituminous	57.1	23.6	3.4	10.6	1.5	0.5	2.3	0.3	0.3	2.04	91.0
Boundary Dam Ash	Saskatch- ewan, Can	Lignite	45.2	21.0	3.4	12.4	3.3	0.4	2.5	0.7	2.1	2.39	96.0
Lakeview Ash	Ontario Canada	Bituminous	42.6	23.4	14.5	4.0	0.3	1.5	1.4	1.4	9.7	2.34	87.0

Table 3.2
Sieve Analysis of Ottawa Sand

ASTM Sieve Designation	Nominal Size of Sieve Opening	% Retained
16	1.18 mm	0
30	600 μ m	2 $\pm$ 2
40	425 μ m	30 $\pm$ 5
50	300 μ m	75 $\pm$ 5
100	150 μ m	98 $\pm$ 2

Table 3.3
Latex Specification

Property	Specification	
	Minimum	Maximum
Solids content, wt%	46.5	49.0
Weight, kg/liter	1.01	1.025
pH	8.5	11.0
Freeze-thaw Stability	2 cycles	
Defoamer Included	Yes	
Description	Dow Latex MODIFIER A is a symbolic styrene-butadiene polymeric emulsion in water for use in modifying Portland cement compositions. It is very low in hazard. The polymer content, expressed as % solids, makes up approximately 48% of the latex emulsion.	

Table 3.4
Mix Proportions

Mix No.	W/C Ratio			Type of Fly Ash				Replacement Levels of Cement by Fly Ash			
	0.47	0.65	0.35 + Latex	Sundance	Forest.	Boundary Dam	Lakeview	0%	35% by Vol.	50% by Vol.	50% by Weight
1	X							X			
2	X			X						X	
3	X			X							X
4	X				X					X	
5	X			X					X		
6	X				X				X		
7			X	X						X	
8			X					X			
9		X						X			
10		X		X						X	
11		X		X					X		
12		X			X				X		
13		X				X			X		
14		X					X		X		

3.4 Manufacture of Specimens

The solid ingredients were placed in a concrete rotary drum mixer and were blended completely before the water was added. Initially, one third of the water was added and mixing continued for one and a half minutes; the remainder of the water was then added. One more minute of mixing followed, then one minute of shutdown, followed by a final one minute of mixing.

From each batch six 50x50x50 mm cubes for strength, (ASTM C109) three 100x250 mm cylinders for chloride permeability (ASTM C192) and twelve truncated cones (see Fig. 3.1) for water and oxygen permeability were cast. Since there is no standard method of how to place mortar into the conical molds, each specimen was vibrated in two separate layers.

Mortar cylinders which were cast for chloride permeability evaluation were later cut into four 50 mm slices as described in the next section. Water and oxygen permeabilities were determined on the truncated-cone specimens. These specimens also required further preparation as described in the following section.

3.5 Curing and Preparation of Specimens

Immediately after casting, the specimens were covered with wet burlap and transferred to the fog room where they were left for 24 hours. They were then demoulded and immersed in lime water at room temperature for further curing. Mortar cubes for compressive strength evaluation were left undisturbed in the curing tank until the test was due. Specimens for water/oxygen and chloride permeability evaluation had to be cut to the proper shape during the curing period. A diamond impregnated circular saw was used. The optimum age of the specimens

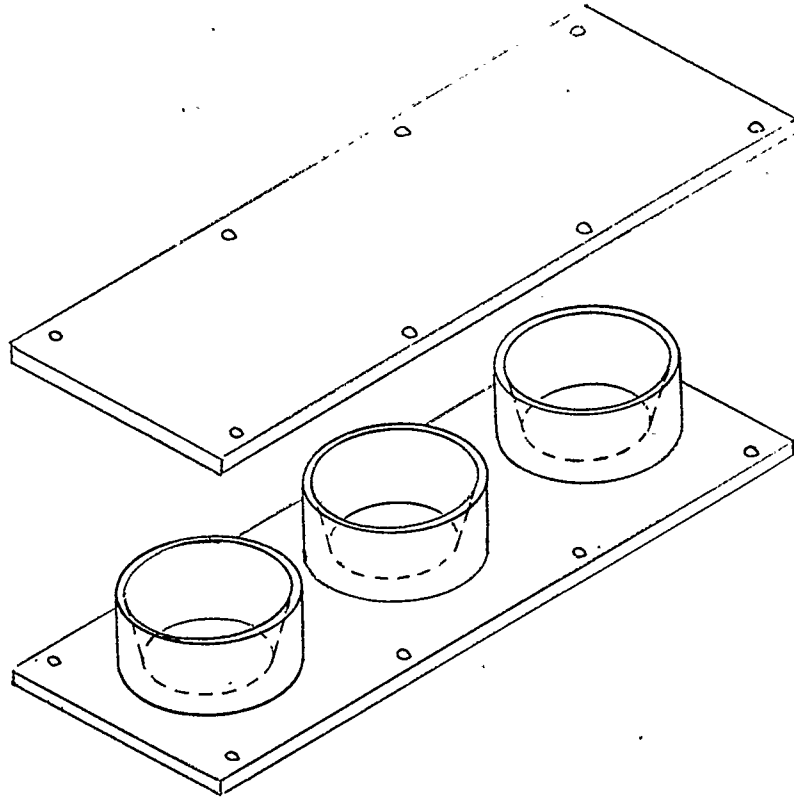


Fig. 3.1 Partially exposed view of permeability specimen mold

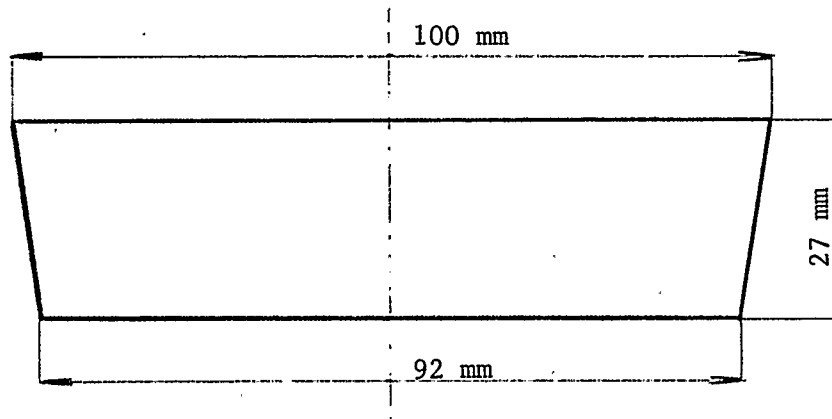


Fig. 3.2 Dimensions of truncated cone specimen after cutting off top and bottom part (actual size)

for cutting was determined by trials to be 7 days. When specimens were cut at earlier ages cracking occurred, especially in blended mortars with the water-cement ratio of 0.65 and in mortars with latex modifier. At higher ages the cutting was more difficult because of hardening of the mortar. Truncated cone specimens for the evaluation of water and oxygen permeabilities were cut to the shape illustrated in Figure 3.2. Cylinders cast for chloride permeability evaluation were cut into four 50 mm slices (see Figure 3.3). The two outer slices were discarded. After cutting, the specimens for water/oxygen permeability tests were placed back into the curing tank.

The specimens for chloride permeability test required further preparation; the periphery of the specimen was coated with rapid-setting epoxy resin to prevent drying of the mortar during testing. By sealing the periphery of the specimen with epoxy, the loss of water was prevented so that specimens remained in a reproducible saturated condition during the test. The procedure of applying the epoxy coating was as follows: the specimens were allowed to surface dry in air for one hour before coating with epoxy resin. The recorded weight loss during this period was in the range of 0.2 to 0.5% from the total weight loss of 10 percent when specimens were dried to constant weight at 80°C. After coating of the specimen's periphery, the epoxy resin was allowed to harden for up to 2 hours. During this period, the bottom and top bases of the slices were covered with plexiglass sheets in order to prevent further loss of water from the specimen. After the curing period, the specimens were placed back into the curing tank.

Specimens for water and chloride permeability determination were

taken from the curing tank a day before the permeability test was to be performed, placed into a beaker in deaerated water and vacuum saturated for 6-8 hours until no visible air bubbles came out of the specimen. These vacuum saturated specimens were left in deaerated water until testing.

Specimens which underwent water permeability testing were also used for evaluation of oxygen permeability. In order to assess oxygen permeability, the specimens had to be dried before testing. Since there is evidence that severe drying may cause damage to the micro-structure of hardened paste (Marsh et al., 1983), two methods of drying were employed in this work. These were:

- a) direct oven drying
- b) solvent replacement method representing less severe drying.

Details of drying techniques are described in Section 4.14.

3.6 Test Methods

3.6.1 Compressive Strength

All specimens were tested in compression at the ages of either 28 or 160 days. Three cubes from each batch were tested at each age. The testing was performed in accordance with ASTM C109, using a Riehle testing frame. The compression test arrangement is shown in Figure 3.4. The subplatens had the same dimensions as the mortar cube specimen.

3.6.2 Water Permeability Measurements

3.6.2.1 Principle

The permeability of concrete can be measured by determining the rate of flow of water through a sample. The flow of water is commonly

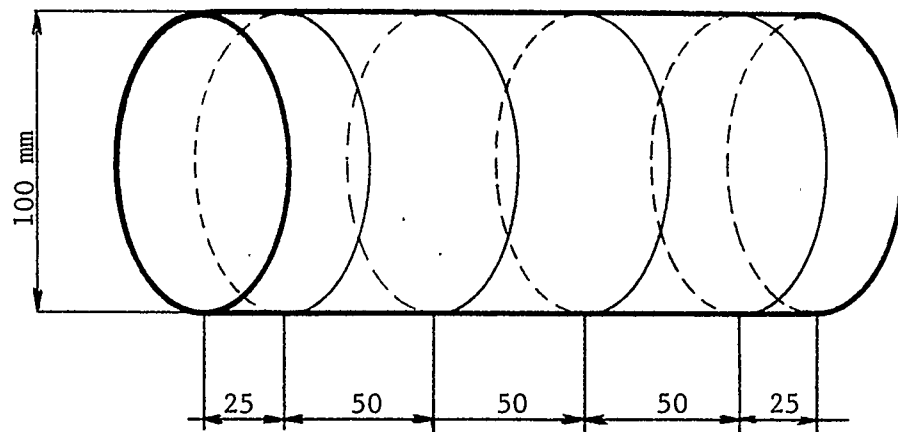


Figure 3.3 Cutting of specimens for chloride permeability test

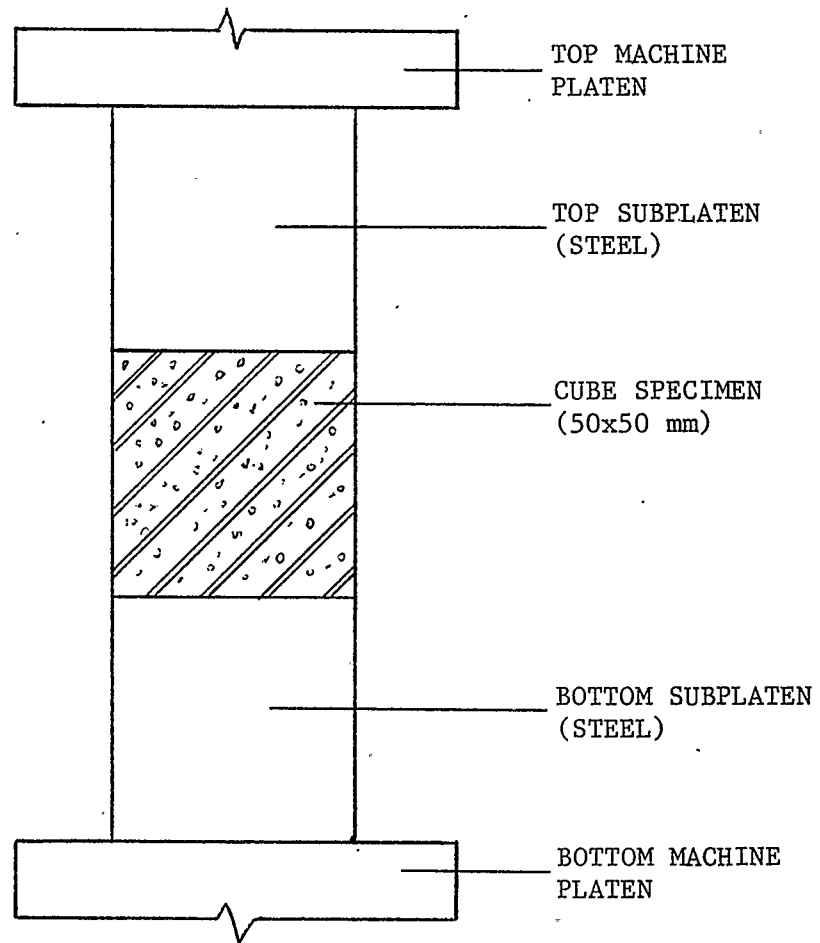


Figure 3.4 Compression test arrangement

assumed to obey Darcy's law for flow through a porous medium.

$$Q = K \cdot A \frac{dh}{L} [m^3 s^{-1}] \quad (3.1)$$

From this equation the coefficient K is given

$$K = \frac{Q}{A \cdot \frac{dh}{L}} [m s^{-1}] \quad (3.2)$$

where

K - coefficient of permeability for cement paste [$m s^{-1}$]

Q - volume outflow rate [$m^3 s^{-1}$]

A - cross-section area of the specimen [m^2]

dh - fluid head [m]

L - path length [m]

The permeability of mortar in this work was measured in the laboratory by means of a simple test. After sealing the specimen in the pressure cell, water under pressure is applied to one surface. When steady-state flow has been reached (see Chapter 2, Figure 2.6) the quantity of water flowing through the specimen in a given time is measured. The coefficient of permeability K, is then calculated using equation 3.2.

3.6.2.2 Apparatus and Procedure

The apparatus used for determination of the water permeability is represented schematically in Figure 3.5. A general view of the apparatus is shown in Figure 3.6. The pressure multiplier pressurizes de-aired distilled water and forces it through metal piping to each permeability cell. The useful pressure range of the apparatus is 5.2 - 13.8 MPa (750 - 2000 psi). Each cell can be connected or disconnected without altering the pressure of the system. This was

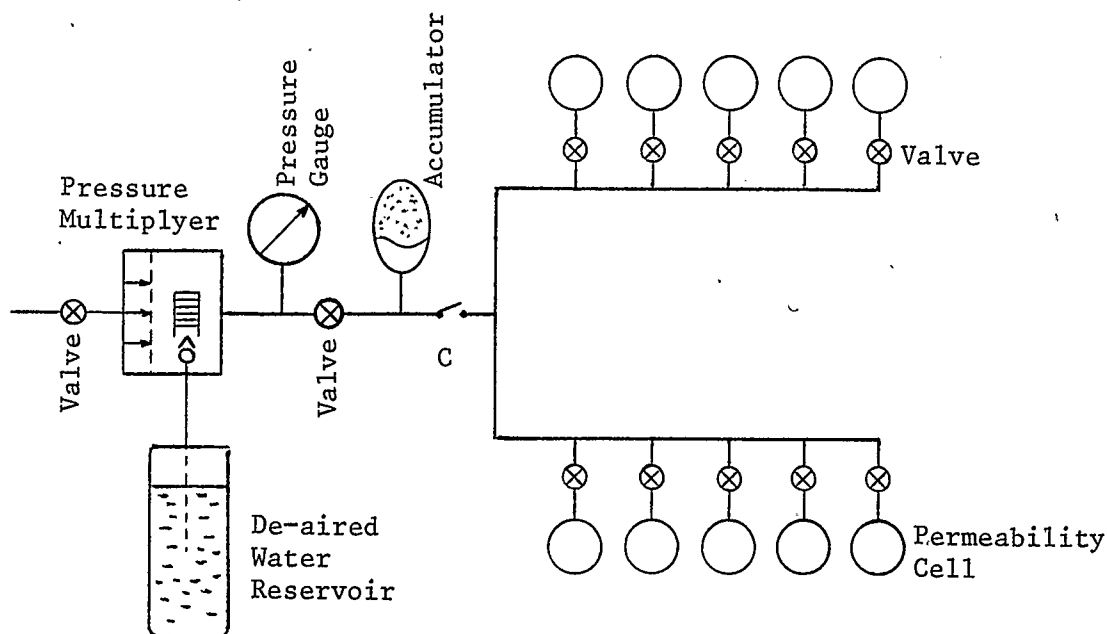


Fig. 3.5 Schematic representation of water permeability apparatus

found to be useful when breakage of any specimen occurred. Partially disassembled and fully-assembled permeability cells with the rubber seals and specimens are shown in Figure 3.7. The rubber seals were manufactured from Flexane rubber in moulds similar in shape to the permeability cells.

At the beginning of permeability measurements, water was poured into the partially assembled cell (without a top lid) to ensure that no air was trapped, so that initial flow through the specimen could be recorded. Then the truncated conical specimens and the rubber seal was pushed into the cell. Some water was poured on the top of the specimen in order to exclude air from the system and the cell was assembled. Afterwards, the pressure was gradually increased to the desired value. After reaching steady-state the flow through the specimen was measured by two techniques:

a) a glass capillary tube of known diameter was used for the mortars

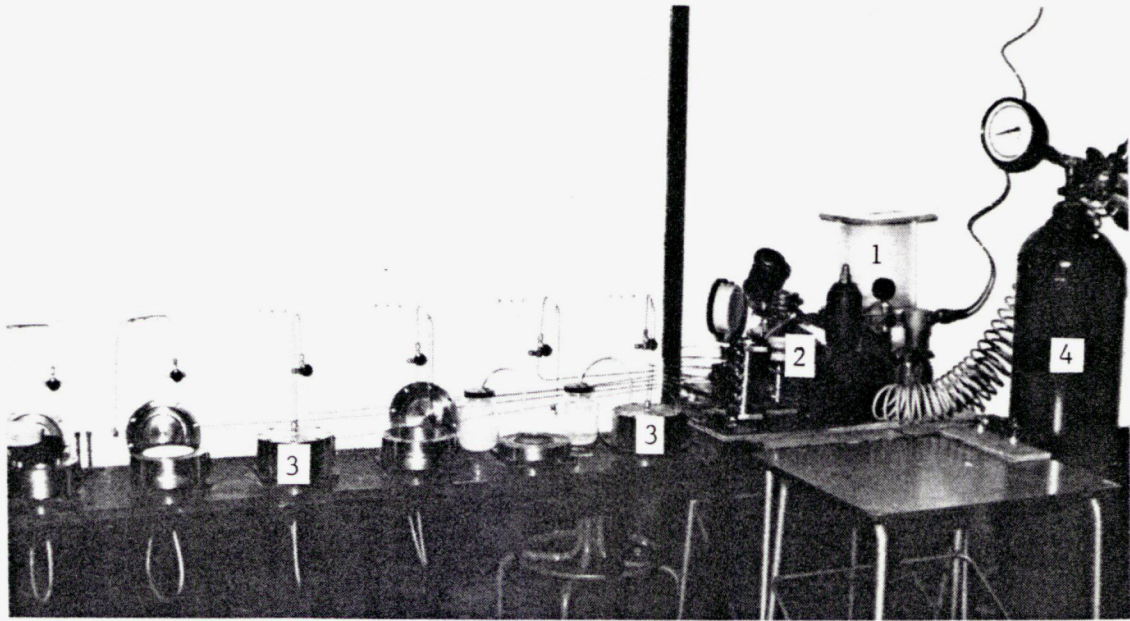


Fig. 3.6 General view of water permeability test apparatus
 (1) water reservoir; (2) pressure multiplier;
 (3) permeability cells; (4) oxygen cylinder

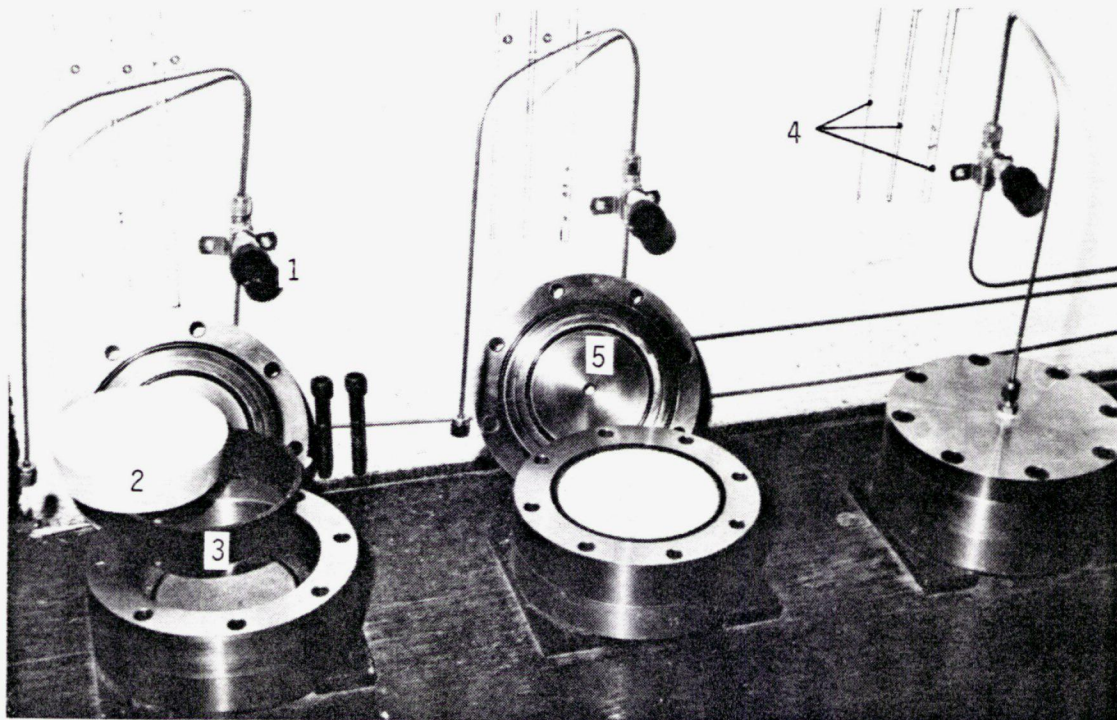


Fig. 3.7 Disassembled and assembled permeability cells
 (1) valve; (2) specimen; (3) rubber seal;
 (4) capillary tube; (5) top lid of the cell

displaying low flow. The rate of flow was determined by timing the water movement of the meniscus between two fixed points on the capillary tube.

b) for moderately and highly permeable mortars the flow was collected in a jar with a lid (in order to prevent evaporation of the water) for a given period of time and then weighed. In this case, the rate of flow $Q[\text{m}^3 \text{ sec}^{-1}]$ equals the weight of water in kilograms divided by the density of water and time in seconds. The density of water was assumed to be 1000 kg/m^3 .

3.6.3 Oxygen Permeability Measurements

For the oxygen permeability determination, the same apparatus was employed. The principle is assumed to be identical to the water permeability assessment. For oxygen permeability, the water supply was disconnected at joint C (see Figure 3.5) and the hose from an oxygen cylinder was connected. To ensure the whole apparatus was free from water, compressed air was first used to blow out any residual water from the system. The procedure of inserting the specimen into the cell was similar to the water permeability procedure; of course, no water was used. A glass capillary tube of known diameter in a horizontal position (unlike the arrangement for water permeability measurements) was employed for the determination of flow rate of oxygen through the specimen. A small amount of water was injected by a syringe into the capillary tube. Then the outflow from the cell was connected to the capillary and by timing the movement of the water between two fixed points, the rate of flow $Q[\text{m}^3 \text{ sec}^{-1}]$ was determined.

3.6.4 The Effect of the Truncated Conical Shape of the Specimens upon Water and Oxygen Permeability Results

Convergent flow through the specimen will occur as a consequence of the specimen's conical shape. It can be expected that aside from the resistance to flow of the specimen itself, resistance due to convergence will occur. The theoretical ratio K_c/K_t can be expressed as (Nyame, 1979):

$$K_c/K_t = (1 - \Delta R_o/R_o)/(1 - \Delta R_o/2R_o)^2$$

where

K_c - coefficient of permeability of a truncated conical specimen
[ms⁻¹]

K_t - coefficient of permeability of an equivalent cylindrical specimen
[ms⁻¹]

R_o - radius of large end of a truncated cone [m]

ΔR_o - difference in radii of the top (large) and bottom (small) bases
of a truncated cone [m]

The ratio K_c/K_t calculated for the specimens used in this project was 0.998. Thus, the effect of convergence is negligible (error is only 0.2 percent).

3.6.5 Chloride Permeability

3.6.5.1 Principle and Apparatus

A study by Slater et al. (1976) indicates that chloride ions can migrate rapidly out of a concrete slab under application of an external electrical field. This principle was utilized in this project for the determination of chloride permeability by reversing the polarity of the current and thus forcing the chloride ions into

the mortar specimens. As reported in Section 2.4.6.2, with the increase in the concentrations of chloride ions the electrical resistivity of mortar decreases (conductivity increases). Thus, a measure of the increase in current with time (i.e. the charge passed through the specimen during a given period) can be correlated with the amount of chloride entering the mortar specimen. The apparatus and procedure were designed in 1981 by Whiting, Construction Technology Laboratories, a division of Portland Cement Association, Skokie, Illinois. Figure 3.8 shows a general view of the apparatus. A schematic representation of the apparatus is displayed in Figure 3.9.

3.6.5.2 Chloride Permeability Measurements

Operation:

A vacuum-saturated specimen having a diameter of 10.0 cm and a height of 5.0 cm is sealed between two halves of the cell. The disassembled cell is shown in Figure 3.10. The seal between the specimen and the cell is secured by rubber rings. Vacuum grease is applied on the interface to prevent any possible leakage. After tightening the halves of the cell together (see Figure 3.11), the left hand side of the cell is filled with 3.0% NaCl solution and the right side of the cell with 0.3 N NaOH solution in order to achieve approximately equal conductances on both sides of the specimen. The cell is then connected into an electrical circuit as shown in Figure 3.9. The d.c. power is set to 60 volts. The current is monitored by placing a digital voltmeter (DVM) across a 100 mV shunt. The sensitivity is 1 mA/0.001 mV. Thus, current in milliamperes can be read directly from the voltmeter. The current vs. time relationship is plotted by the chart recorder for the duration of the test. The test proceeds for 6 hours.

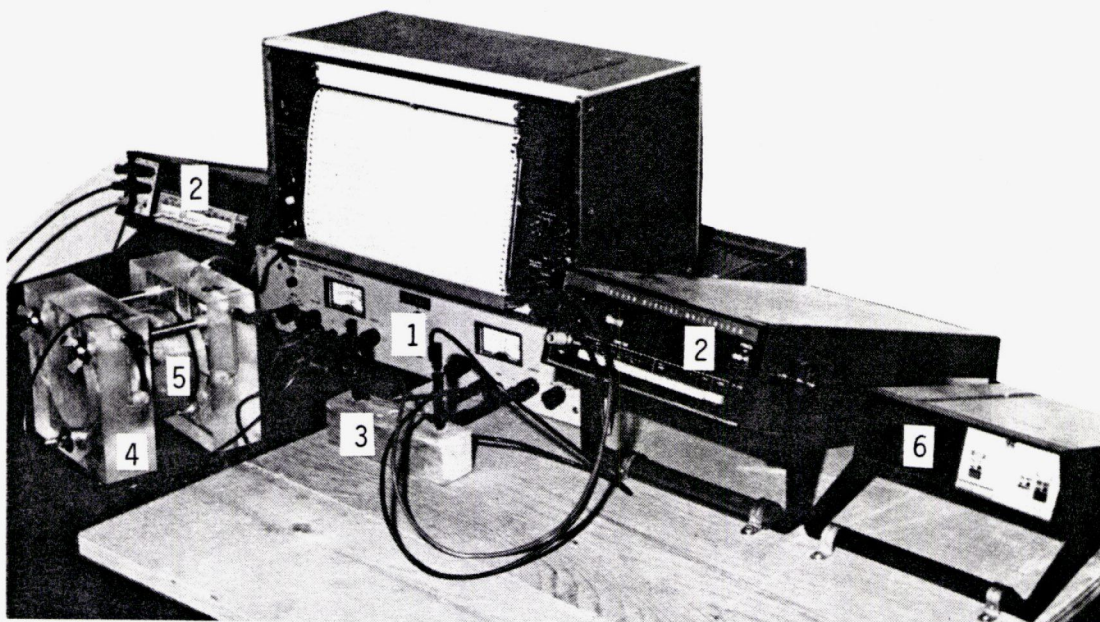


Fig. 3.8 General view of chloride permeability apparatus
 (1) constant voltage power supply; (2) digital voltmeter (DVM); (3) 100 mV shunt; (4) applied voltage cell; (5) specimen; (6) thermometer; (7) chart recorder

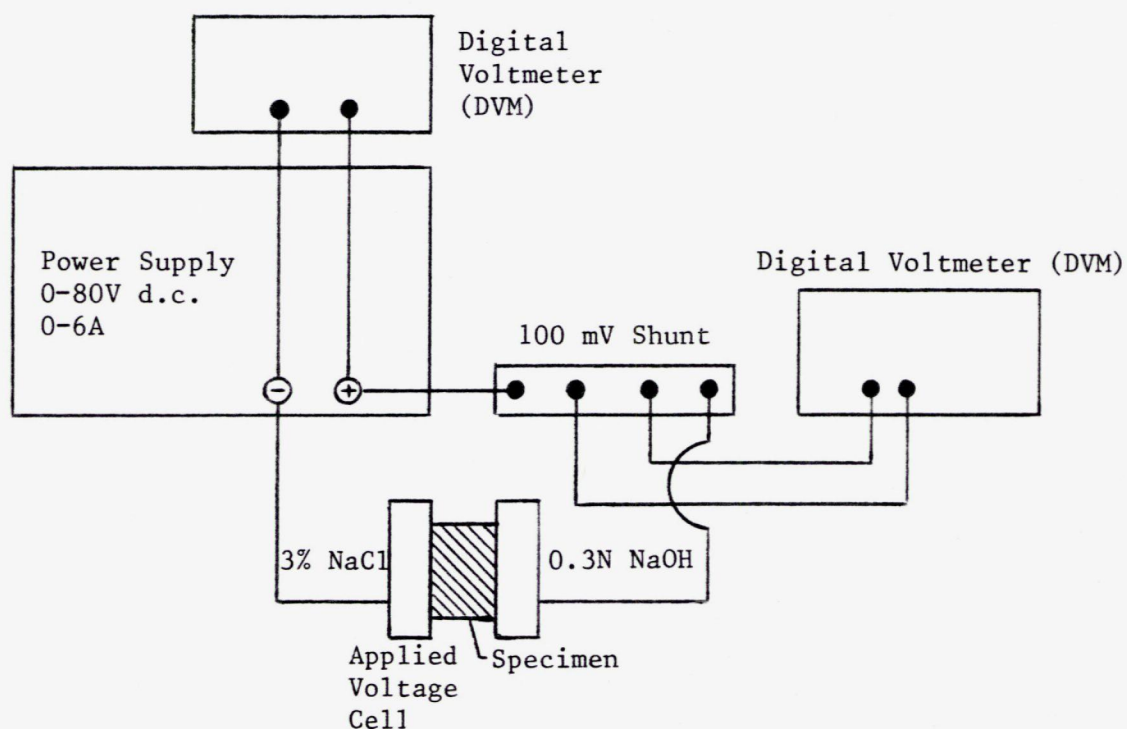


Fig. 3.9 Schematic representation of chloride permeability apparatus

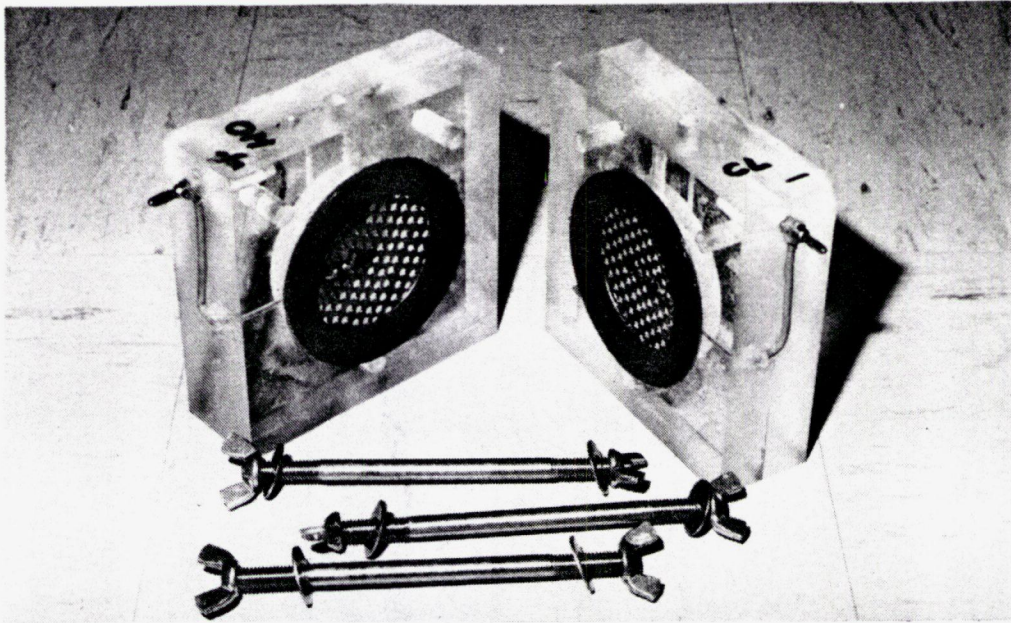


Fig. 3.10 Disassembled chloride permeability cell

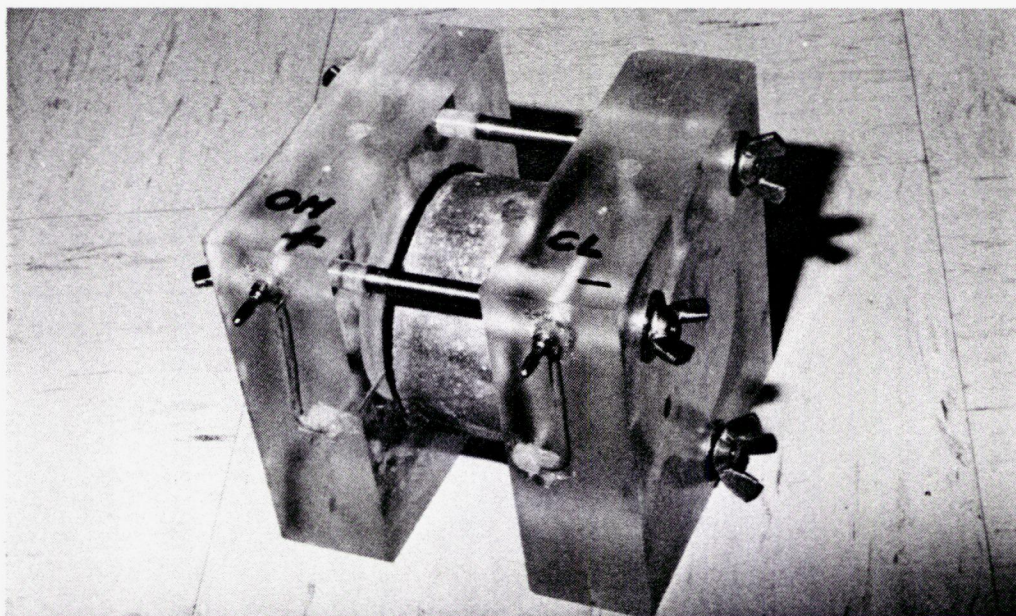


Fig. 3.11 Assembled permeability cell

Typical plots of current vs. time are presented in Figure 3.12. It was noted that in mortar with a water-cement ratio of 0.65, there was a peak in a current vs. time curve. In mortars with w/c ratio < 0.65 , the current increased continuously with time at various rates. The peak is attributed to the effect of temperature rise in mortars with high permeability.

By integrating the area under the curve, the charge passed through the specimen within a given period of time is obtained. A planimeter was used for the integration. Whiting (1981) divided permeability of concrete to chloride ions into five categories, from negligible to high, depending on the charge passed through the specimen during the test (see Table 3.5). For the evaluation of chloride permeabilities in this work, Whiting's classification was used.

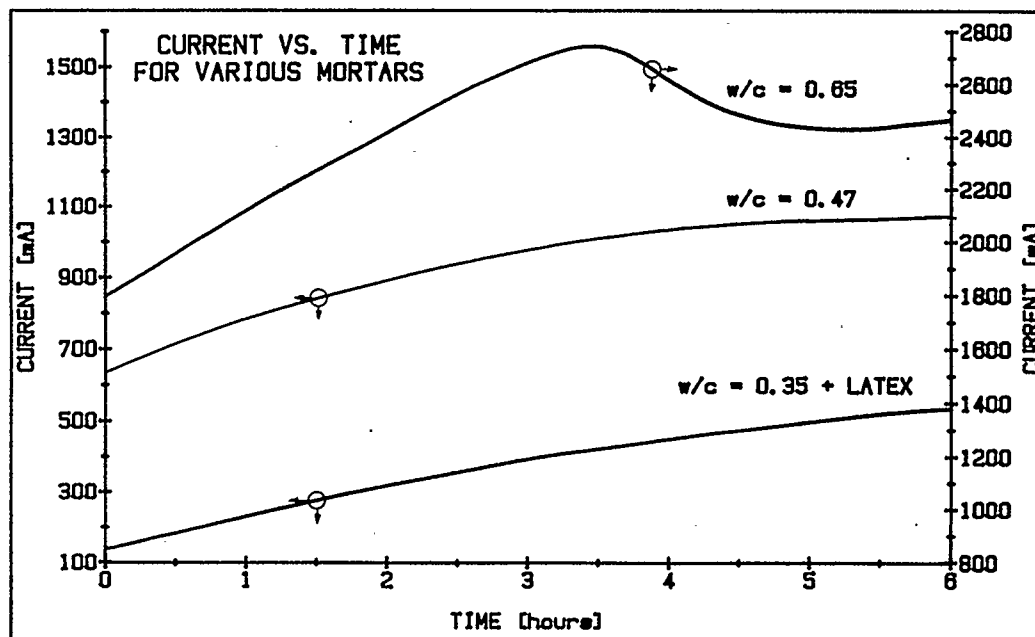


Fig. 3.12 Current vs. time relationship

<u>Chloride Permeability</u>	<u>Charge Passed (coulombs)</u>	<u>Type of Concrete</u>
High	4,000	High water-cement ratios (≥ 0.6)
Moderate	2,000-4,000	Moderate water-cement ratio (0.4-0.5)
Low	1,000-2,000	Low water-cement ratios "Iowa" dense concrete
Very Low	100-1,000	Latex modified concrete Internally sealed concrete
Negligible	100	Polymer impregnated concrete Polymer concrete

Table 3.5 Interpretation of chloride permeability from charge passed (Whiting, 1981)

3.7 Conclusion

This chapter covered mixing procedures, preparation of specimens and details about methods employed to evaluate engineering properties. For each particular method, the principle and description of apparatus were given. Calculations and interpretation of data were also presented. The results of engineering tests are presented in Chapter 5.

CHAPTER FOUR

DETERMINATION OF MICROSTRUCTURAL CHARACTERISTICS

4.1 Introduction

Hardened cement paste is a porous material. Porosity and pore structure of cement paste have a significant influence upon the physical properties of mortars and concretes. Powers (1958) observed that permeability of concrete is not a simple function of its porosity but depends also on the size, distribution and continuity of pores. To examine the microstructure of mortar specimens, mercury porosimetry was used in this work.

The progress of the pozzolanic reaction between fly ash and cement is easily determined by monitoring calcium hydroxide content. This can be done by various techniques such as differential thermal analysis, thermogravimetry, X-ray diffraction or solvent extraction. In this work, thermogravimetry was employed because this method has been shown to be accurate (Midgley, 1979) and is easy to perform.

4.2 Mercury Intrusion Porosimetry

This technique was used to examine changes in the porosity and pore size distribution of mortar specimens. The changes result from the effect of water cement ratio, hydration, the level of cement replacement by fly ash and the use of latex modifier. Basically, the technique consists of measuring the extent of mercury penetration into an evacuated, porous-solid as a function of applied pressure. The technique is simple in principle and with commercially available equipment is easy to perform. The range of pore sizes determined by mercury porosimeters usually spreads from a radius $r_p \sim 3.5 \text{ nm}$ ($35 \text{ \AA}$)

to $r_p \sim 7.5 \mu\text{m}$ ($75\,000 \text{ \AA}$) depending on the pressure employed (Gregg and Sing, 1982). In the Quantachrome porosimeter, used throughout this work, the pore size range is extended down to pore radius $r_p \sim 1.8 \text{ nm}$ ($18 \text{ \AA}$) by increasing the maximum applied pressure to 413.7 MPa (60 000 psi) and is extended on the upper end to a pore radius $r_p \sim 70 \mu\text{m}$ ($700\,000 \text{ \AA}$) by reducing the applied pressure below atmospheric (see Washburn equation in the next section).

4.2.1 Theory

Washburn (1921) first proposed that the technique of mercury intrusion under pressure can be used to determine pore size distribution and derived the relationship between the applied pressure and the pore radius for cylindrical pores:

$$P = \frac{-2\gamma \cos \theta}{r}$$

where P = pressure applied

γ = surface tension of mercury

r = pore radius

θ = contact angle

The computation of pore size distribution from this equation essentially involves several assumptions described in the following section.

4.2.2 Sources of Error

a) Contact Angle

Auskern and Horn (1973) suggested that using a constant value of contact angle may not be valid due to heterogeneity of cement paste. They also mentioned the possibility that the contact angle may change with pressure. Values of the contact angle in the literature show a

considerable variation. Gregg and Sing (1982) pointed out that, according to different sources, the contact angle of mercury lies between 135° and 150° . If one compares the values of $\cos 135^\circ$ and $\cos 150^\circ$, which are -0.707 and -0.866 , respectively, and then substitutes these values into the Washburn equation, it is obvious that the value chosen for contact angle can significantly affect the results. Nevertheless, most workers have followed Ritter and Drake (1945) in assuming that $\theta = 140^\circ$ is valid for all solids. In the present work, the contact angle was assumed to be 140° .

b) Surface Tension

Different values of surface tension of mercury in vacuum are also found in the literature. The lack of consistency is presumably because mercury is unusually prone to contamination (Gregg and Sing, 1982). Ritter and Drake in 1945 recommended a value of surface tension of mercury of 480 mN/m and this value is still the most commonly used for routine determinations. This value was adopted in the present study.

c) Ink Bottle Effect

A pore with a smaller entry radius than that of the pore body is known as an ink bottle pore (Fig. 4.1).

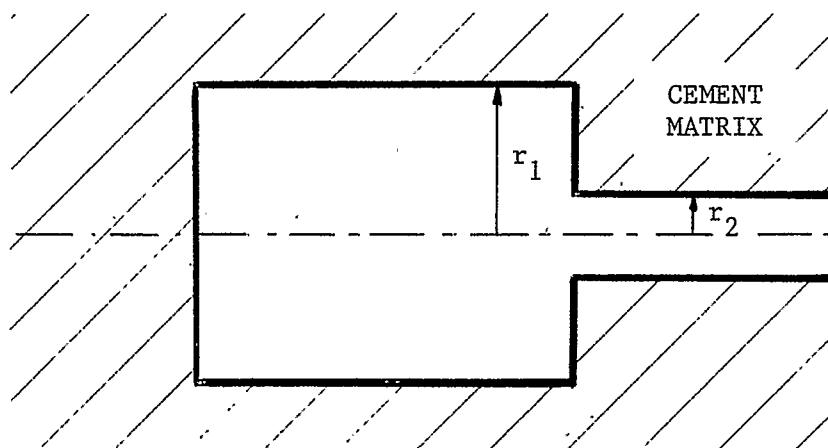


Fig. 4.1 Ink Bottle Pore

The ink bottle hypothesis was proposed by Kraemer (1931) and McBain (1935). An ink bottle pore will not be intruded at the pressure corresponding to the radius r_1 (see Fig. 4.1). Only when the pressure is high enough to fill pores of radius r_2 , will the mercury fill the whole pore. The volume of mercury intruded into this ink bottle pore will be attributed to the radius of the entry r_2 . Thus, when this type of pore is present, the pore size distribution curve will be shifted towards the fine-pore region.

d) Pore Structure Damage

Mercury is forced under pressure into the pores of the material. Damage to the pore structure can occur when high pressure is applied. Feldman (1984) and Shi and Winslow (1985) investigated possible damage to the pore structure of hydrated Portland cements. Pore size distribution obtained from the first intrusion of the sample was compared to that from the second intrusion of the same sample. Feldman observed, after repeated mercury intrusion, that the pore size distribution for the hydrated cements changed marginally, but for blended cements changed significantly; the blended pores displayed a coarser distribution on second intrusion. From this observation, Feldman concluded that mercury enters the pores of cement-paste blends by breaking the blockage formed by hydrates resulting from pozzolanic reaction.

Marsh (1984) examined the microstructure of plain and blended cement pastes by mercury porosimetry and helium pycnometry. The trends reported by Marsh from the comparison of results from these two techniques are in agreement with Feldman's conclusions.

It is important to point out that it is not necessary to measure

the exact volume of pores; a relative indication of the porosities of various porous materials is also valuable. Hence, the mercury porosimetry technique is enjoying increasing popularity as a device for the comparative study of pore structures.

4.2.3 Specimen Preparation for Mercury Porosimetry

For mercury intrusion porosimetry, it is essential that the specimen is free of evaporable water. Different modes of drying of cement paste may have a significant impact on its microstructure.

Direct oven drying is a common preparation technique; it is fast and easily performed. Much of the published work dealing with microstructure was performed on specimens prepared by this method. When direct oven drying is employed for removal of the evaporable water, water menisci are formed in the pores. Retreat of these menisci is likely to cause disruption of the fragile pore structure because of high surface tension of water and its attraction to the paste.

To obtain a more authentic indication of the original state of microstructure, the solvent replacement technique can be used to dry specimens. The solvent replacement technique was first applied to cement paste to prepare specimens for sorption tests (Litvan, 1976). Marsh et al. (1982) made comparisons of specimens dried in the oven with those which were solvent-replaced. It was observed that the two drying methods produced different representation of pore size distribution of hardened cement paste. Results from their work are presented in Figure 4.2. It follows that direct oven drying of the paste causes disruption to the pore structure for pores of radii less than about 8 nm ($80 \text{ \AA}$). On the other hand, the solvent replaced

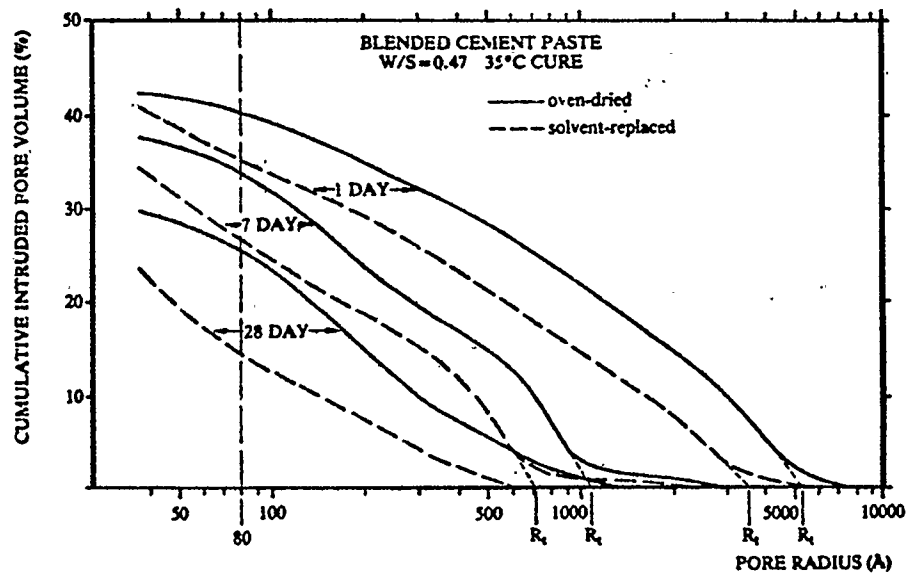
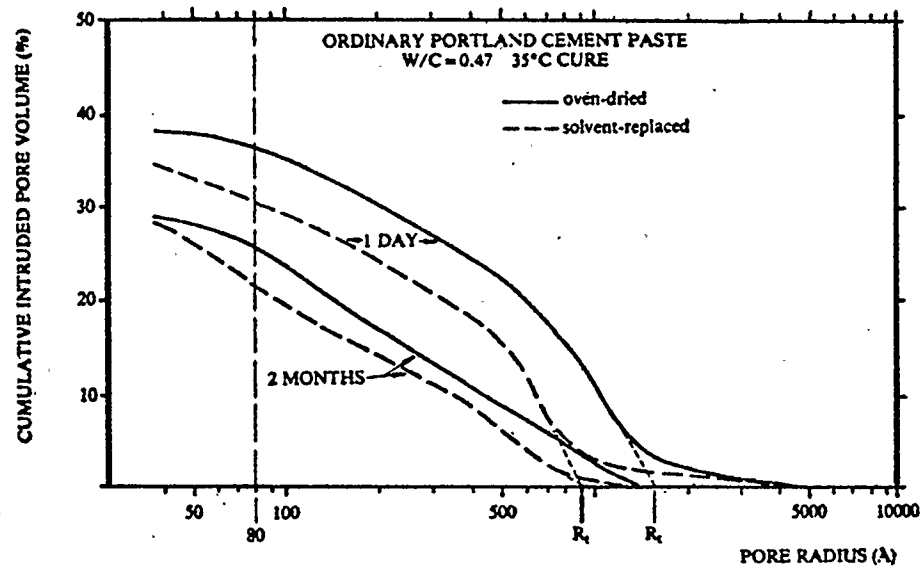


Fig. 4.2 Typical mercury porosimetry results for ordinary and blended cement pastes (Marsh et al., 1982)

pastes retained a considerable pore structure in this range. Solvent replaced specimens showed fewer pores in the large pore size region. It was concluded that the solvent replacement technique tends to preserve the pore structure of the original material better than direct oven drying. The procedure of both methods is described in the next section.

4.2.4 Details of Drying Techniques

a) Direct Oven Drying

The water saturated specimens were weighed and placed in an oven at 80°C ¹. Through the oven a flow of dry, CO_2 -free air was circulated. After reaching a constant weight, the specimens were removed for oxygen permeability measurements and microstructural examination.

b) Solvent Replacement Method

Specimens were weighed and placed in a plastic vessel containing approximately 1250 ml of 2-propanol. There were three specimens in each container. The weight loss of each specimen was recorded and the propanol was renewed after 7 days. After an additional 14 days, when there was no further weight loss, the specimens were placed into a desiccator and vacuum dried for 2 days. After vacuum drying, the specimens were placed in an oven and dried at 80°C in a CO_2 -free atmosphere until weight equilibrium.

The final drying at the same temperature meant that the amount of

-
1. Preference was given to the drying at 80°C over that at 105°C since it represents less severe drying and still removes all the water in the capillary pores.

evaporable water loss for solvent replaced and oven dried samples was approximately the same (Marsh and Day, 1985). The final 80°C drying stage also allowed the use of a single value of contact angle for mercury, regardless of the specimen preparation technique, and thus enabled direct comparison of results between these two drying methods.

4.2.5 Apparatus and Procedure

A "Quantachrome Autoscan-60 Mercury Intrusion Porosimeter" was employed to determine porosity and pore size distribution. The Quantachrome porosimeter uses hydraulic oil to transfer the pressure to the mercury.

A sample, dried by one of the techniques described in Section 4.2.4, is placed into a glass sample cell. The cell is filled with mercury to about 1 cm below the top of the stem (see Figure 4.3). A metal sheath is placed around the stem and the sample cell is inserted into the high pressure cell. Mercury acts as one plate of a capacitor and the metal sheath as the second plate. Thus, when the pressure is applied, mercury is forced into the sample and the corresponding drop of mercury in the stem leads to a fall in the capacitance. The change in capacitance is calibrated to indicate change in volume. This change in volume is the volume of mercury intruded into the sample.

4.2.6 Correction for Volume Changes of Mercury

During pressurization mercury tends to be compressed. Thus, the mercury level in the stem decreases and this leads to a false intrusion signal. The compression effect is largely offset by heat flow into the mercury, due to heating of oil during the pressurization, which causes the mercury in the stem to rise. The

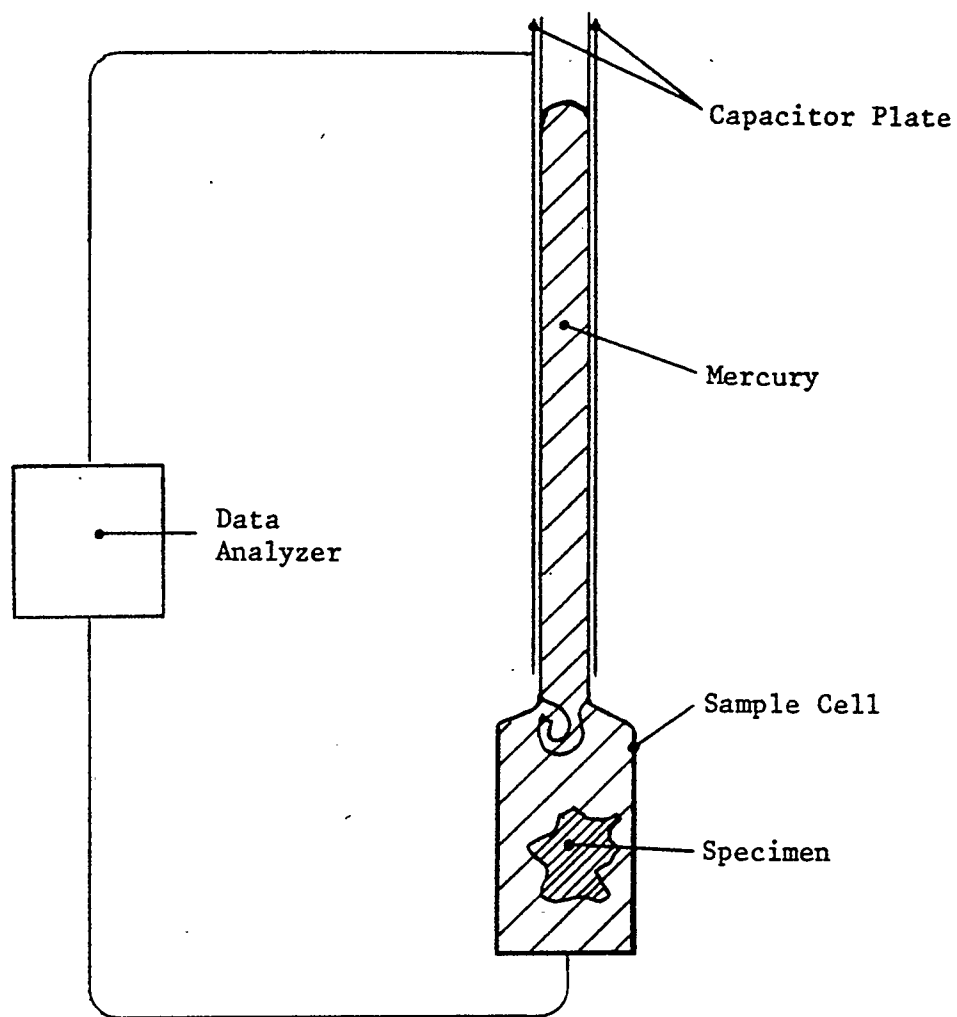


Fig. 4.3 Sample cell with the specimen and mercury

heating of mercury leads to an apparent extrusion signal.

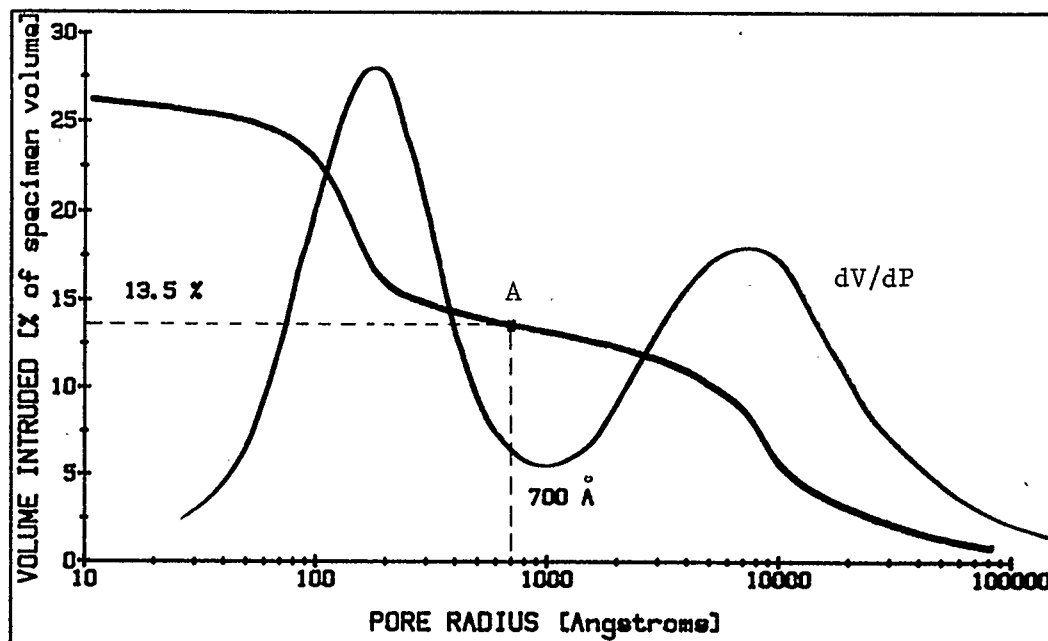
The effect of the temperature rise and the compression in this work was examined by a "blank run" (i.e. pressurization of sample cell containing mercury only). Since the volume changes of mercury from the blank run accounted for less than 1%, it was concluded that no corrections were necessary.

4.2.7 Analysis of Results

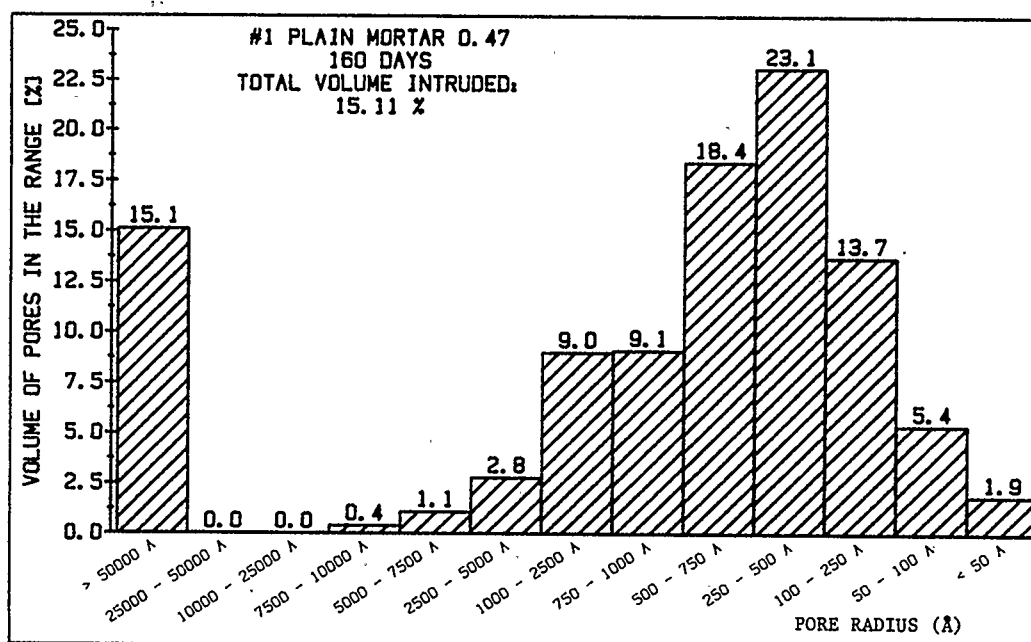
The results from mercury porosimetry are presented in three forms illustrated in Figure 4.4.

- a) Cumulative intruded pore volume, expressed by the volume intruded by mercury (as a portion of the total volume of specimen) versus $\log r$. Point A on the curve in Figure 4.4a shows that 13.5 percent of the specimen volume exists as pore space in the pore range above 70 nm (700 Å).
- b) Derivative plot dV/dP is presented as an example also in Figure 4.4a. This graph shows that significant intrusions occurred at pore sizes of 20 nm (200 Å) and 750 nm (7 500 Å).
- c) Bar Chart

The bar chart is the most illustrative when pore size distribution is to be examined. The two preceding curves are plotted during or after each mercury porosimetry run. The bar chart is obtained only after further analysis of the data. Figure 4.4.b presents an example of a typical bar chart. It can be seen that 23.1 percent of the total pore volume occurs in the range of pores between 25 to 50 nm (250 to 500 Å) and there were no pores present in the pore size range from 1 μm to 5 μm (10 000 to 50 000 Å). This representation of the data was used most frequently in this work for interpretation



a) Cumulative curve and derivative of the cumulative



b) Bar chart

Fig. 4.4 Various forms of representation of mercury porosimetry results

of results from microstructural examination.

4.3 Thermogravimetry and Derivative Thermogravimetry

Mackenzie (1969) defined thermogravimetry (TG) as "a technique whereby the weight of a substance, in an environment heated or cooled at a controlled rate, is recorded as a function of time or of temperature", and derivative thermogravimetry (DTG) as "any technique yielding the first derivative of the TG curve with respect to either time or temperature". It is obvious that these methods can be used only for materials which undergo a weight change on heating.

4.3.1 Equipment for Thermogravimetry

In this work a "Dupont Thermogravimetric Analyser type 951 TGA" was used. The 951 TGA operates on a null-balance principle. The null-balance thermogravimetric analyser is shown diagrammatically in Figure 4.5. Briefly, the principle can be described as follows: the crucible and sample are maintained in a constant position by applying an electromagnetic field to the central coil in order to offset the twist in the suspension ribbon as the sample weight changes. The value of this electromagnetic field is then electronically processed and displayed as a weight change.

4.3.2 Principle

When a hardened cement paste is heated the weight loss observed can be divided into four parts:

- a) Evaporation: the weight loss up to 105°C is attributed to the depletion of evaporable water.
- b) Dehydration: due to loss of chemically combined water from the gel products. This occurs over the temperature range 105-1005°C.

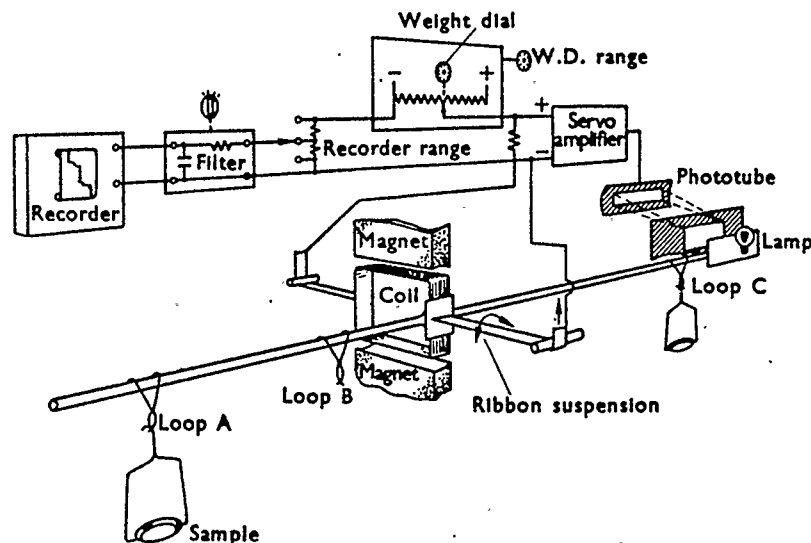
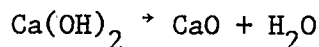


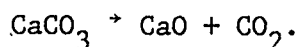
Fig. 4.5 Diagrammatic sketch of the null-balance type thermogravimetric analyser (from Redfern 1970)

Biffen (1956) observed that the evolution of chemically combined water from calcium silicate hydrates represents itself as a gently sloping straight-line TG curve over the range 350 to 650 °C.

c) Dehydration of calcium hydroxide: due to loss of water from the calcium hydroxide. The dehydration of Ca(OH)_2 takes place at the temperature range of 420-550°C. Thus, any divergence from the straight-line TG plot within this temperature range is attributed to the dehydration of calcium hydroxide. The reaction involved is:



d) Decarbonation: This is due to decomposition of calcium carbonate over the temperature range 600-750°C, according to the reaction:



Calcium carbonate is present in the paste due to reaction between Ca(OH)_2 and carbon dioxide in the atmosphere. The weight loss due to

decarbonation will be negligible if care is taken to eliminate carbon dioxide during specimen preparation.

4.3.3 Test Methods

Three thermogravimetric methods for quantitative determination of calcium hydroxide content in Portland cement paste are in current use.

a) Dynamic Method:

The sample is heated at a constant rate over the entire temperature range while the weight loss is simultaneously monitored.

b) Semi-Isothermal Method:

From the very beginning the sample is heated at a constant rate. When the rate of weight change reaches a maximum (at DTG peak), the dynamic heating is switched to the isothermal state for a certain period of time. The temperature of the isothermal state is about 2-5°C higher than the peak temperature. At the end of the isothermal period, the heating is switched back to dynamic heating.

El-Jazairi and Illston (1977), who developed this method, used a duration of 30 minutes for the isothermal condition. According to these authors three features of the semi-isothermal method show its superiority over the dynamic method:

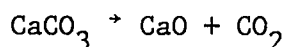
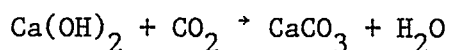
- 1) the separation of some overlapping reactions which are otherwise undistinguishable by the dynamic method;
- 2) the accurate determination of temperatures at which compounds decompose or dehydrate;
- 3) the accurate monitoring of weight changes for each compound or group of compounds associated with particular peaks.

Nevertheless, Marsh (1984) stated that the main disadvantage of this method is the impossibility of separating weight loss due to

dehydration of Ca(OH)_2 from weight loss due to dehydration of the C-S-H in the temperature range 400-560°C.

c) Carbonation Method:

This method is applicable to partly carbonated specimens. It is based on deliberate carbonation of all calcium hydroxide present in cement paste. Thus, the difficulties with Ca(OH)_2 content determination which might be caused by overlapping peaks due to dehydration and decarbonation of calcium hydroxide are eliminated. The reactions involved are:



It can be seen that a weight loss of one mole of carbon dioxide (44 g) corresponds to one mole of the original calcium hydroxide (74 g).

Butler and Morgan (1980) heated samples of Ca(OH)_2 containing 10.2% CaCO_3 in nitrogen atmosphere up to 200°C until the evolution of water was negligible. Then the atmosphere was changed to a mixture of 80% nitrogen and 20% carbon dioxide. They showed that the carbonation reaction became rapid as the water was lost from the Ca(OH)_2 . After the carbonation reaction was completed at about 700°C, the atmosphere was changed back to nitrogen to facilitate the decomposition of CaCO_3 . The weight loss in the range of 700-800°C was then due to decomposition of the CaCO_3 formed from the Ca(OH)_2 and CaCO_3 originally present. Butler and Morgan showed that 93 percent of the Ca(OH)_2 had been converted into CaCO_3 .

The disadvantage is that this method depends upon no reaction between hydrated calcium silicates or aluminates and carbon dioxide during the run. Also, two changes of atmosphere within each run bring

about practical difficulties.

In this work preference was given to the dynamic method for the following reasons:

- Specimens were prepared with care to prevent any carbonation; moreover, only samples taken from the center of the specimen prior to each run were examined in order to exclude any accidental carbonation. Thus, it was assumed that no CaCO_3 was present. Experimental results confirmed this assumption since no weight loss was recorded between 600-750°C.
- Using the assumption that weight loss due to dehydration is a sloping straight line over the temperature range 350-650°C (Biffen, 1956), it is possible to separate weight losses due to dehydration of Ca(OH)_2 and dehydration of C-S-H respectively by the graphical method described in Section 4.3.5.
- There was no need to change atmosphere during the run.

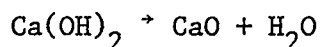
4.3.4 Procedure

Calcium hydroxide content was determined on the samples taken from the oven dried remnants of the specimens which were examined for compressive strength. Care was taken not to take samples from the outer layer, as mentioned above. Ground mortar of a total weight of approximately 50 mg (as recommended by the manufacturer) was loaded into the thermobalance crucible. The sand-cement ratio in all mortars was 2.75. Care was taken to select a sample representing both ingredients. Weight loss was recorded in a flowing atmosphere of nitrogen as temperature was raised at the rate of 20°C/min. At 105°C the temperature was held constant for 10 minutes in order to drive off

evaporable water. After this period of time, the specimen was heated at 20°C/min to 1005°C. Here, the temperature was held until no further weight loss was recorded.

4.3.5 Interpretation of Results

A typical output from a dynamic TG run is shown in Figure 4.6a. Figure 4.6b explains the graphical technique employed for separating the weight losses due to dehydration of Ca(OH)_2 . The vertical line drawn at the mid-point (length $\overline{AB}$) equals the water loss from Ca(OH)_2 decomposition (see Fig. 4.6b). Pilot tests using specimens of known Ca(OH)_2 composition showed this method to be accurate (Day, 1987, personal communication). The original amount of calcium hydroxide was back-calculated from the monitored weight loss of water according to the reaction



In order to compare results from different mortars the Ca(OH)_2 content was expressed as a percentage of ignited weight of the Portland cement present in the sample.

$$W_{\text{CH}} = \frac{\text{weight loss due to dehydration of } \text{Ca(OH)}_2 \times 4.113}{\frac{\text{ignited weight at } 1005^\circ\text{C}}{C}} \times [100\%]$$

$$W_{\text{CH}} = \frac{\overline{AB} \times 4.113 \times C}{W_{1005}} \times 100 [\%]$$

where

W_{CH} = weight of Ca(OH)_2 as a percentage of weight of cement

W_{1005} = ignited weight of the sample at the temperature of 1005°C

C = sand compensation factor. Since sand-cement ratio is 2.75, the sand compensation factor equals 3.75.

$\overline{AB}$ = water loss from Ca(OH)_2

Sample: SUNDANCE 50X .47 7 DAYS
 Size: 50.10 mg
 Rate: 20C/MIN
 Program: General Analysis V1.0

TGA

Date: 2-Mar-88 Time: 22:44
 File: CA/OH/2.08 LK DISK#1
 Operator: L.KONECNY
 Plotted: 3-Mar-00 1:24:35

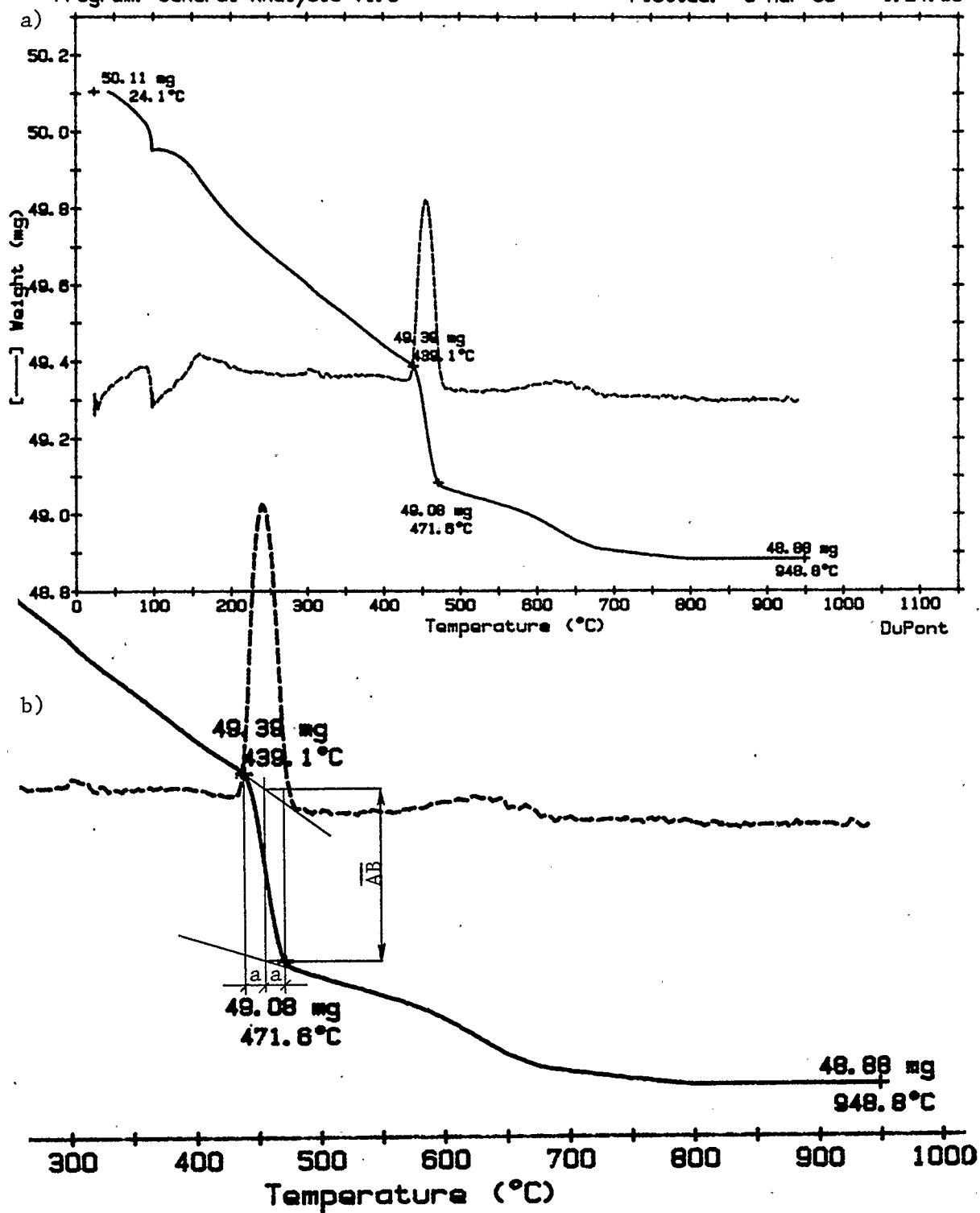


Fig. 4.6 Typical TG plot (a) and graphical method employed for separating the weight losses (b)

4.4 Other Measurements

4.4.1 Bulk Specific Gravity

Bulk specific gravity was determined according to ASTM standard D2726 on all mortar specimens at the age of 160 days.

$$\text{Bulk specific gravity} = \frac{A}{B-C}$$

where

A = weight of dry specimen in air

B = weight of saturated surface dry specimen in air

C = weight of the specimen in water

Bulk specific gravity values were used for calculation of volume intruded by mercury per unit volume of specimen.

4.5 Conclusion

The purpose of this chapter was to choose and describe the most appropriate methods for the microstructural examination carried out in this work. Two techniques were selected; these were mercury intrusion porosimetry and thermogravimetry. The testing procedure and principle of each particular technique were presented. The advantages and limitations were discussed. After the evaluation of available TG methods, the most suitable one for this work was chosen. The examples of print-out data in the form of graphs and their interpretation are shown for each technique.

The scanning electron microscopy technique is not discussed in this chapter since it was used only infrequently to better illustrate the results from selected specimens. The same can be said about X-ray diffraction; this technique was used only to determine whether any reaction occurred between permeating Cl^- ions and the cement matrix.

CHAPTER FIVE

RESULTS AND DISCUSSION - ENGINEERING PROPERTIES

5.1 Introduction

This chapter contains the results from examination of engineering properties as a function of water-cement ratio, age, replacement level of cement by fly ash, type of fly ash and latex content. The following engineering properties were determined: water, oxygen and chloride permeabilities and compressive strength. An attempt to find correlations between various engineering properties was made. Standard statistical methods were used to evaluate the significance of particular observed relationships.

As described in Chapter 3, fourteen different mixes were cast (see Table 3.4). Mixes are denoted by numbers from 1 to 14 according to the same table. Nevertheless, for clarity a notation system is introduced here as follows:

Fly ashes:

Sundance as SUN

Forestburg FOR

Lakeview L*V

Boundary Dam B*D

Water-cement ratio 0.47 as 0.47

35% replacement by volume as 35V

50% replacement by weight as 50W

Thus, for example, mix #4 with Forestburg fly ash, $W/C = 0.47$ and replacement level of 50% by volume is denoted as

FOR-0.47-50V.

5.2 Compressive Strength

Compressive strength results at ages of 28 and 160 days are presented in Figure 5.1. The average values of standard deviation of strength results were 0.65 and 0.61 MPa at 28 and 160 days respectively.

a) Mortars with Water-Cement Ratio 0.47

The control mix in this group attained strength of 34 MPa at 28 days and 38 MPa at 160 days. Twenty-eight day strengths of all blended mortars within this group are less than that of the control; nevertheless, at 160 days two blended mortars #3 (SUN-0.47-50W) and #6 (FOR-0.47-35V) achieved comparable strengths to that of the plain mortar. In one case the strength of blended mortar #5 (SUN-0.47-35V) exceeded that of the control.

In the group of specimens with water-cement ratios of 0.47 only sub-bituminous fly ashes were employed. If one compares blended mortars with the same replacement levels within this group, it follows that mortars with Sundance fly ash are superior to those with Forestburg fly ash [compare specimens #2 (SUN-0.47-50V) to #4 (FOR-0.47-50V) and #5 (SUN-0.47-35V) to #6 (FOR-0.47-35V)]. It was observed that mortars with the replacement level of 35% by volume attained higher strengths than those with 50% by volume replacement at both ages. Surprisingly, mortar #3 (SUN-0.47-50W) with the highest content of fly ash, displayed compressive strength values at 28 and 160 days -- similar to those of mortar #6 (FOR-0.47-35V).

The compressive strength of mortar #3 (SUN-0.47-50W) is higher than that of mortar #2 (SUN-0.47-50V) with the same cement content. This is because there is a higher volume of cementitious material

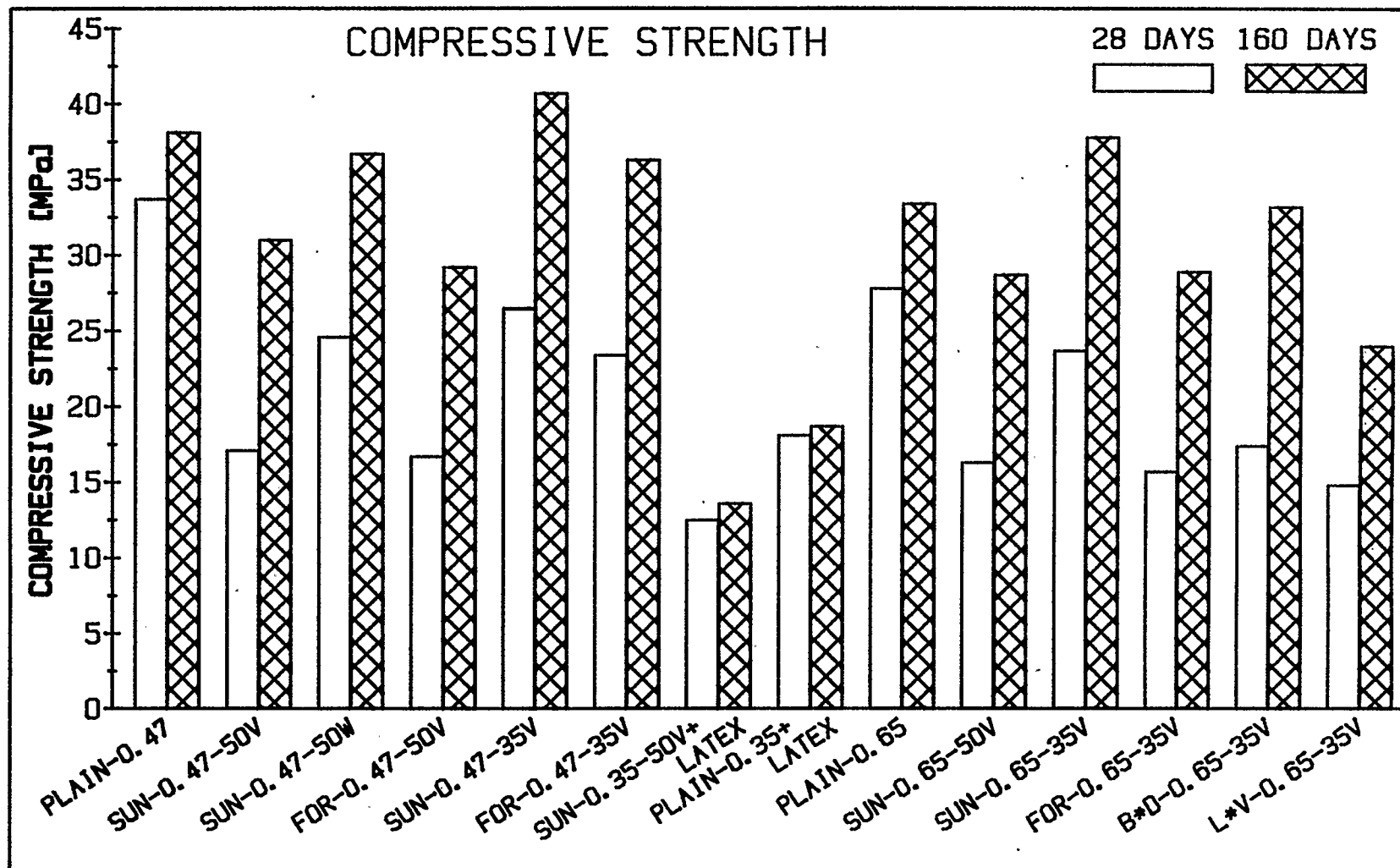


Fig. 5.1 Compressive strength at the ages of 28 and 160 days

(i.e. cement + fly ash) available in the former mortar because of lower specific gravity of fly ash than that of cement.

For illustration, one cubic meter of cement weights 3140 kg. By replacing 50 percent of cement (i.e. 1570 kg) with an equal weight of Sundance fly ash (specific gravity 2040 kg m⁻³), the total volume of cement plus fly ash is 1.27 m³. This means a 27 percent increase in volume of cementitious material, provided the cement content is the same, compared to the mix with replacement by volume.

b) Mortars with Water-Cement Ratio 0.65

In this group, fly ashes from four sources were employed: Sundance (sub-bituminous), Forestburg (sub-bituminous), Boundary Dam (lignite) and Lakeview (bituminous). The control mix #9 (PLAIN-0.65) attained a 28 day strength of 28 MPa which was the highest strength within this group at this age. At 160 days, the control mix strength was exceeded by mix #11 (SUN-0.65-35V). Blended mortar #13 (B*D-0.65-35V) displayed the same strength as the control. In mixes #10 (SUN-0.65-50V) and #11 (SUN-0.65-35V) two levels of Sundance fly ash were employed. The compressive strength of the mix with the lower replacement level is superior to that of the mix with replacement of 50 percent.

For mixes #11 through #14 one replacement level of cement by fly ash was employed so that the effect of fly ashes from various sources could be compared. From this group of blended mortar with 35 percent replacement, the highest compressive strength at 28 and 160 days is displayed by mortar with Sundance fly ash. Mortar with Boundary Dam fly ash showed the second highest strength at both ages followed by mortar with Forestburg fly ash. The lowest values of compressive

strength at 28 and 160 days were obtained with the use of Lakeview fly ash.

In summary, sub-bituminous and lignitic fly ashes attained higher values of strength at 28 and 160 days than the bituminous ash. This finding indicates that the former fly ashes, both from Western Canada, are more reactive than bituminous ones from Eastern Canada. The reactivity of fly ash is influenced to a large extent by the proportion of amorphous phase present in the fly ash (see Chapter 2).

c) Mortars with Latex Modifier

According to the manufacturer of latex (Dow Chemical Canada Ltd.), the Latex Modifier increases the strength of concretes. This was not observed in the present project. Both mixes incorporating latex displayed far lower values of compressive strength than the other mortars, despite having the lowest water-cement ratio employed. The latex increases workability so the water necessary in the mixing process is reduced; therefore, a relatively low water-cement ratio could be employed¹.

It is necessary to point out that Latex Modifier also acted as an effective air entrainment admixture although a defoamer was included in latex (see Table 3.3). This effect was not mentioned by the manufacturer. Although air content was not measured on fresh mortars, the evidence of air bubbles is clear from electron microscopic observation (see Figure 5.2). Increased air content is also obvious when comparing specific bulk gravities of mortars (see Table 5.1). It

1) According to the manufacturer, the highest recommended W/C ratio in latex mixes is 0.37.

is well established that the use of air entrainment in mortars reduces early as well as ultimate strength. Mindess & Young (1981) state that for most air entrained concretes, a strength loss of 10-20% can be anticipated. According to Dow Chemicals Ltd., latex added to concrete bonds chemically to the surface of aggregate and "seals off" the voids and cracks. While this chemical action reduced the penetration of some corrosive chemicals into mortar, as presented later in this chapter, it did not increase strength. It might be possible that the sealing effect of latex hinders or retards the pozzolanic reaction or even the hydration of cement itself because the strength loss is higher than that reported by Mindess and Young. At 160 days, the strength of mortar #8 (PLAIN-0.35+LATEX) was about one half (49%) of that of mortar #1 (PLAIN-0.47). The strength of mortar #7 (SUN-0.35-50V+LATEX) reached only 44 percent of that of comparable mortar #2 (SUN-0.47-50V) at the age of 160 days.

In latex modified mortars the monitoring of Ca(OH)_2 content was not feasible by the thermogravimetric method which was employed in this work; the reason is discussed in Chapter 6. Thus, no indication about the progress of the pozzolanic reaction was obtained.

5.2.1 Summary of Strength Results

If 28 day strength values of latex mortars #7 (SUN-0.35-50V+LATEX) and #8 (PLAIN-0.35+LATEX) are compared, mortar #7 displays lower strength than mortar #8. This is in agreement with the observation of plain and blended mortars which did not contain latex. The early strength is lower for blended mortars than for corresponding plain mortars because blended mortars contain less cement and the pozzolanic reaction is not appreciable at early ages (see Chapter 6).

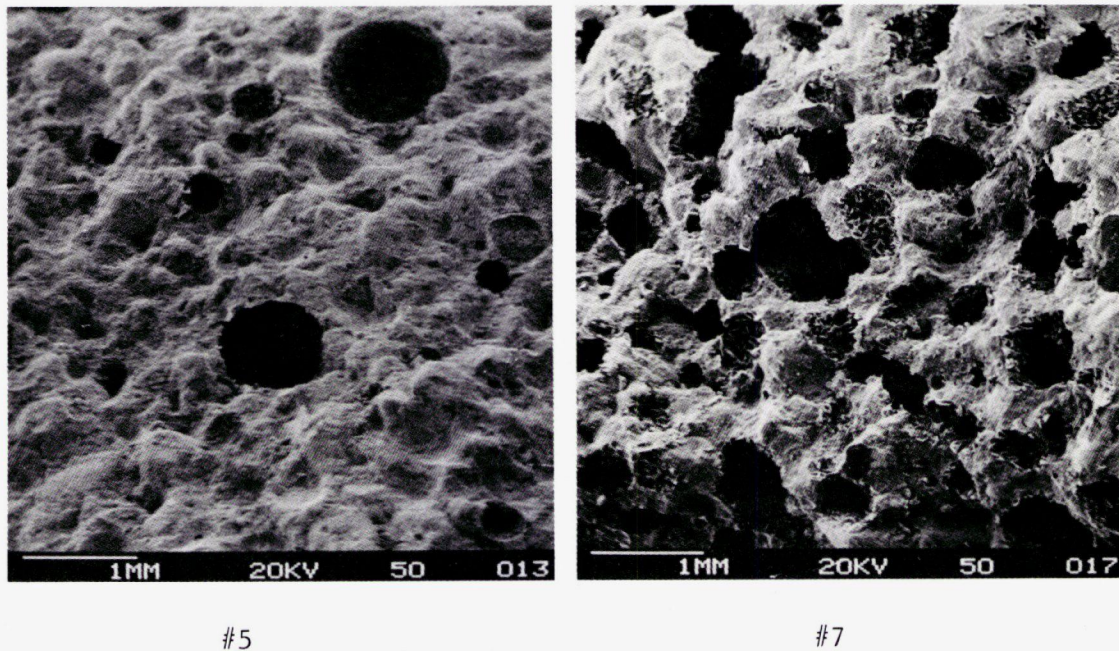


Figure 5.2 SEM micrographs of blended mortar #5 (SUN-0.47-35V) and latex-modified blended mortar #7 (SUN-0.35-50V+LATEX)

Table 5.1

Specific gravity of mortars at the age of 160 days

Mix No.	Description	Bulk Specific Gravity at 160 Days [kgm^{-3}]
1	PLAIN-0.47	2049.5
2	SUN-0.47-50V	1960.9
3	SUN-0.47-50W	1948.3
4	FOR-0.47-50V	1958.4
5	SUN-0.47-35V	2016.6
6	FOR-0.47-35V	1996.6
7	SUN-0.35-50V+LATEX	1646.7
8	PLAIN-0.35+LATEX	1691.5
9	PLAIN-0.65	1970.8
10	SUN-0.65-50V	1950.0
11	SUN-0.65-35V	1901.5
12	FOR-0.65-35V	1881.8
13	B*D-0.65-35V	2005.3
14	L*V-0.65-35V	1959.5

An insignificant strength gain for both latex mortars was recorded between the ages of 28 and 160 days compared to the other mortars. From the examination of compressive strength, it is concluded that: a) latex impedes the pozzolanic reaction between the ages of 28 and 160 days [compare strength gains of mortars #2 (SUN-0.47) and #7 (SUN-0.35-50V+LATEX)], and b) latex might also hinder the hydration of cement in the same period of time [compare mortars #1 (PLAIN-0.47) and #8 (PLAIN-0.35+LATEX)].

To determine whether latex hinders or just slows down the hydration and pozzolanic reaction, more examination at later ages (higher than 160 days) is necessary.

The compressive strength observation of latex mortars is in agreement with that of Steinberg (1974). Steinberg reported that the strengths obtained from polymer-cement concrete (PCC) can be disappointing. He also stated that the improvement of compressive strength over conventional concrete is obtained only with higher polymer concentration of about 30%. There is no reference about the curing regime.

Riley and Razl (1974) report that better properties of latex mortars are achieved by allowing the latex components to dry. They also advise that the best curing procedure is to keep latex mortars saturated for about two days, in order to improve the hydration of cement, and then allow them to dry.

Since water and chloride permeability examinations in this work were performed on saturated specimens, latex mortars were cured together with other specimens in lime water. No specimens were air cured. The mortar remnants from compressive strength tests were saved

for microstructural examination. Thus, any trends in water and/or chloride permeability values could be interpreted in terms of microstructural characteristics of identically cured specimens.

5.3 Water Permeability

Coefficients of water permeability of mortars with water-cement ratio of 0.47 and 0.35 are presented in Figure 5.3. Figure 5.4 shows water permeabilities of mixes with water-cement ratio 0.65. Mortars with $w/c = 0.65$ were not tested at 7 days because of difficulties to prepare specimens (see Section 3.5). For easier comparison, permeabilities of all mixes at the ages of 28 and 160 days are presented in Figure 5.5.

Values on the y-axis are logarithms (base 10) of the coefficient of permeability values. This was done for the convenience of plotting and subsequent correlation with engineering properties and microstructural characteristics. For example, the logarithm of the coefficient of permeability $K = 3.162 \times 10^{-12} \text{ ms}^{-1}$ equals -11.5 ms^{-1} . Higher absolute values on the y-axis correspond to lower permeability and vice versa.

Coefficient of variation of permeability results approached 100 percent in some cases; nevertheless, the average coefficient of variation was 72 percent. The variation may appear to be high but it is a common feature of permeability results. The variation in this work was not higher than those observed by Nyame (1979) and Marsh (1984).

a) Mortars with Water-Cement Ratio 0.47

While at 7 days the coefficient of permeability of mortar #1 (PLAIN-0.47) displays the lowest value (i.e. between 10^{-12} and 10^{-13} ,

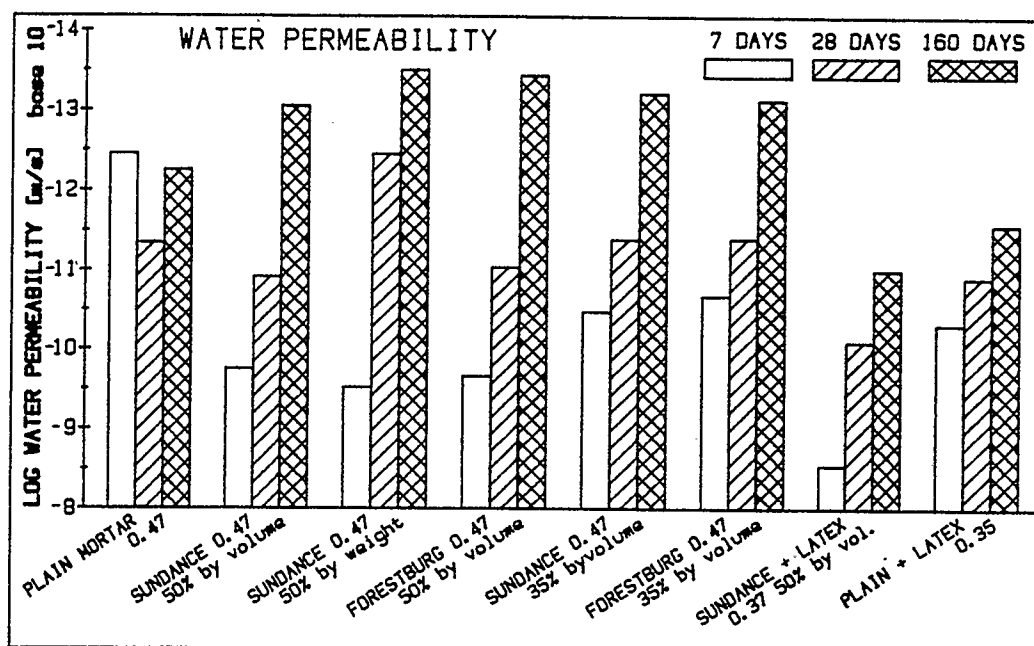


Fig. 5.3 Water permeability values for mortars with w/c = 0.47 and 0.35

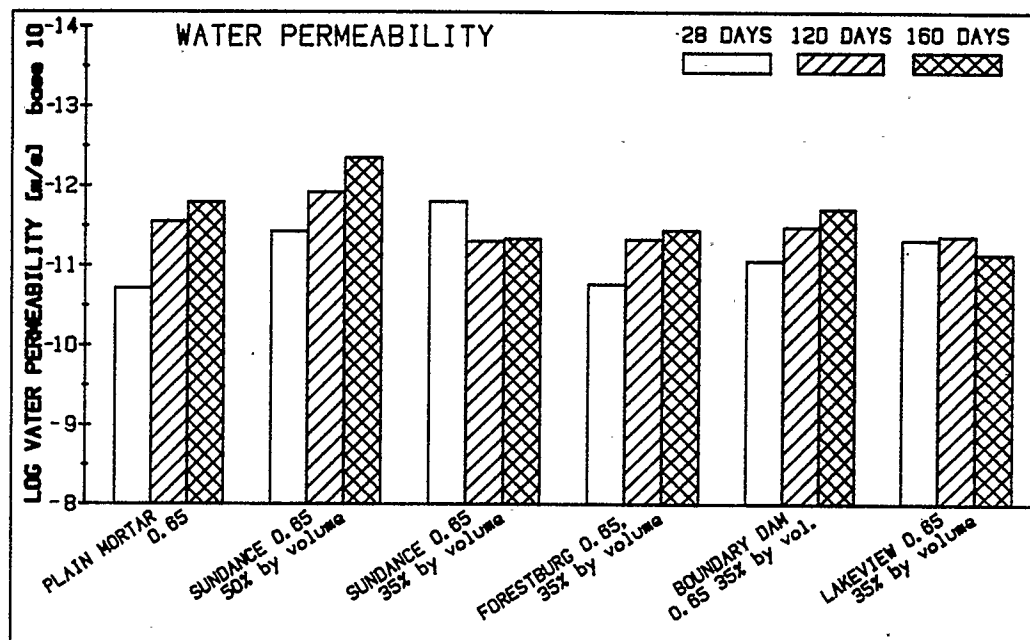


Fig. 5.4 Water permeability values for mortars with w/c = 0.65

see Figure 5.3), at 28 days the gap between the control mix and blended mortars of the same w/c ratio is reduced. In one case, blended mortar #3 (SUN-0.47-50W) is less permeable. At the age of 160 days, all blended mortars show much lower values of coefficient of permeability than that of plain mortar. This indicates significant progress in the pozzolanic reaction.

For illustration of the effect of pozzolanic reaction on permeability, it might be helpful to describe Li and Roy's (1986) hypothesis. They assumed that the gelatinous hydrates of calcium silicate and calcium aluminate resulting from pozzolanic reaction deposit to block the pores, instead of just depositing on the surface. Their schematic model showing the impermeable gel plug formed by the pozzolanic reaction is shown in Figure 5.6.

b) Mortars with Water-Cement Ratio 0.65

At 28 days, all blended mortars with water-cement ratio of 0.65 display similar or lower permeabilities than the control mix (see Figure 5.4). At the ages of 120 and 160 days, however, only the mortar #10 (SUN-0.65-50V) with the highest replacement level within this group displayed lower values of the coefficient of permeability than the control mix. Mortar #13 (B*D-0.65-35V) shows similar values of permeability at 28 and 160 days as plain mortar. All remaining blended mortars with the replacement level of 35% show higher permeabilities than the plain mix. A mortar with a high w/c ratio contains a larger volume of large pores than that with a lower w/c ratio. Clearly, water can move much easier through the former mortar than it can through the latter.

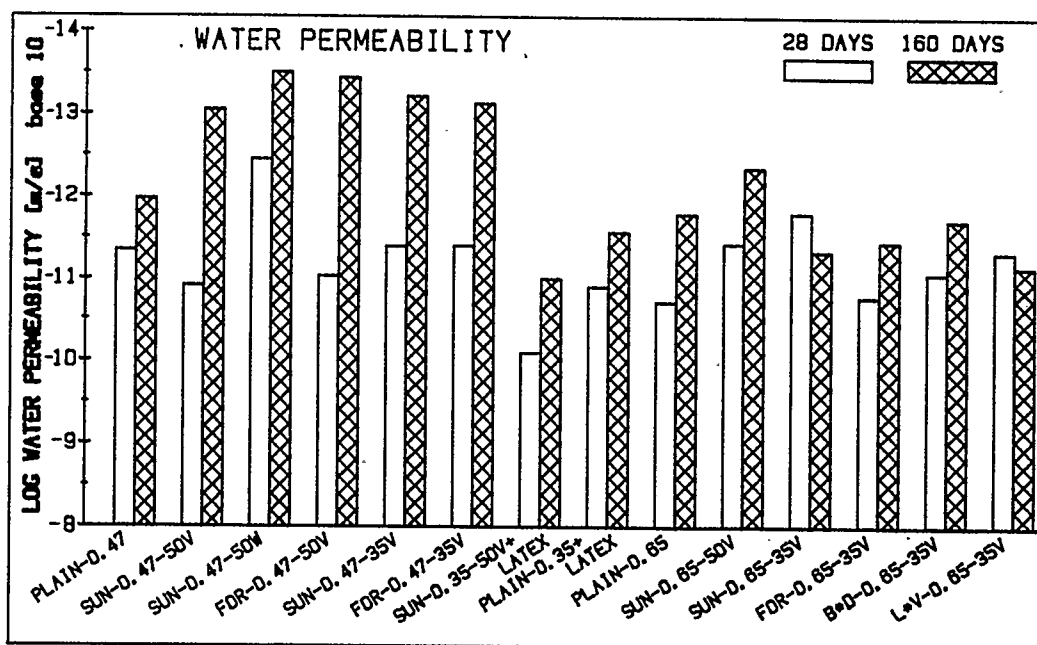


Fig. 5.5 Water permeability of all examined mortars at the age of 28 and 160 days

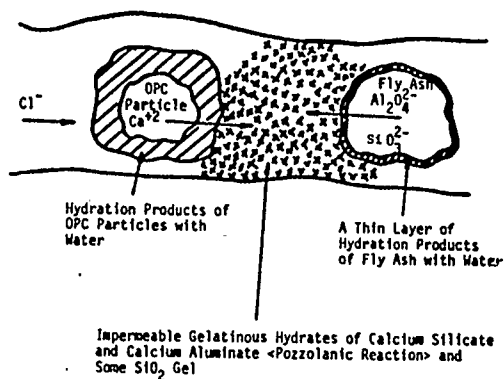


Fig. 5.6 Schematic model showing impermeable gel plug forming in the pore (Li and Roy, 1986)

c) Mortars with Latex Modifier

Figure 5.3 also shows that mortars with latex modifier did not perform well compared to mortars with a water-cement ratio of 0.47. It is interesting to point out that while permeability values of blended mortars were lower than that of plain mortar at 160 days when no latex was employed, the reverse is true for mortars with latex modifier [see mortars #7 (SUN-0.35-50V+LATEX) and #8 (PLAIN-0.35+LATEX)]. This finding supports the author's suggestion that latex, acting as an internal seal, may hinder or slow down the reaction between calcium hydroxide and fly ash (see Section 5.2).

The effect of air entrainment was not considered here because the addition of latex acting as an air entraining admixture results in discrete isolated air voids in the mortar (see Figure 5.2); therefore, it was assumed that these discrete air voids do not take part in permeability flow.

5.3.1 Summary of Water Permeability Results

Despite increased permeabilities at early ages, blended mortars with water-cement ratio of 0.47 were superior to the plain one at 160 days. It was shown that the replacements of up to 50 percent by weight of cement by fly ash in mixes with $w/c = 0.47$ is a necessity to attain low permeable mortar.

From examination of mixes with $w/c = 0.65$, it is concluded that only 50 percent replacement of cement by fly ash reduced mortar permeability.

Plain and blended mortars incorporating latex modifier displayed

higher values of permeability than did corresponding mortars without latex.

5.4 Oxygen Permeability

Specimens which underwent water permeability measurements were dried and afterwards investigated for oxygen permeability. Not very many specimens withstood removal from the high pressure permeability cell at 7 and 28 days undamaged. For this reason, the oxygen permeability was determined at the age of 160 days only.

Permeability tests were determined on specimens dried by the two techniques described in Section 4.1.3. The results of oxygen permeability measurements are presented in Figure 5.7. From this figure, it follows that the two different drying techniques are equivalent with respect to the determination of coefficients of permeability for oxygen.

The relationship between water and oxygen permeabilities for oven-dried mortars is shown in Figure 5.8. Because there is a positive correlation (correlation coefficients of 0.893 and 0.887 for oven- and solvent-dried plain mortars respectively), oxygen permeabilities of blended mortars will not be interpreted here. It would be a mere restatement of what is already described in Section 5.3 dealing with water permeability.

Oven-dried specimens can be examined for oxygen permeability immediately after reaching a constant weight; the solvent drying is about three times more time consuming than oven-drying. Thus, for rapid prediction of water permeability from oxygen permeability results, the oven-drying technique is more appropriate. Plain mortars and mortars with latex modifier were not included in the regression

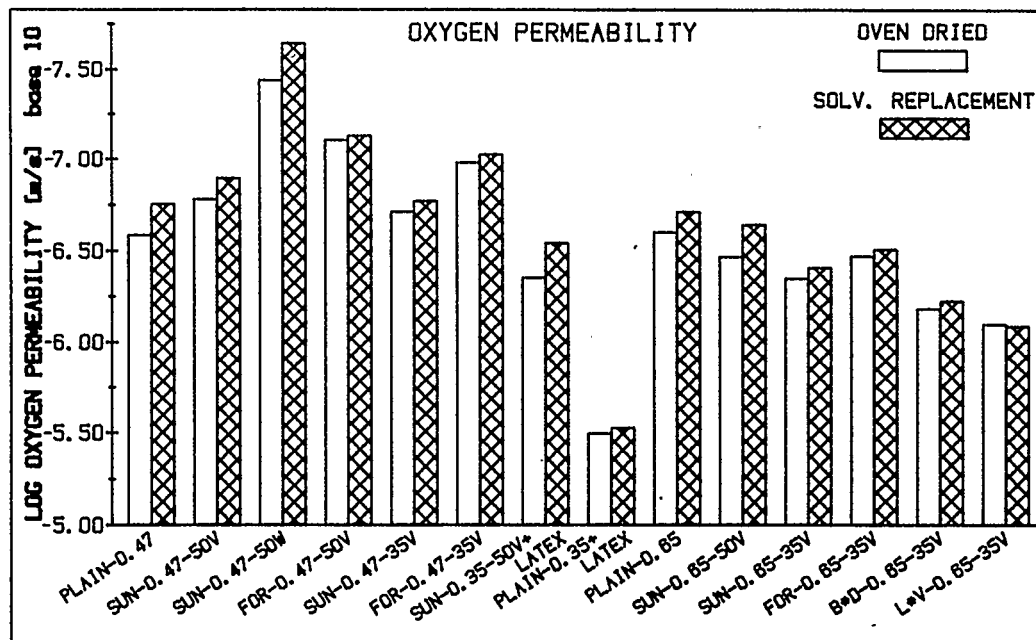


Fig. 5.7 Oxygen permeability at the age of 160 days

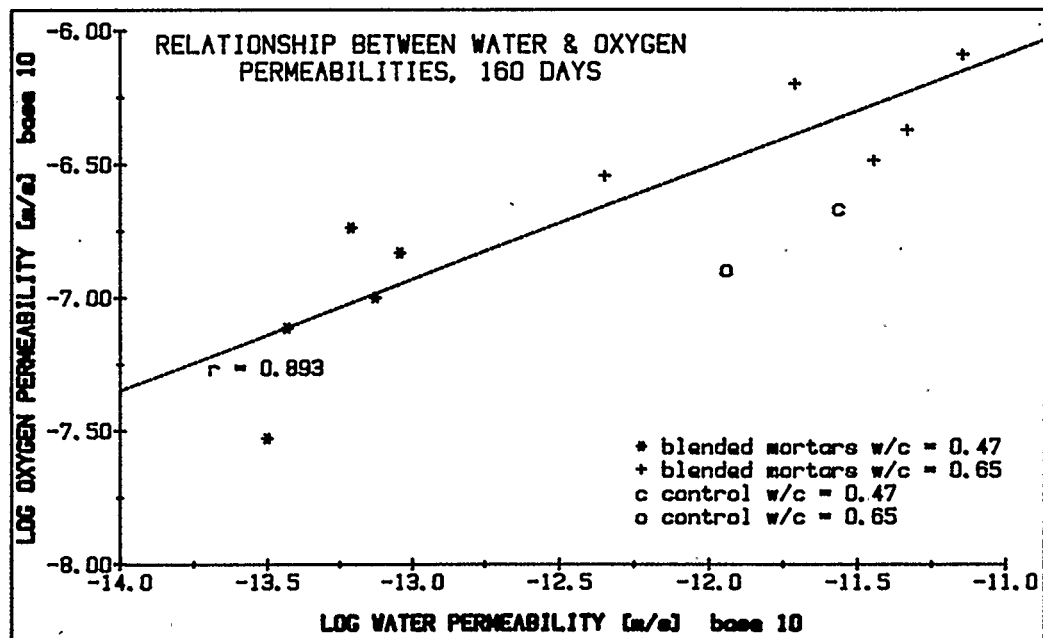


Fig. 5.8 Relationship between water and oxygen permeabilities

analysis because of their distinct microstructural differences from those of blended mortars (see Chapter 6). For this reason, plain and latex mortars are discussed here.

a) Plain Mortars

Plain mortar #1 with a water-cement ratio of 0.47 shows similar or higher permeability at the age of 160 days compared to blended mortars with the same w/c ratio. From a group of specimens with w/c ratio 0.65, the coefficient of permeability to oxygen of plain mortar #9 (PLAIN-0.65) displays the lowest value. Surprisingly, mortar #1 (PLAIN-0.47) shows a similar value of permeability coefficient as mortar #9 (PLAIN-0.65), contrary to the lower water-cement ratio employed.

From the comparison of plain mortars with blended mortars of the same w/c ratio it follows that the beneficial effect of pozzolanic reaction on the reduction of oxygen permeability of blended mortars is effective only for mixes with the lower water-cement ratio of 0.47.

b) Mortars with Latex Modifier

Generally, mortars with latex did not perform well (see Figure 5.7). The value of coefficient of permeability to oxygen of mortar #7 (SUN-0.35-50V+LATEX) is similar to those of blended mortars with w/c ratio 0.65; mortar #8 (PLAIN-0.35+LATEX) is the most permeable of all that were examined.

When comparing the oxygen and water permeability results of latex mortars #7 and #8, there is some controversy. Water permeability results at 28 and 160 days show mortar #8 (PLAIN-0.35+LATEX) less permeable than mortar #7 (SUN-0.35-50+LATEX). From oxygen permeability results mortar #8 is much more permeable than mortar #7 (see

Figures 5.5 and 5.7). This extremely interesting behaviour might be due to the drying procedure which is necessary for the preparation of specimens for oxygen permeability examination. Both drying techniques employed in this work consist of final drying at 80° (see Section 4.1.3).

Further discussion from the microstructural point of view is presented in the chapter dealing with microstructure-engineering properties.

5.5 Chloride Permeability

The principles and test procedure for evaluation of chloride permeability are described in Chapter 2 and Chapter 3, respectively. As shown in Section 2.4.6.2, permeability of mortar to chloride ions is proportional to the charge passed through the specimen during the test. Thus for the purpose of comparison, the term "more permeable" means, with respect to this work, mortar with a higher value of charge passed. In Table 3.5, chloride permeability of concretes is divided into five categories depending on the charge passed.

Values of charge passed through the specimens during a six-hour period, are presented in Figures 5.9, 5.10 and 5.11. Figure 5.9 presents chloride permeabilities of mixes with $w/c = 0.47$ and mixes with Latex Modifier, Figure 5.10 of mixes with $w/c = 0.65$. Figure 5.11 shows a summary of all results at 28 and 160 days.

a) Mortars with Water-Cement Ratio of 0.47

At 7 days, all blended mortars within this group show similar or higher values of charge passed than the control mix; at 28 days, some blended mortars display a lower and some a higher charge passed. At

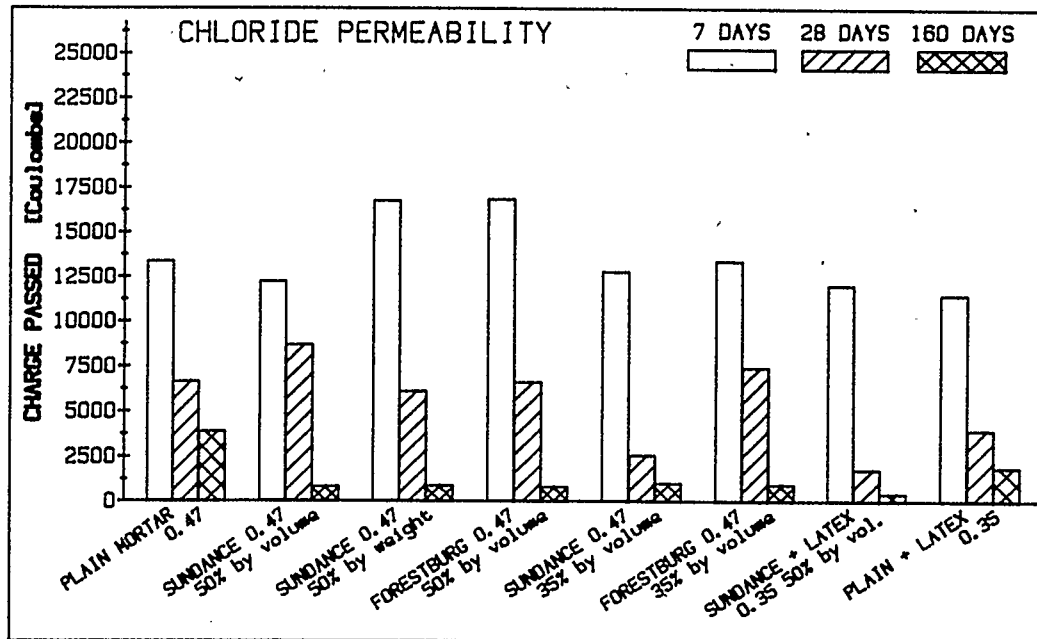


Fig. 5.9 Chloride permeabilities of mortars with w/c = 0.47 and 0.35

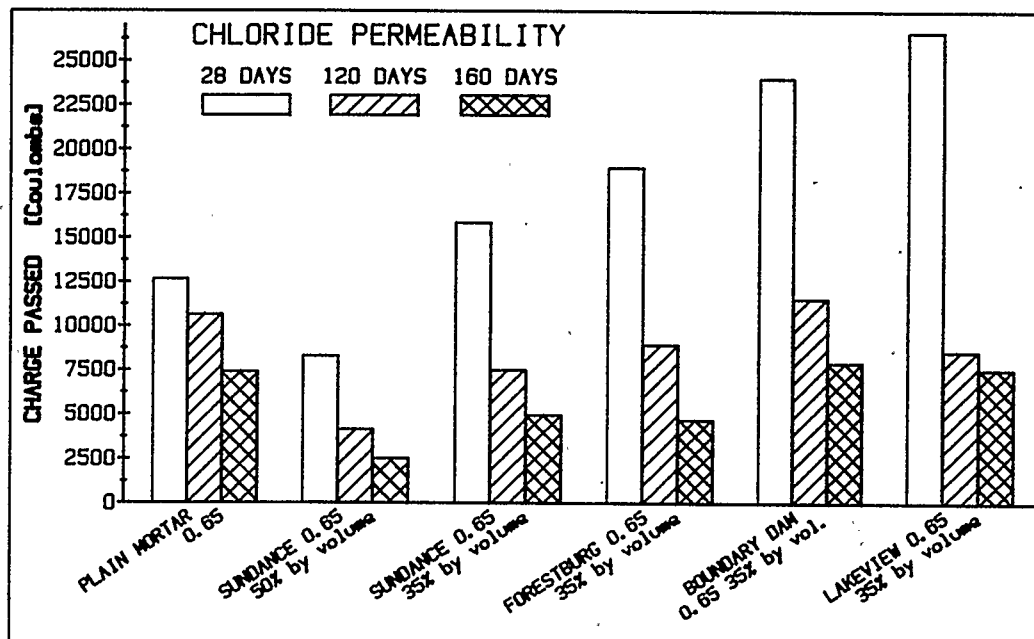


Fig. 5.10 Chloride permeabilities of mortars with w/c = 0.65

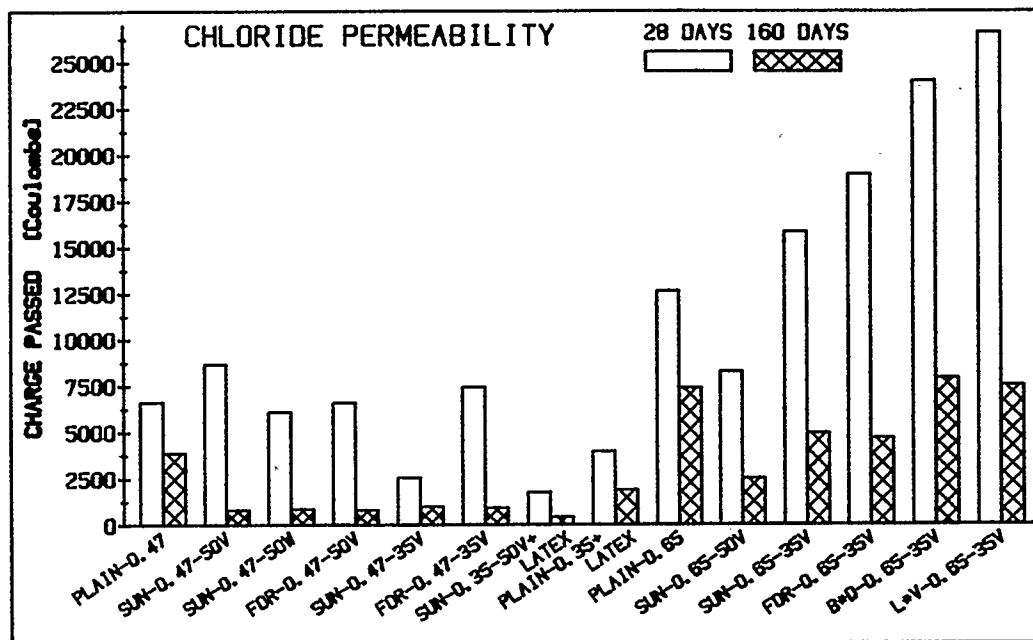


Fig. 5.11 Chloride permeabilities of all examined mortars at the ages of 28 and 160 days

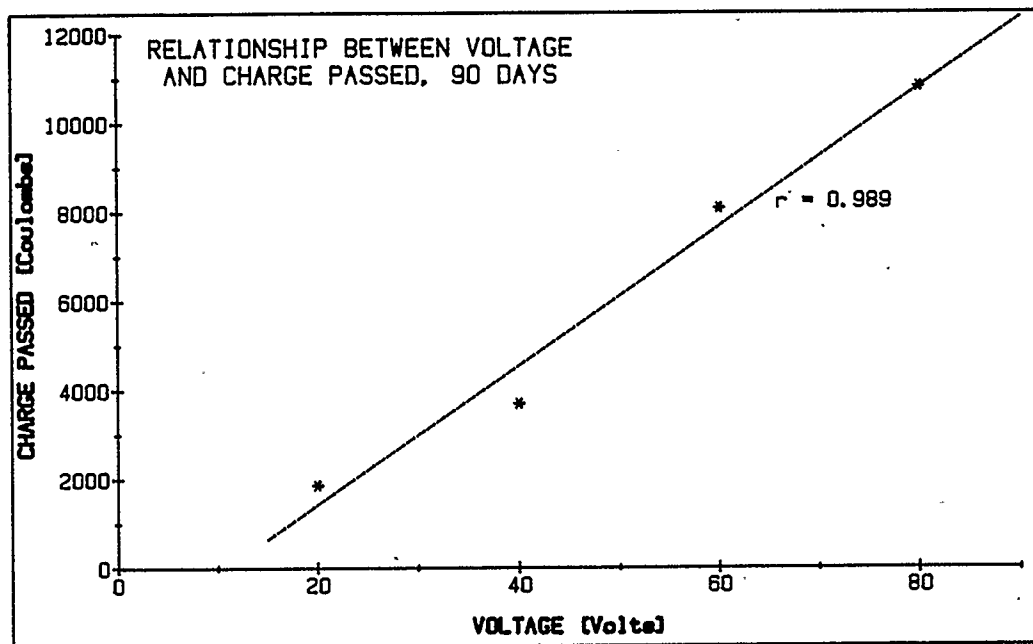


Fig. 5.12 Applied voltage vs. charge passed

the age of 160 days all blended mortars show a much lower permeability to chloride ions than the control mix. The replacement levels and type of fly ash employed within this group apparently did not affect significantly the values of charge passed at the age of 160 days, in contrast to the observation at earlier ages.

b) Mortars with Latex Modifier

The least permeable mortar to chloride ions from all mixes examined at 160 days was mortar #7 (SUN-0.35-50V+LATEX). The charge passed through mortar #8 (PLAIN-0.35+LATEX) was about one half of that passed through the control mix #1 with w/c ratio of 0.47. Similar reduction in charge passed was recorded in mortar #7 (SUN-0.35-50V+LATEX) when compared to mortar #2 (SUN-0.47-50V). The presence of latex modifier together with lower w/c ratio reduces by about 50% the charge passed through the specimen when w/c = 0.47. The reduction will be different for mortars with other w/c ratios than that of 0.47 as seen from Figure 5.10.

c) Mortars with Water-Cement Ratio 0.65

Figure 5.10 presents a value of charge passed through the mortar specimens with w/c = 0.65 at 28, 120 and 160 days. Generally, all mixes within this group, including the control mix, display higher permeabilities than mortars with w/c ratio of 0.47 (Fig. 5.11). Since the mixes with higher w/c ratios contain higher proportion of large pores compared to the identical mixes with lower w/c ratio (see Chapter 2), the effect of water-cement ratio on permeability is evident. It follows that the lowest permeability to chloride ions at the age of 160 days was recorded for specimen #10 (SUN-0.65-50V) which had the highest replacement level. Specimens #11 (SUN-0.65-35V)

and #12 (FOR-0.65-35V), both with sub-bituminous fly ashes, performed better than specimens #13 (B*D-0.65-35V) and #14 (L*V-0.65-35V) with lignite and bituminous fly ashes.

The values of charge passed at 28 days for the three most permeable specimens (i.e. #12, #13 and #14) were calculated at 40 volts. The reason for this was that the recorded temperature in these specimens during pilot testing reached 88°C. According to Whiting (1981), when the temperature reaches 88°C, the test should be discontinued in order to avoid damage to the cell. A different approach was taken in this project where these three specimens were tested at 40 volts, in order to keep the temperature of the specimen low. As shown in Figure 5.12, the correlation coefficient for the relationship between voltage and charge passed for blended mortar with $w/c = 0.65$ was $r = 0.99$. Therefore, the charge through the specimen at 60 volts was calculated from a simple proportion of the charge passed at 40 volts in order to enable direct comparison with the rest of the specimens.

5.5.1 Summary of Chloride Permeability Results

From the comparison of values of charge passed through the specimens at 28 and 160 days (see Figure 5.11) it is observed that the drop in charge is more profound for blended mortars than for control mixes. All blended mixes benefitted from pozzolanic reaction regardless of w/c ratio employed, however for mixes #13 and #14, there is only an economical benefit from the replacement of cement by fly ash since the chloride permeabilities of these two mixes were not less than the control mix #9. Classification of all mortars according to Table 3.5 is presented in Table 5.2.

In some mixes, the charge passed through the specimens at 160

Table 5.2 Classification of Chloride Permeabilities
of Examined Mortars in this Work

MIX	DESCRIPTION	AGE (DAYS)			
		7	28	120	160
1	PLAIN 0.47	H	H		M
2	SUN-0.47-50V	H	H		VL
3	SUN-0.47-50V	H	H		VL
4	FOR-0.47-50V	H	H		VL
5	SUN-0.47-35V	H	M		L
6	FOR-0.47-35V	H	H		VL
7	SUN-0.35-50V-(LATEX)	H	L		VL
8	PLAIN-0.35-(LATEX)	H	M		L
9	PLAIN-0.65		H	H	H
10	SUN-0.65-50V		H	H	M
11	SUN-0.65-35V		H	H	H
12	FOR-0.65-35V		H	H	H
13	B*D-0.65-35V		H	H	H
14	L*V-0.65-35V		H	H	H

H - High

M - Moderate

L - Low

VL - Very Low

days was as low as 9% of that at 28 days. Such a large reduction in permeability was not recorded during water or oxygen permeability tests.

Li & Roy (1986) investigated Cl^- diffusion of blended cement pastes. They noticed that the concentration of Ca^{2+} , Al^{3+} and Si^{4+} cations in pore solution was about 2.5 times higher in the fly ash cement system than in normal Portland cement paste. These cations lower the diffusion rates and thus restrict the mobility of Cl^- ions. The concentration of cations K^+ (cations K^+ increase Cl^- ion mobility) was decreased in the fly ash cement system by one half.

It is concluded that the observed reduction in chloride permeability of blended mortars is caused by:

- a) the discontinuity of pores resulting from the pozzolanic reaction as was in the case of water and oxygen permeability (see Fig. 5.6);
- b) the presence of those cations which hinder Cl^- movement and by the reduced amount of those cations which promote the diffusion of Cl^- ions;
- c) the presence of latex. On account of the non-conductive property of latex, the saturated mortars incorporating latex are reasonably expected to be less conductive than saturated ones without latex.

5.6 Relationship between Engineering Properties

A statistical analysis was carried out to examine whether correlation existed between the engineering properties determined in this work. Regression analyses were performed for these relationships:

compressive strength - water permeability

compressive strength - oxygen permeability
compressive strength - chloride permeability
water permeability - oxygen permeability
water permeability - chloride permeability
oxygen permeability - chloride permeability

Results of regression analyses are presented in Figures 5.13, through 5.16. Analyses indicate that the highest correlation coefficient of 0.91 exists for the relationship between water and chloride permeabilities¹⁾, followed by those of 0.89 for water permeability vs. oxygen permeability and 0.86 for oxygen permeability vs. chloride permeability. The 'goodness-of-fit' was reduced for relationships between compressive strength and water permeability ($r = 0.77$) and between compressive strength and chloride permeability ($r = 0.70$). Since correlation at the 95% confidence level exist for $r \geq 0.63$, the relationship between compressive strength and oxygen permeability ($r = 0.59$) was rejected and therefore is not shown here.

It is concluded that good correlation exists between compressive strength and water permeability, and between compressive strength and chloride permeability. Significant correlation exists for the relationships between water-oxygen and oxygen-chloride permeabilities. No general relationship exists between water and chloride permeabilities; however, significant correlations were observed between these permeabilities at the age of 160 days.

1) While the correlation for the combined data between water and chloride permeability at 28 and 160 days was rejected ($r = 0.62$), there does exist a significant correlation of $r = 0.91$ for the relationship when 160 days data only are considered.

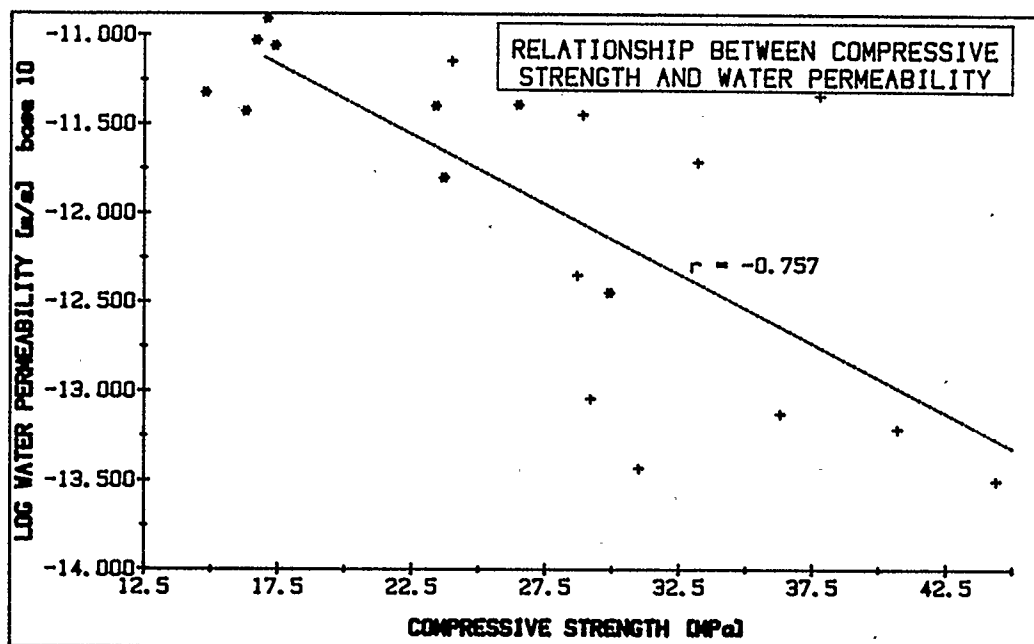


Fig. 5.13 Relationship between compressive strength and water permeability

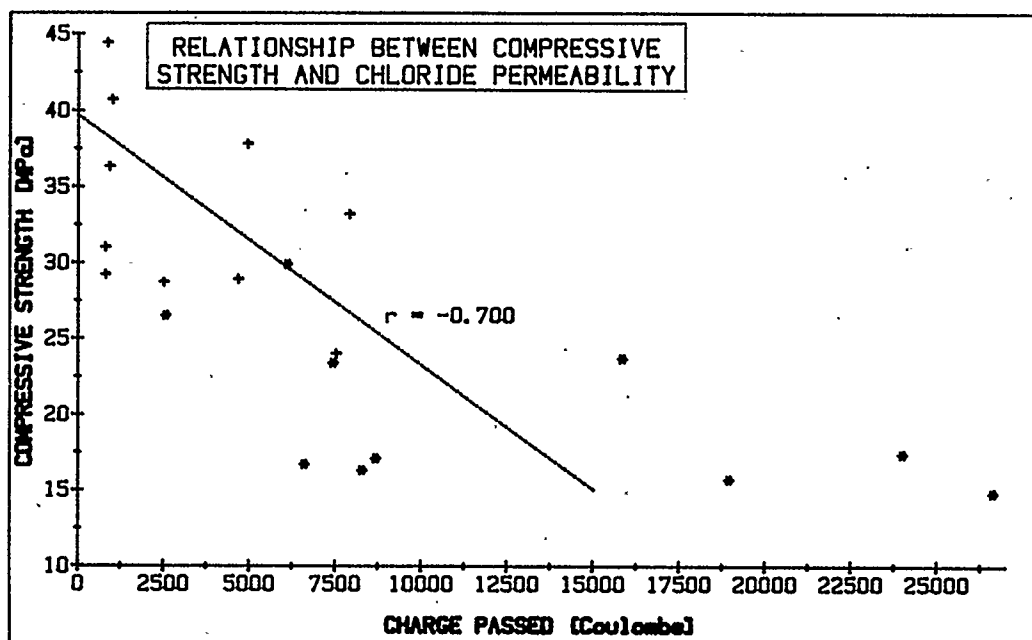


Fig. 5.14 Relationship between chloride permeability and compressive strength

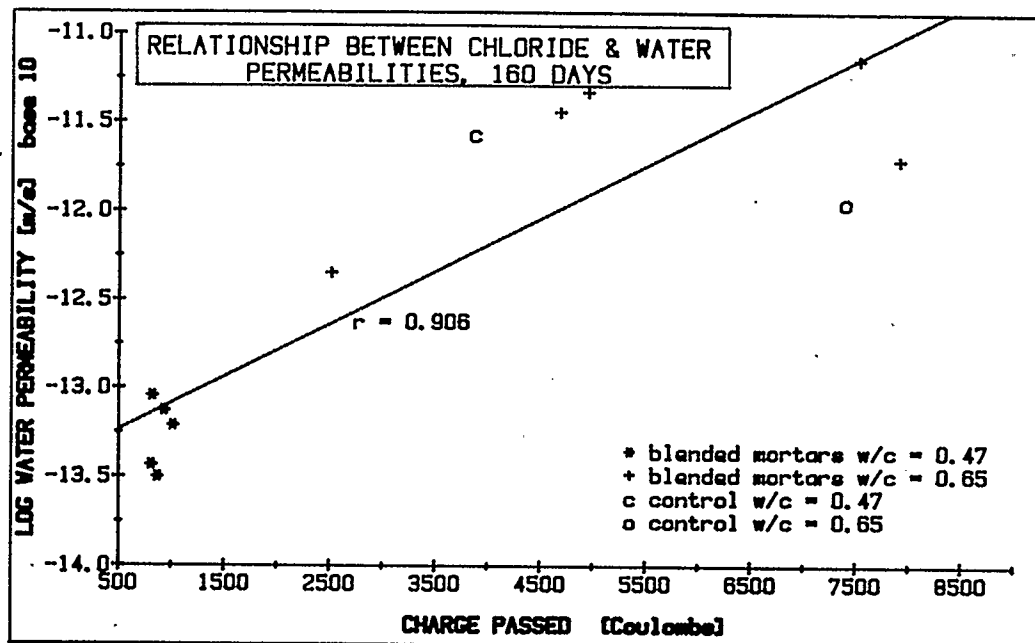


Fig. 5.15 Relationship between chloride and water permeabilities

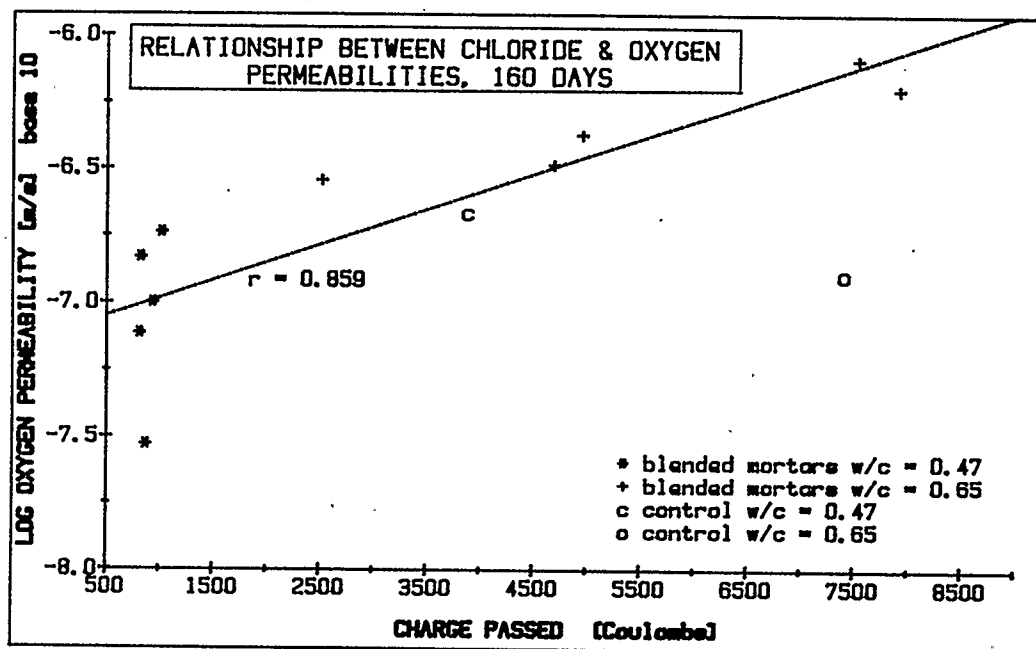


Fig. 5.16 Relationship between chloride and oxygen permeabilities

5.7 Conclusions

The conclusions based upon the results of Chapter 5 are as follows:

- 1) Both plain and blended mortars with a w/c ratio of 0.47 showed better compressive strengths, and lower water, oxygen and chloride permeabilities than those with a w/c ratio 0.65.
- 2) The compressive strength values of some blended mortars, although lower at early ages, were similar or higher than those of plain mortars at the age of 160 days.
- 3) Mortars with latex modifier had only 50% of the strength of comparable mortars without latex at 160 days.
- 4) The water, oxygen and chloride permeabilities of blended mortars with w/c = 0.47 are generally much lower at 160 days than those of the control mortar without any fly ash. The improvements are not so profound for mortars with w/c = 0.65 when compared to the corresponding control mix.
- 5) While latex mortars displayed relatively high water and oxygen permeabilities, in the case of chloride permeability latex modifier significantly decreased the diffusion of Cl^- ions in mortars.
- 6) Good correlations exist for relationships between: compressive strength and water permeability (correlation coefficient $r = 0.76$), compressive strength and chloride permeability ($r = 0.70$).
- 7) Significant correlations exist at the age of 160 days for relationships between water and oxygen permeabilities ($r = 0.89$), chloride and water permeabilities ($r = 0.91$) and chloride and oxygen permeabilities ($r = 0.86$).

CHAPTER SIX

RESULTS AND DISCUSSION - MICROSTRUCTURAL CHARACTERISTICS

6.1 Introduction

This chapter presents results from microstructural examination of the mortars tested for strength and permeability. Total porosity is defined in this work as the total volume of pores intruded by mercury at the maximum pressure of 413.7 MPa corresponding to the volume of pores down to a radius of 1.8 nm (18 Å). Since the permeability of mortar is related to the volume of larger pores (see Chapter 2, Table 2.2), volumes intruded into the pores down to a radius of 100 nm (1000 Å) and down to 18 nm (180 Å), (corresponding to pressures of 7.45 and 41.4 MPa respectively), are presented for the purpose of correlation with permeability results.

Maximum continuous pore radius (Nyame and Illston, 1980) and threshold radius (Manmohan and Mehta, 1981) were also determined from the intrusion curves. Maximum continuous pore radius (MCPR) is defined as the pore radius at which dV/dP has a maximum value and the threshold radius (TR) as the pore radius at which significant intrusion begins (see Figure 6.10). It was felt that more realistic parameters for correlation with permeabilities might be the volume intruded into pores above the MCPR or the TR. These volumes were also included as possible "measures" of the pore structure.

Different pore size distributions resulting from the two drying techniques (oven-drying and solvent-replacement) were obtained for each specimen; examples are presented.

Effects of other variables such as water-cement ratio, replacement level of cement, type of fly ash, latex modifier and age of

specimens on porosity and pore size distribution are examined and discussed in this chapter.

Values of calcium hydroxide content in blended and plain mortars are also presented.

6.2 Calcium Hydroxide Content

The dynamic thermogravimetry described in Chapter 4 was used to determine calcium hydroxide (CH) content in mortars. Figures 6.1 and 6.2 show values of CH content as a percentage of the weight of cement at the ages of 7, 28, 120 and 160 days. Each value is an average of at least 3 measurements. The method for calculation of CH content is presented in Section 4.3.5.

At 7 days the CH content in most blended mortars was comparable to that in plain mortar, except for mix #4 (FOR-0.47-50V) which showed an unusually high content (see Figure 6.1). As hydration of cement continues, CH content will rise. On the other hand, the pozzolanic reaction involves consumption of free CH, by the reaction with the silica and/or alumina phases presented in fly ash to form C-S-H and/or C-A-H.

From the CH values shown in Figure 6.1, it is clear that the pozzolanic reaction in blended mortars with $w/c = 0.47$ started as early as 7 to 28 days; further decrease in CH content was recorded between 28 and 160 days.

Similar trends were observed for plain mortar and most blended mortars with w/c 0.65 (see Figure 6.2). Only mortar #13 (B*D-0.65-35V) shows no consumption of CH by the pozzolanic reaction after 28 days. Certainly, most ashes at high w/c are not as reactive between 28 and 160 days as those at a w/c of 0.47.

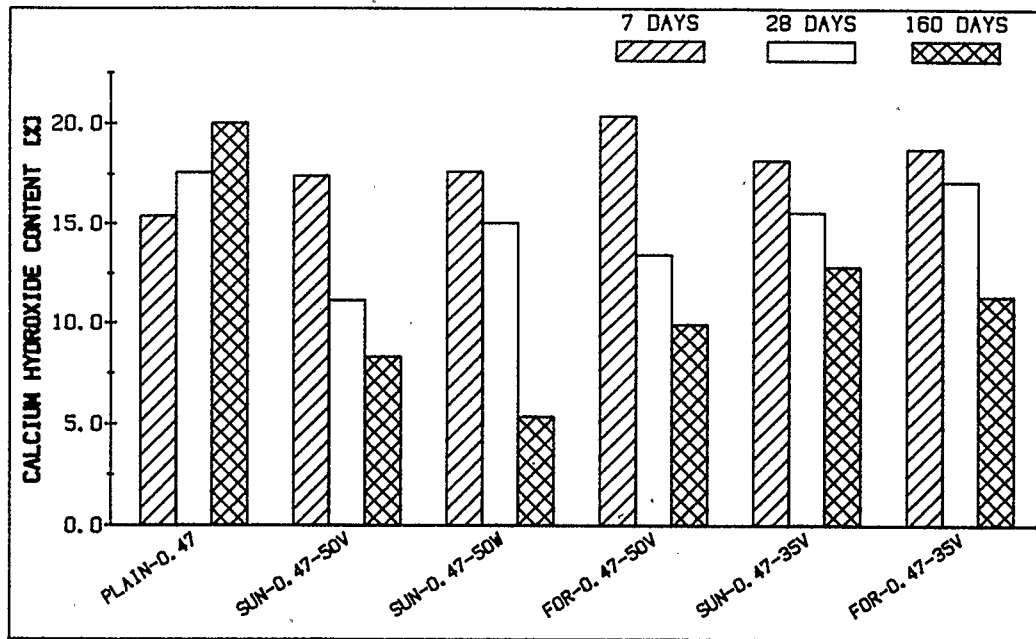


Fig. 6.1 Calcium hydroxide content of mortars with w/c = 0.47

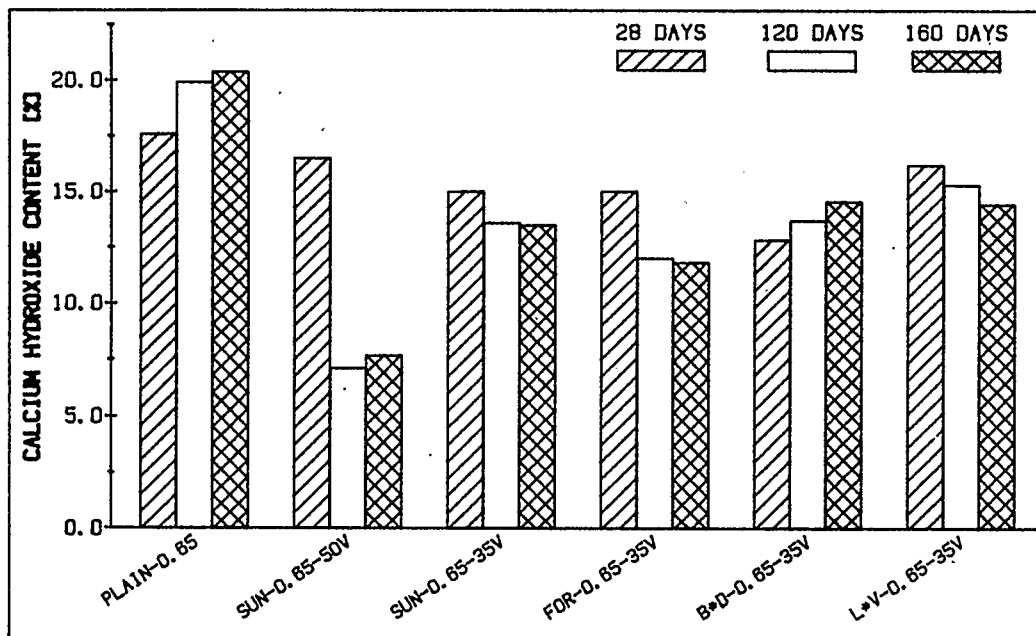


Fig. 6.2 Calcium hydroxide content of mortars with w/c = 0.65

For easier comparison of results at the age of 160 days, the CH content of the blended mortars is expressed as a percentage of the plain mortar (see Table 6.1). From the comparison of corresponding mortars with the same replacement levels, it follows that the different water-cement ratios did not affect the relative values of CH content after 160 days (compare mixes #2 and #10; #5 and #11; #6 and #12). Also, values of CH content in both plain mortars are comparable (see Figures 6.1 and 6.2). The CH content in latex mortars was not

Table 6.1 Calcium hydroxide contents at the age of 160 days

Mix No.	Description	CH Content [%]
1	PLAIN-0.47	100
2	SUN-0.47-50V	42
3	SUN-0.47-50W	27
4	FOR-0.47-50V	50
5	SUN-0.47-35V	64
6	FOR-0.47-35V	57
7	SUN-0.35-50V+LATEX	-
8	PLAIN-0.35+LATEX	-
9	PLAIN-0.65	100
10	SUN-0.65-50V	38
11	SUN-0.65-35V	66
12	FOR-0.65-35V	58
13	B*D-0.65-35V	72
14	L*V-0.65-35V	71

determined in this work as explained later in this section.

Since insignificant changes in CH content were observed between 120 and 160 days, it is assumed that the pozzolanic reaction and/or hydration is well-advanced at the age of 160 days. Thus, the effect of variables (different fly ashes and replacement levels) which influence the CH content will be discussed at this age only.

The lowest value of CH at the age of 160 days occurs in mortar #3 (SUN-0.47-50W) with the highest replacement level (see Table 6.1) followed by mortars #10 (SUN-0.65-50V), #2 (SUN-0.47-50V) and #4 (FOR-0.47-50V). The rest of blended mortars with 35% replacement level of cement by fly ash show higher values of CH content since less fly ash was available for the pozzolanic reaction. From Table 6.1, it also follows that lignitic and bituminous fly ashes employed in mixes #13 and #14 are less reactive than the sub-bituminous ones.

In specimens with latex modifier, calcium hydroxide content could not be detected by the thermogravimetric technique. During pilot testing it was found that the latex decomposes over the same temperature range as the decomposition of CH (Figure 6.3). Future tests should employ another method to determine the CH content. It is suggested that the carbonation method involving conversion of calcium hydroxide to calcium carbonate, as described in Section 4.2.3, might be utilized.

6.3 Porosity and Pore Size Distribution

Porosity and pore size distribution were determined by mercury porosimetry.

A different representation of the pore structure was obtained for identical specimens which were dried by the two different techniques -

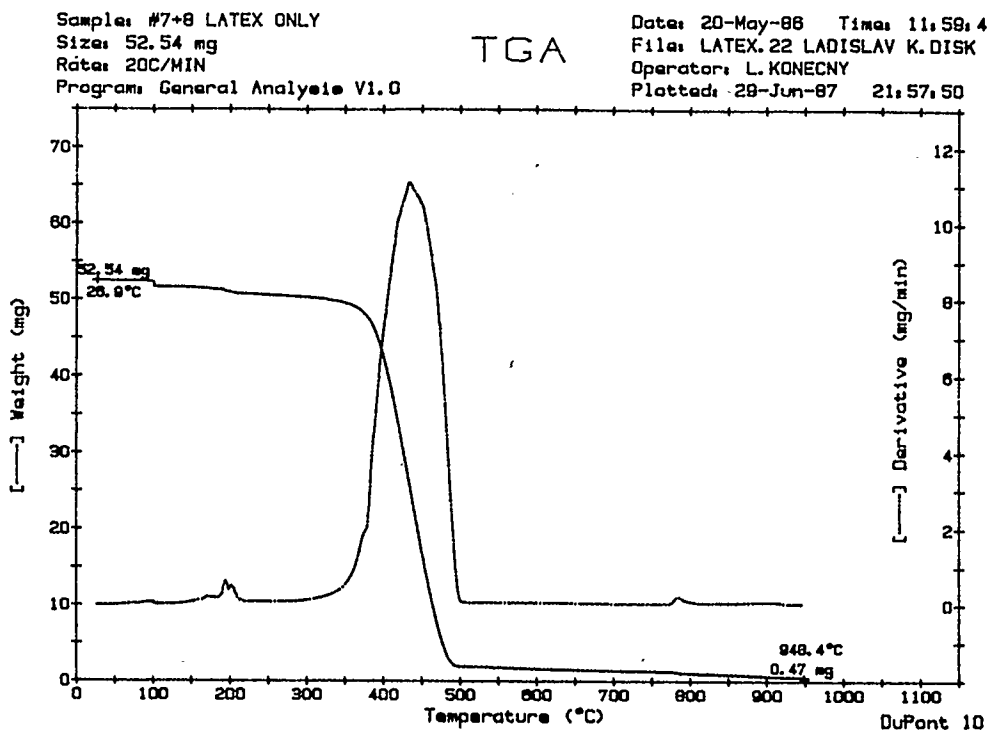


Figure 6.3 TG curve representing weight loss of latex over the temperature range of 0 to 1000°C

i.e. oven drying and solvent replacement. For this reason, before discussion of the effect of the various parameters on the microstructure of mortars, the impact of the different drying techniques on microstructure is discussed.

6.3.1 The Effect of Drying Technique on Microstructure

The two drying methods employed (oven drying at 80° and solvent replacement) produce different representation of the pore structure of the material. Figures 6.4 to 6.7 show the pore size distributions of three blended and one plain mortar. Two mortars contain latex

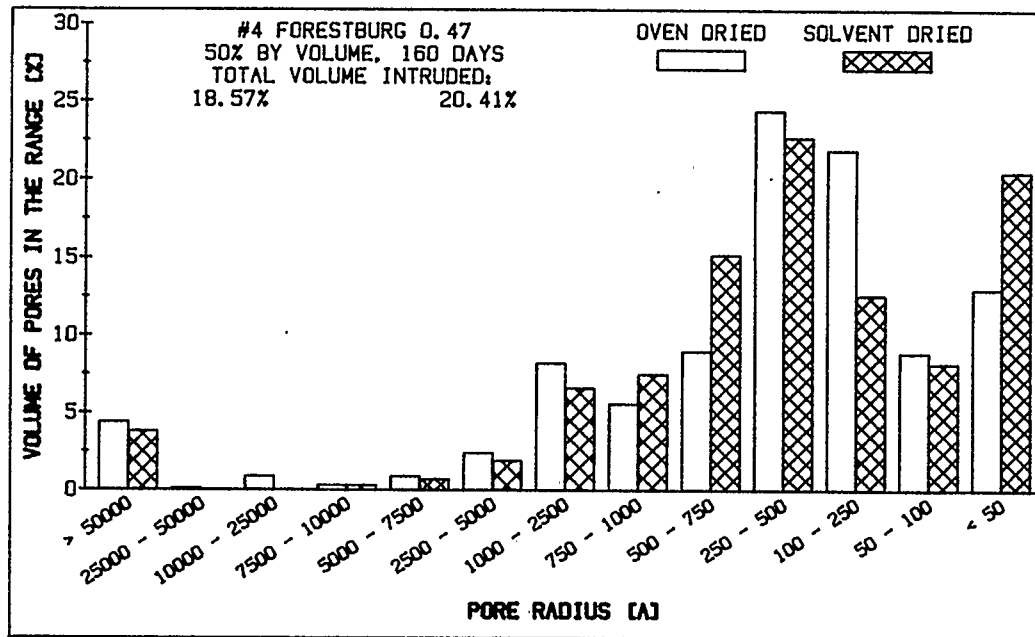


Fig. 6.4 Pore size distributions resulting from different drying techniques of blended mortar ($w/c = 0.47$)

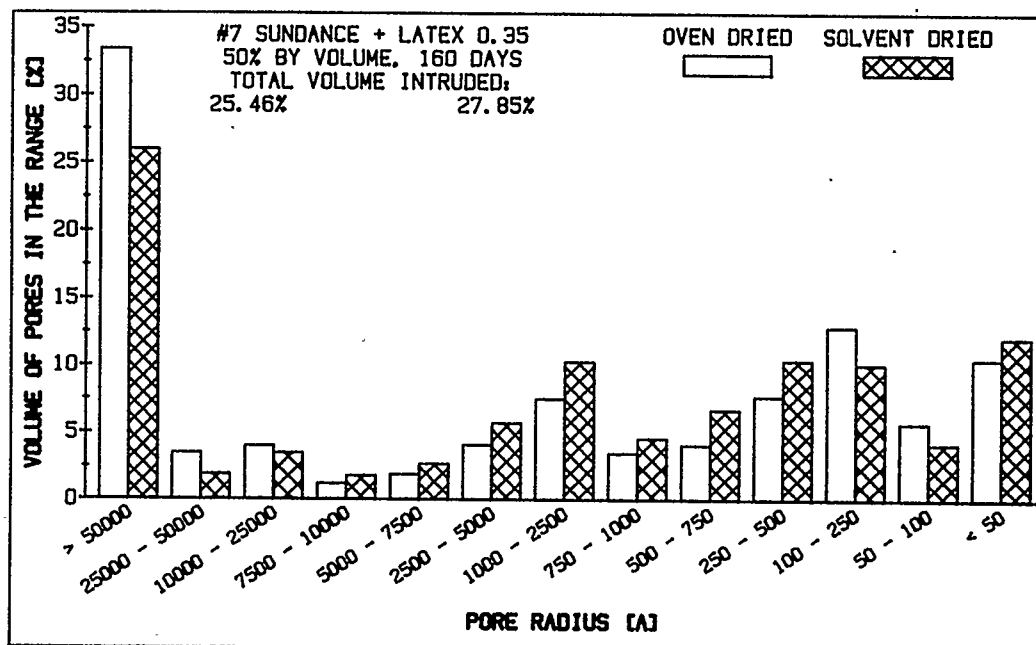


Fig. 6.5 Pore size distributions resulting from different drying techniques of blended mortar with latex ($w/c = 0.35$)

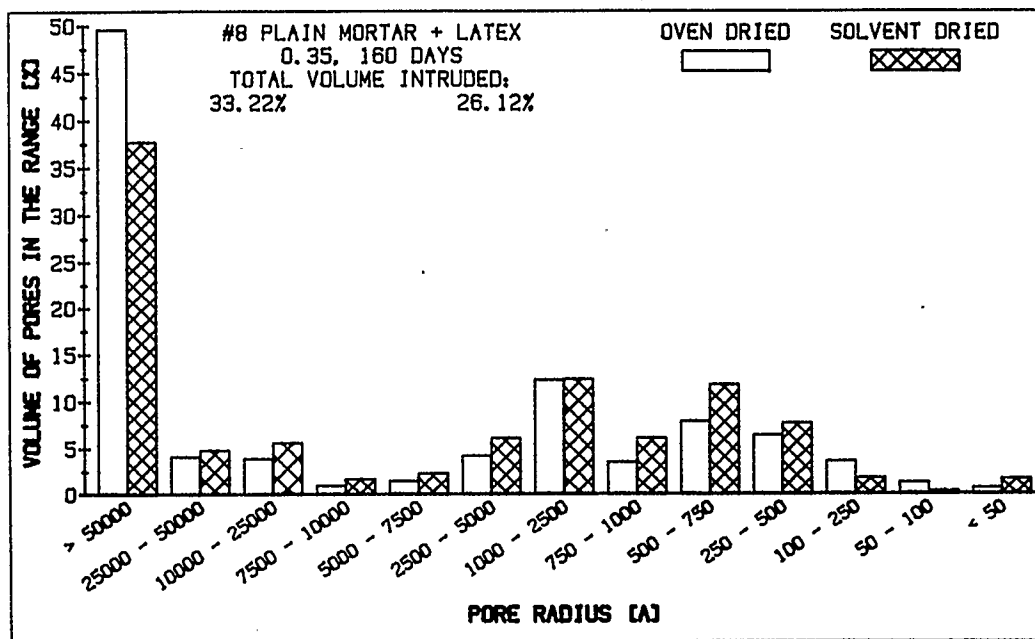


Fig. 6.6 Pore size distributions resulting from different drying techniques of latex modified plain mortar ($w/c = 0.35$)

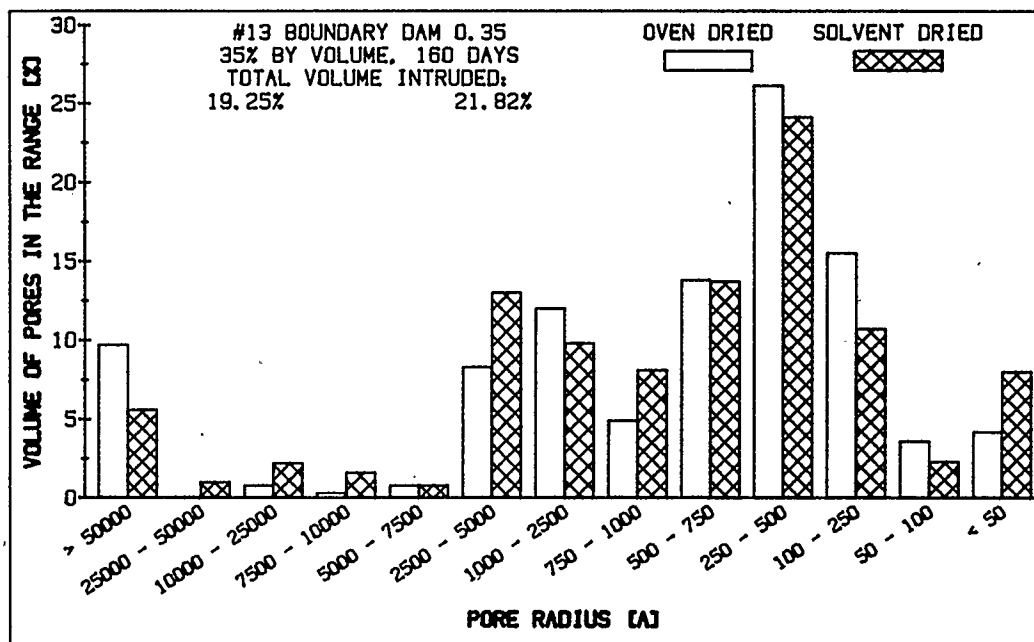


Fig. 6.7 Pore size distributions resulting from different drying techniques of blended mortar ($w/c = 0.65$)

modifier. These mortars represent mixes with various replacement levels and three w/c ratios.

Oven dried specimens have more pores in the large pore size range (> 5000 nm) and fewer pores in the very fine range (< 5 nm) than solvent-dried specimens. This indicates that direct oven drying of the mortar causes disruption of the pore structure for pores of radius less than about 5 nm ($50 \text{ \AA}$). On the other hand, the solvent replaced mortars retain a considerable volume of pores in this fine pore size range. The solvent-replacement technique tends to preserve the pore structure of the original mortar better than direct oven drying. Therefore, for further discussion only solvent-replaced specimens will be considered.

6.3.2 The Effect of Pozzolanic Reaction on Pore Size Distribution

Pore size distributions at the age of 28 and 160 days are presented in Figures 6.8 and 6.9, respectively.

Pore size distributions of all blended mortars regardless of age are shifted towards the finer pore size region, compared to those of plain mortars. The reaction between calcium hydroxide and fly ash causes refinement of the pore structure of blended mortars. In blended mortar #7 with latex modifier (SUN-0.35-50V+LATEX), the refinement of the pore structure is also evident when compared to the mix #8 (PLAIN-0.35+LATEX) at both ages. The refinement of pore structure for all blended mortars is more far-reaching at the age of 160 days; nevertheless, at 28 days the trend is also observable.

As shown in Figures 6.1 and 6.2, the CH content in mortars changed significantly during the early period of curing. Since these changes indicate progress in hydration and pozzolanic reaction, the

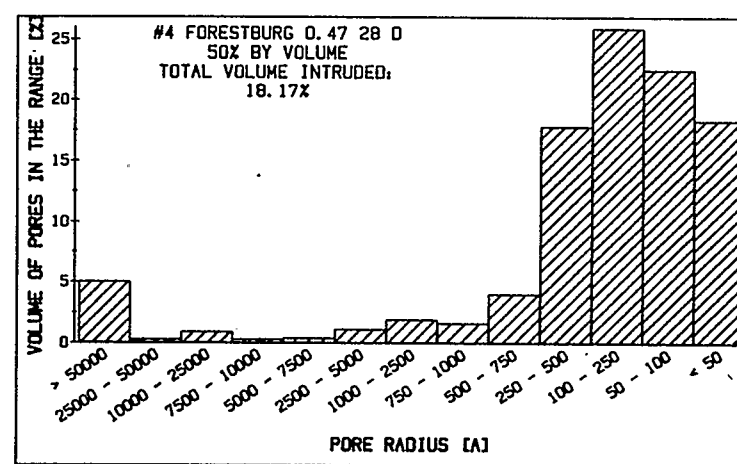
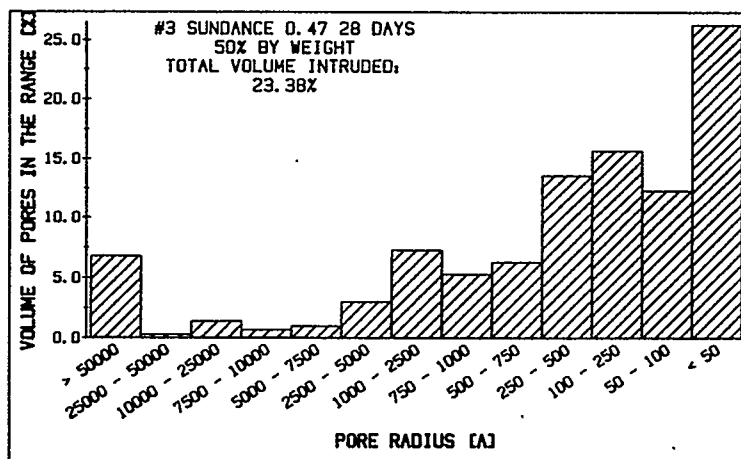
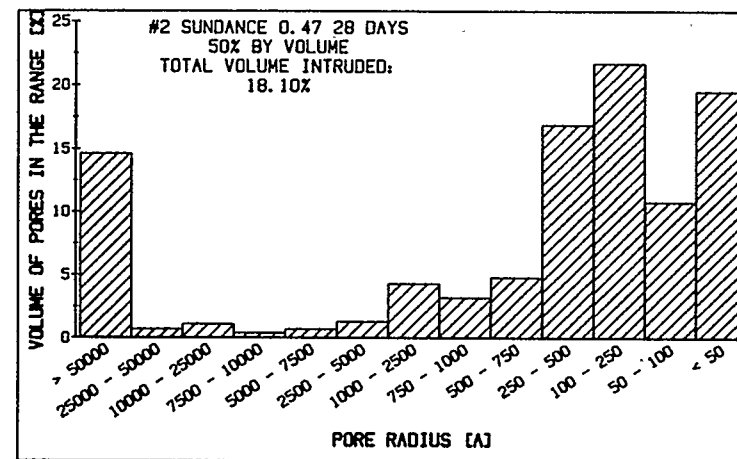
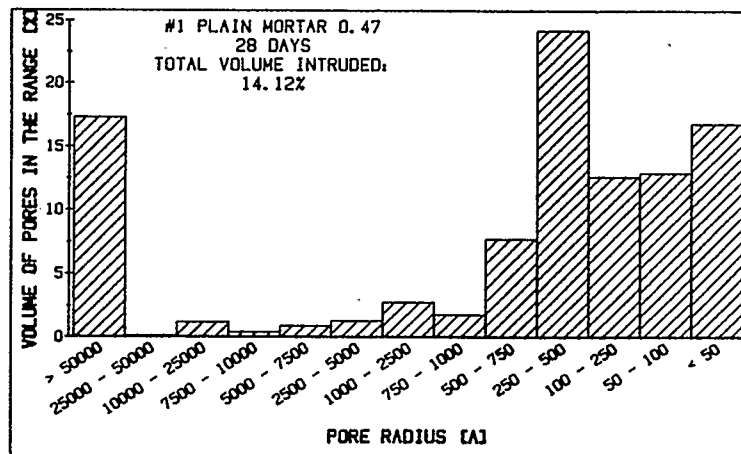


Fig. 6.8 Pore size distributions of mortars at the age of 28 days

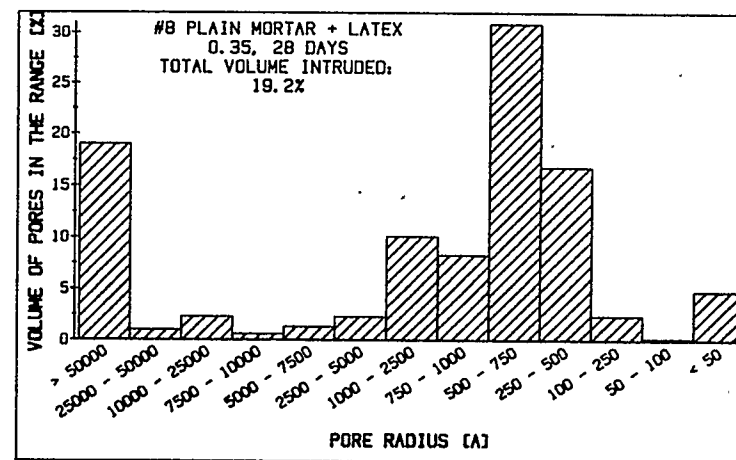
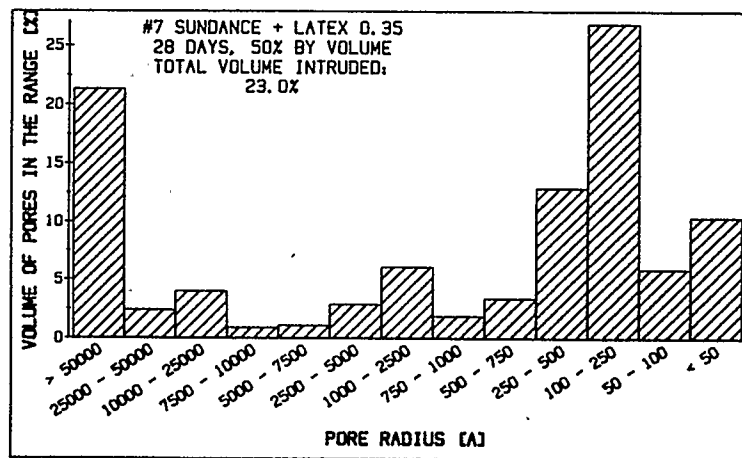
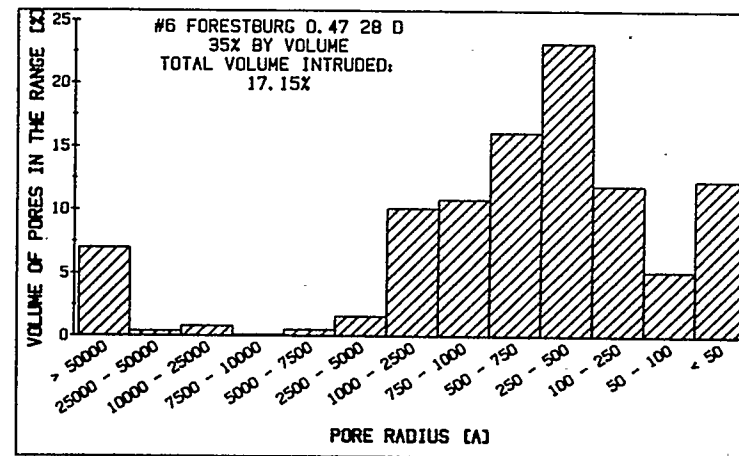
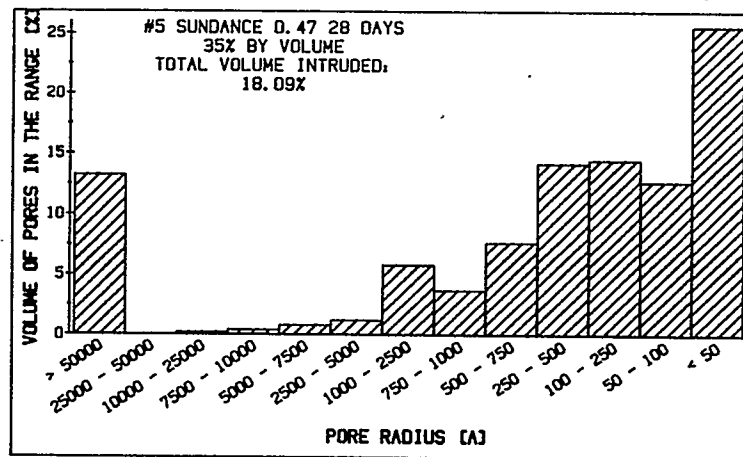


Fig. 6.8 (continued)

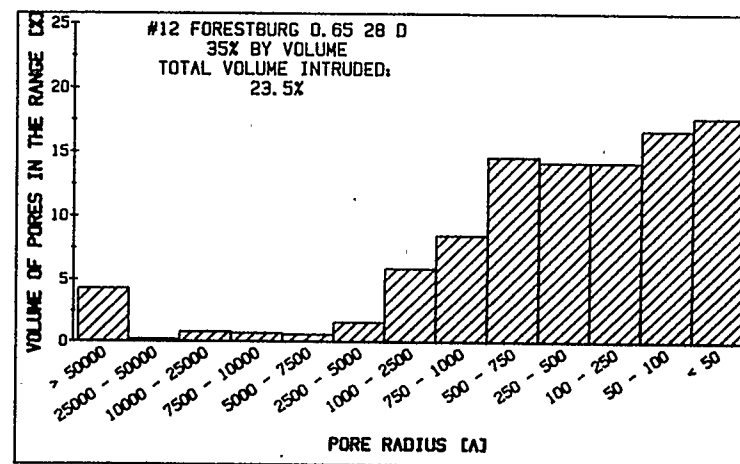
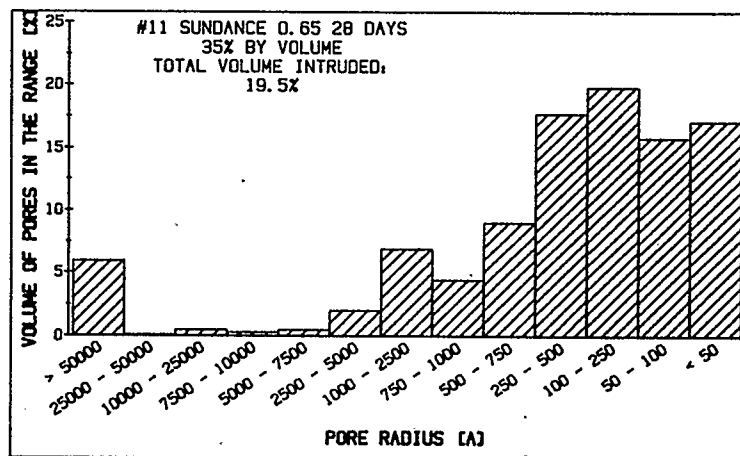
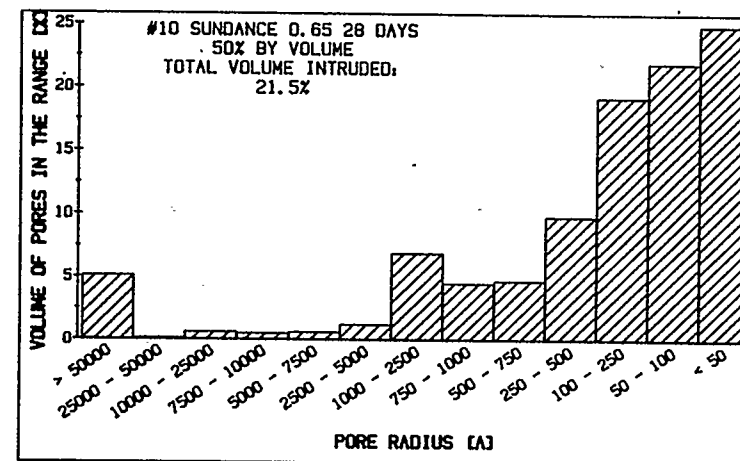
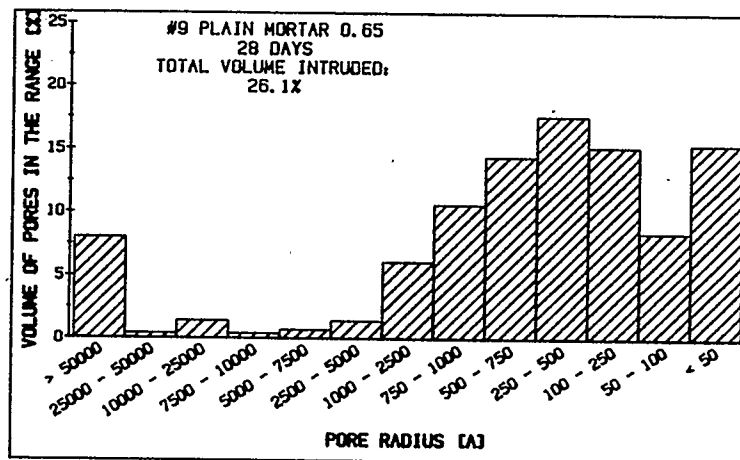


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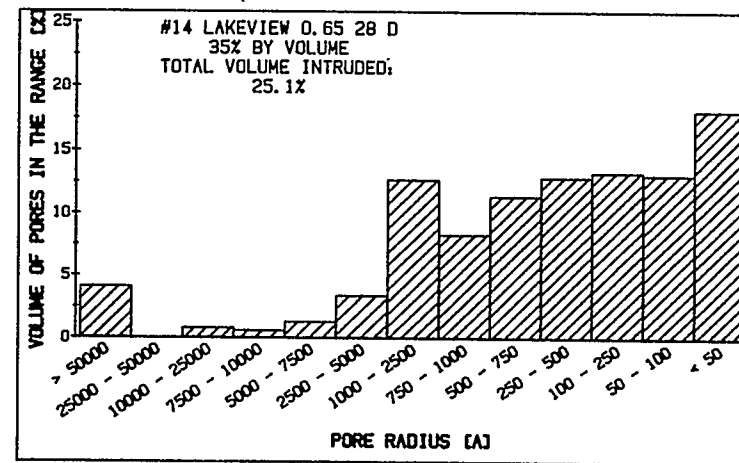
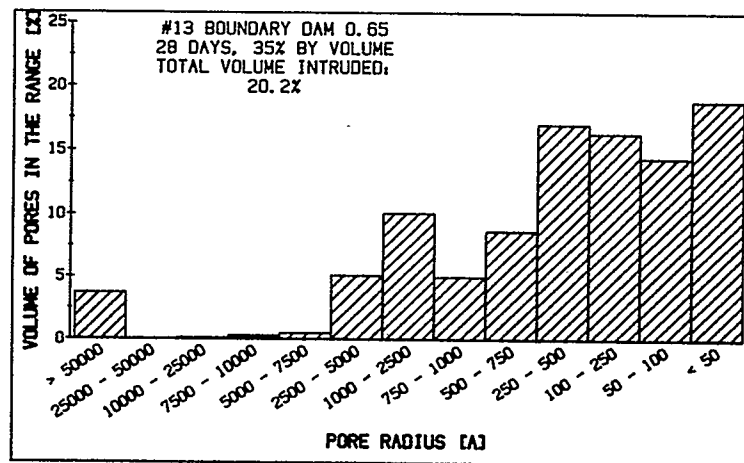


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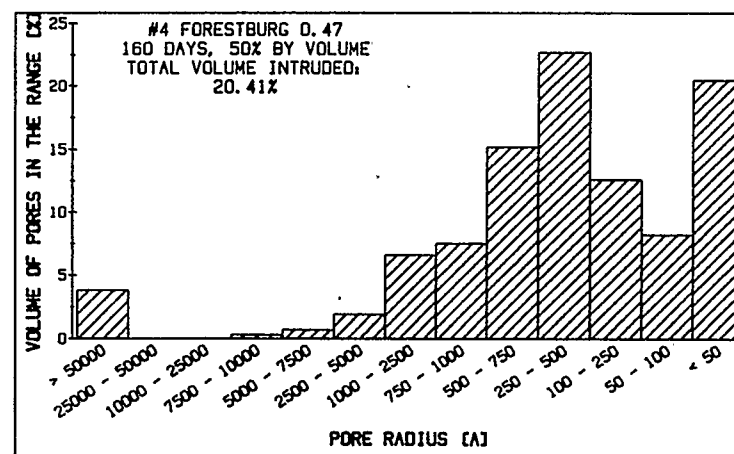
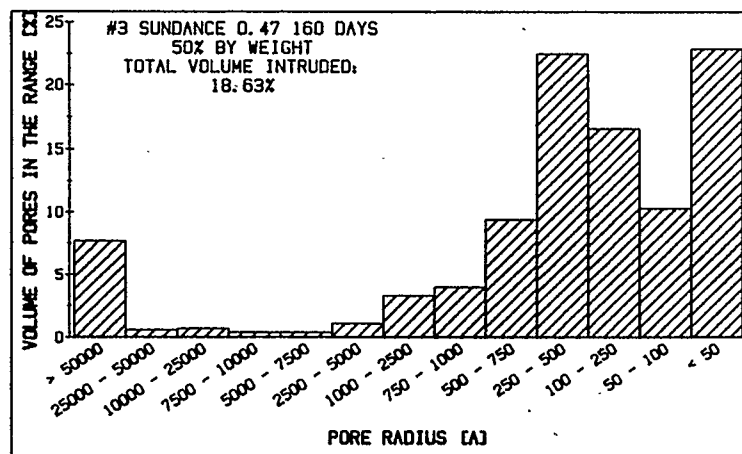
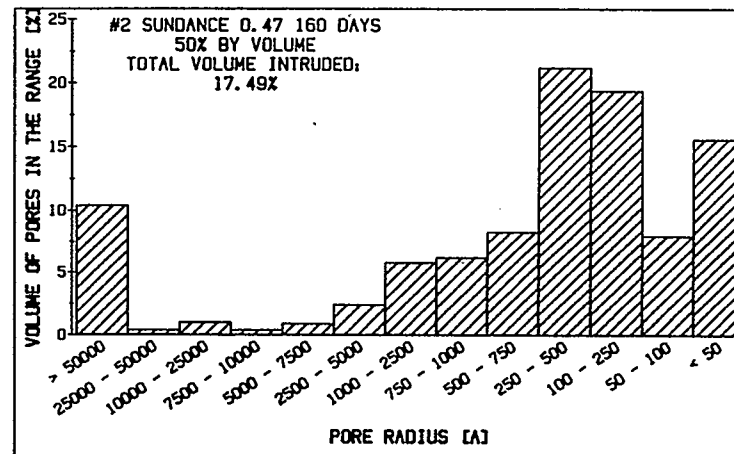
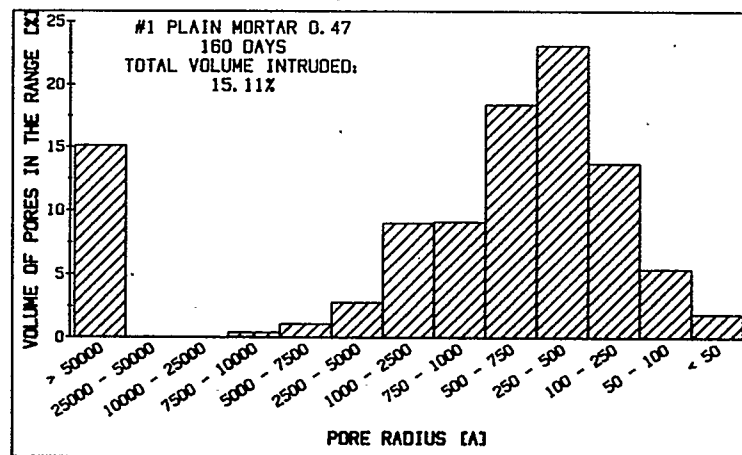


Fig. 6.9 Pore size distribution of mortars at the age of 160 days

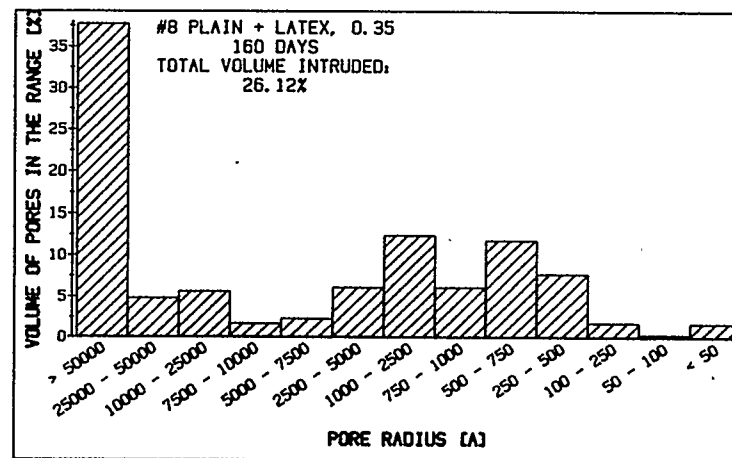
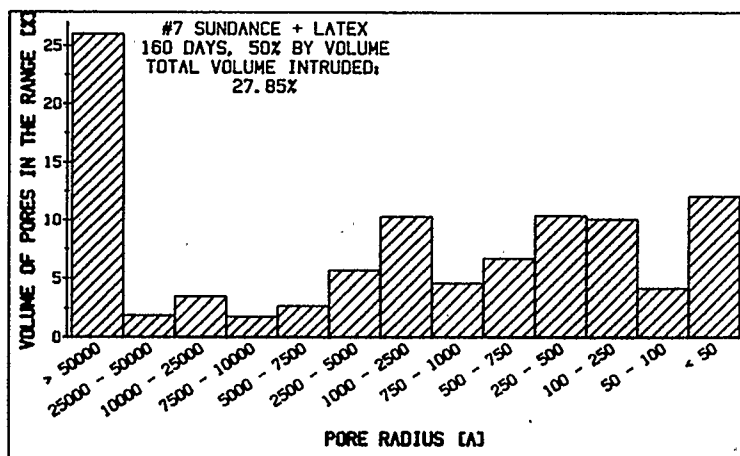
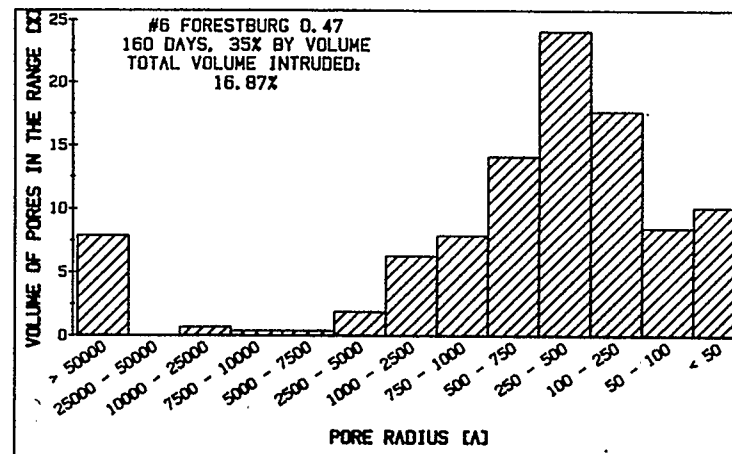
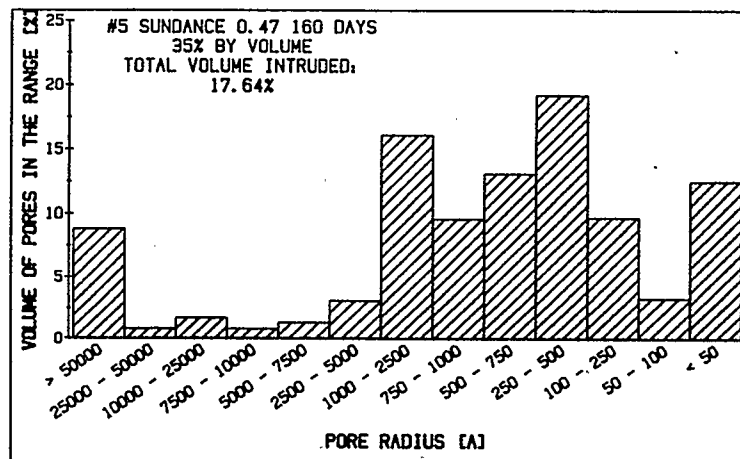


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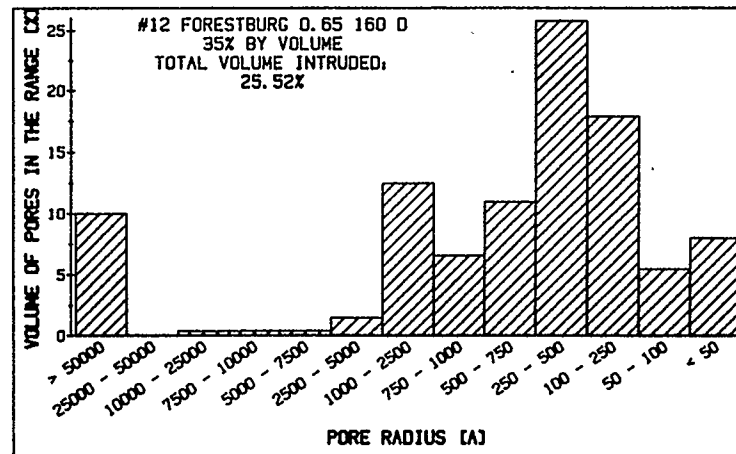
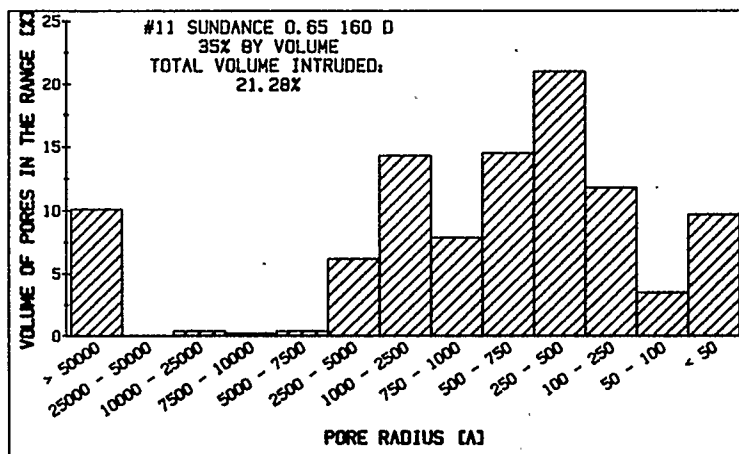
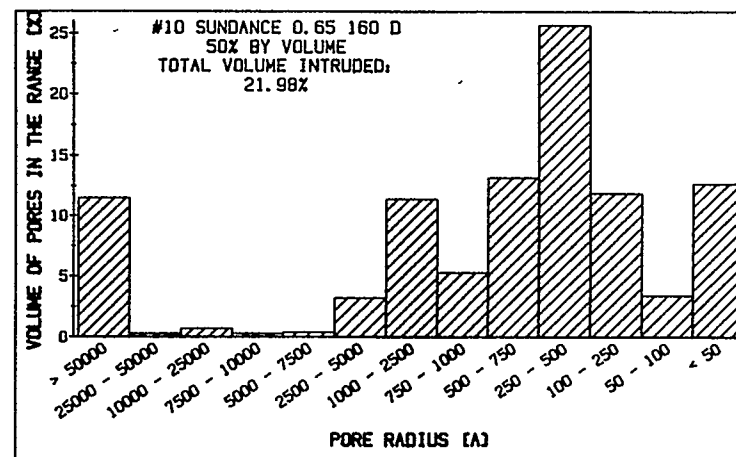
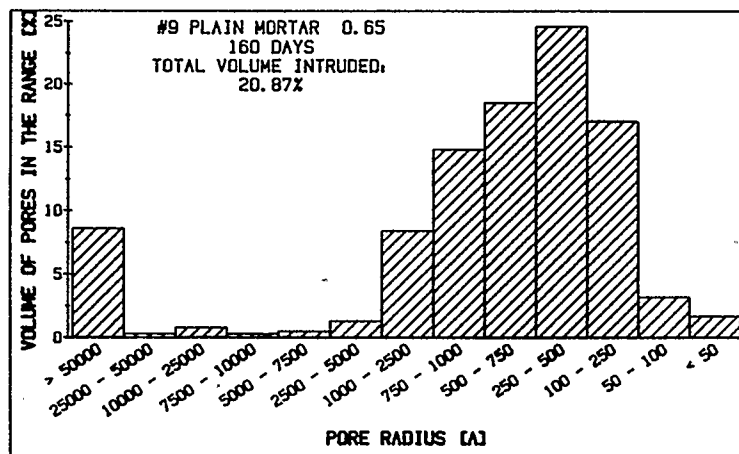


Fig. 6.9 (continued)

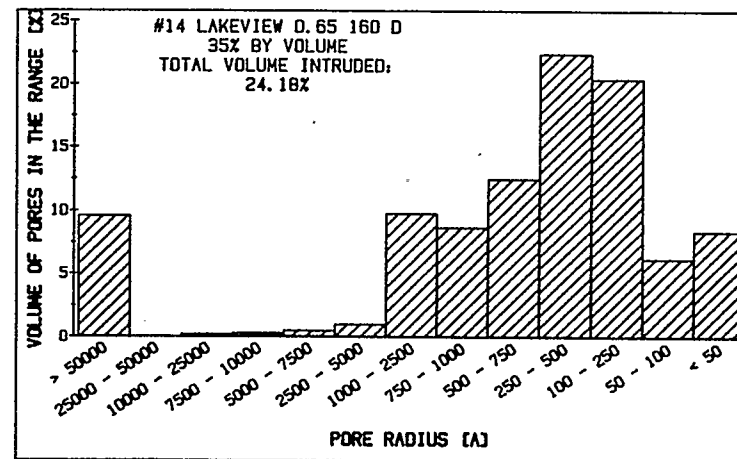
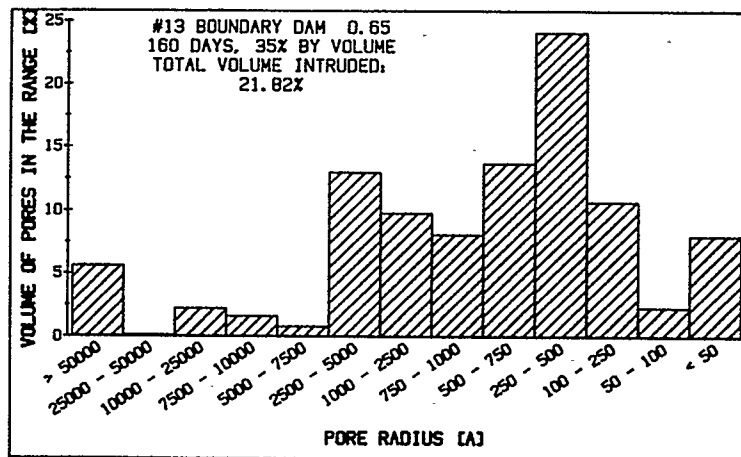


Fig. 6.9 (continued)

pore structure is also changing during this period of time. The CH content did not alter notably between 120 and 160 days, so that it is reasonable to expect that most changes in microstructure have occurred by the age of 160 days. On this account, the effects of variables employed in this work on pore size distribution will be discussed at the age of 160 days only.

6.3.3 The Effect of Replacement Levels on Pore Size Distribution

a) Mortars with Water-Cement Ratio 0.47

Figure 6.9 shows that the mortar #3 (SUN-0.47-50W) with the highest replacement level contains the highest volume of pores in the finest pore size range $< 5 \text{ nm}$ ($50 \text{ \AA}$). The volume of pores in the finest pore size range is smaller for mortars with 50% by volume replacement followed by those with 35% replacement by volume. The lowest volume of the finest pores was observed in control mortar #1 (PLAIN-0.47). The control mortar #1 displayed also the largest volume of pores in the range $> 5000 \text{ nm}$ ($50\,000 \text{ \AA}$).

b) Mortars with Water-Cement Ratio 0.65

As in the case of specimens with $w/c = 0.47$ similar trends resulting from the different replacement levels were observed for mortars within this group. Mortar #10 (SUN-0.65-50V) with the highest replacement level of cement by fly ash displays the largest volume of pores in the fine pore size range $< 5 \text{ nm}$ ($50 \text{ \AA}$). Here, the control mortar #9 (PLAIN-0.65) has only a small volume of pores in the same fine pore size range.

It was noted that the volumes of large pores in the pore size range $> 5000 \text{ nm}$ ($50\,000 \text{ \AA}$) were not reduced by the pozzolanic reaction for most blended mortars within this group as it was in the case of

mortars with $w/c = 0.47$.

c) Mortars with Latex Modifier

The presence of latex significantly affected the pore size distribution of both plain and blended mortars. From the comparison of mortars #8 (PLAIN-0.35+LATEX) and #1 (PLAIN-0.47), it follows that in the latex modified mortar the volume of pores in the pore size range of 5-250 nm ($50-2500 \text{ \AA}$) was reduced and the volume of pores of radii larger than 500 nm ($5000 \text{ \AA}$) was increased. Latex has an opposite effect on pore structure than the pozzolanic reaction. The coarsening of the pore structure, caused by latex, was partially offset in mortar #7 (SUN-0.35-50V+LATEX) by the pozzolanic reaction where an increase in volume of fine pores of radii $< 50 \text{ nm}$ ($500 \text{ \AA}$) and a decrease in volume of pores of radii larger than 2500 nm ($25\ 000 \text{ \AA}$) was detected.

The coarsening effect of latex on pore structure is also clear from comparison of blended mortars #2 (SUN-0.47-50V) and #7 (SUN-0.35-50V+LATEX). The volume of pores of radii $< 50 \text{ nm}$ ($500 \text{ \AA}$) was reduced and the volume of pores of radii $> 500 \text{ nm}$ ($5000 \text{ \AA}$) was substantially increased in latex mortar #7.

Since increased water-cement ratio in mortars is accompanied by increased capillary porosity (Mehta and Manmohan, 1980), the mortar with $w/c = 0.35$, if no latex were present, would show lower capillary porosity than those with w/c ratio of 0.47. Therefore, the coarsening effect of Latex Modifier would be even more profound for mortars with $w/c > 0.35$.

It is concluded that the presence of Latex Modifier in mortars results in coarser pore structure with a significant increase in

volume of pores of radii $r > 5000 \text{ nm}$ ($50,000 \text{ \AA}$).

6.4 Threshold Pore Radius and Maximum Continuous Pore Radius

Typical intrusion curves from mercury porosimetry for plain and blended mortars are shown in Figure 6.10. The intrusion of mercury into both plain mortars (with $w/c = 0.47$ and 0.65) and blended mortars with $w/c = 0.47$ increased steadily once significant intrusion began. The pore size where the intrusion started is denoted as the threshold radius (TR). In blended mortars with $w/c = 0.65$ the curves show two step intrusion or an intermediate plateau. Here the threshold pore radius was defined as the pore radius where the more significant intrusion developed and after which the intrusion continuously increased.

The maximum continuous pore radius (MCPR) corresponds to the pore size radius where dV/dP displays the highest value. Figure 6.10 also explains the graphical technique employed for the determination of TR and MCPR. These two microstructural parameters were determined for the purpose of correlation with engineering properties as presented in Chapter 7.

6.5 Significance of Inclusion of Low Pressure Porosimetry for Latex Mortars

Figures 6.11 and 6.12 show total porosities, as determined by the mercury porosimetry, with and without the inclusion of low pressure porosimetry. The low pressure apparatus enables one to determine the volume of pores of radii up to $70 \text{ }\mu\text{m}$ ($700\,000 \text{ \AA}$).

Significant differences between porosities which included the volume of large pores and those which did not were observed for latex mortars, especially at the age of 160 days. The differences for

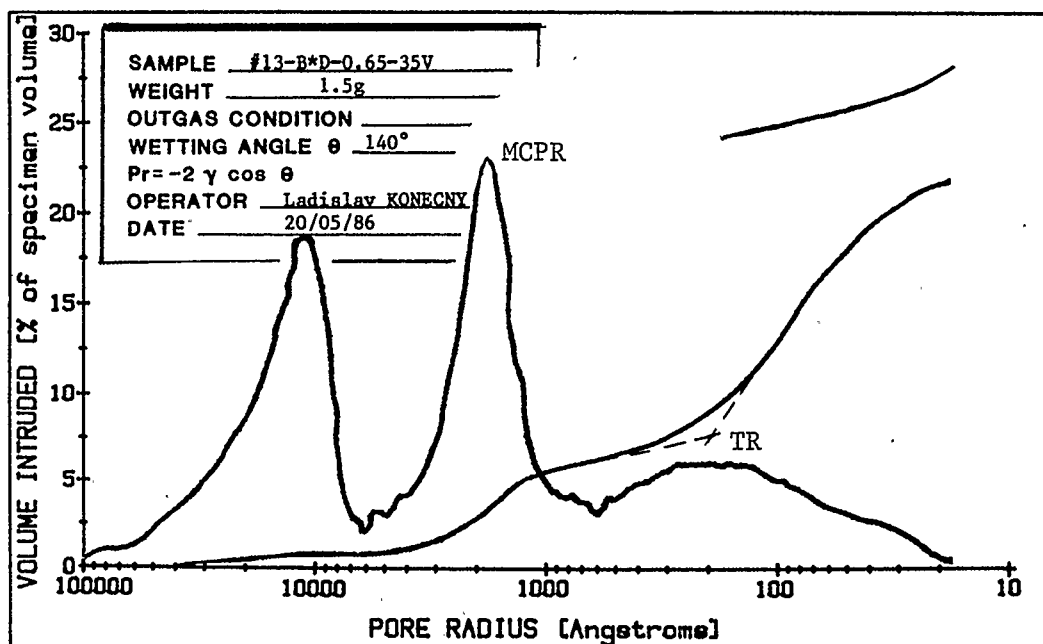
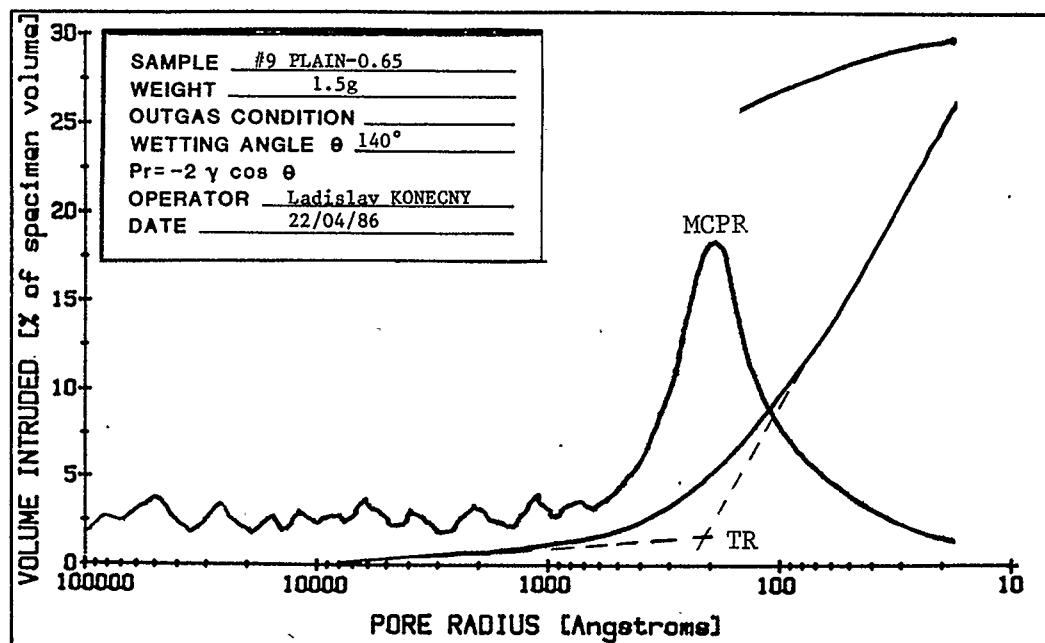


Fig. 6.10 Typical mercury intrusion curves for plain and blended mortars

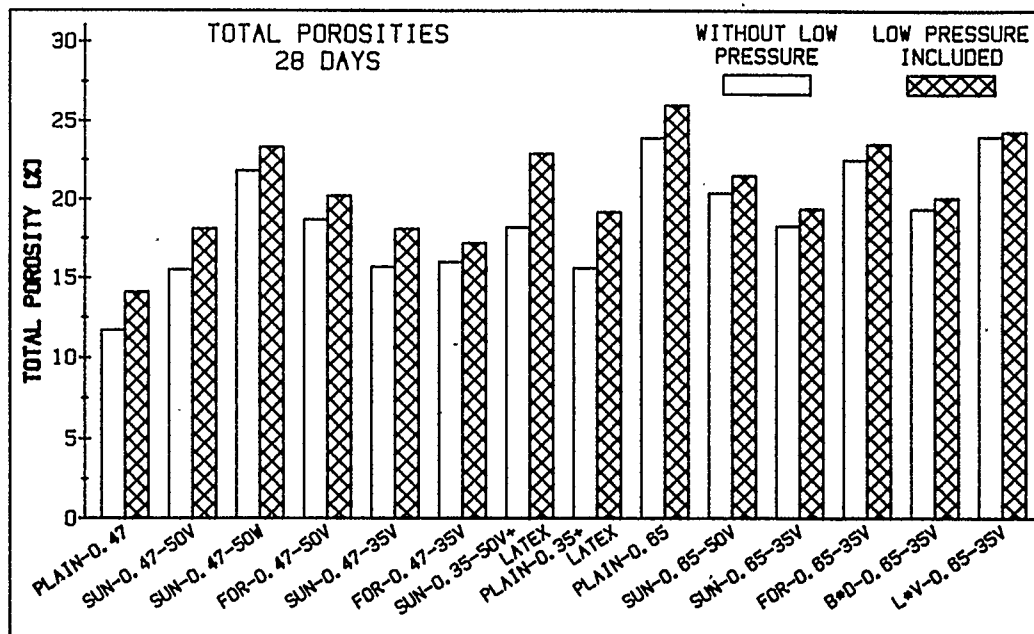


Fig. 6.11 Total porosities of mortars at the age of 28 days (with and without low pressure porosimetry)

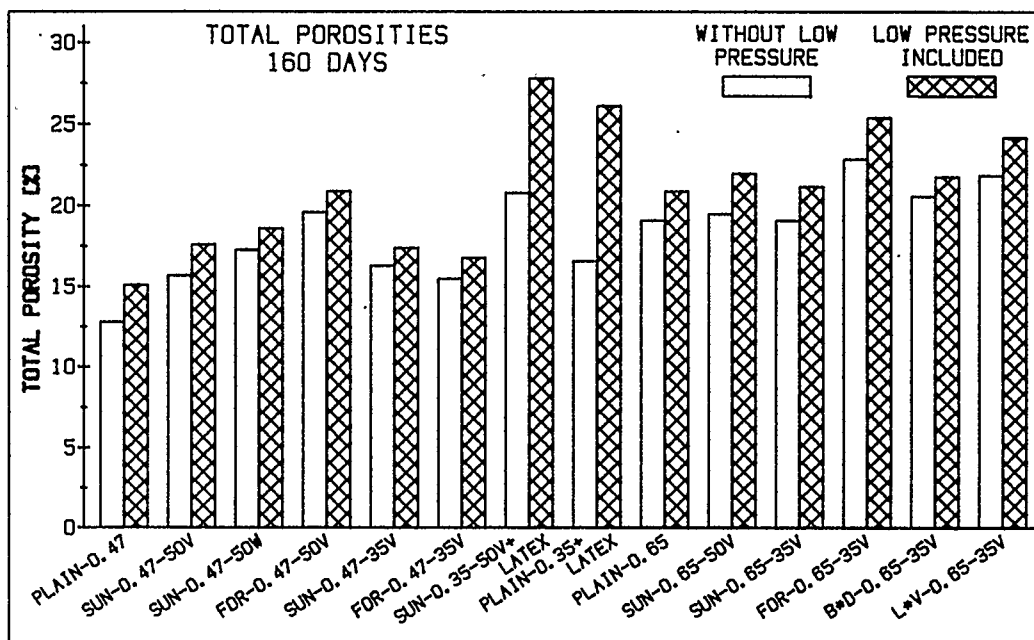


Fig. 6.12 Total porosities of mortars at the age of 160 days (with and without low pressure porosimetry)

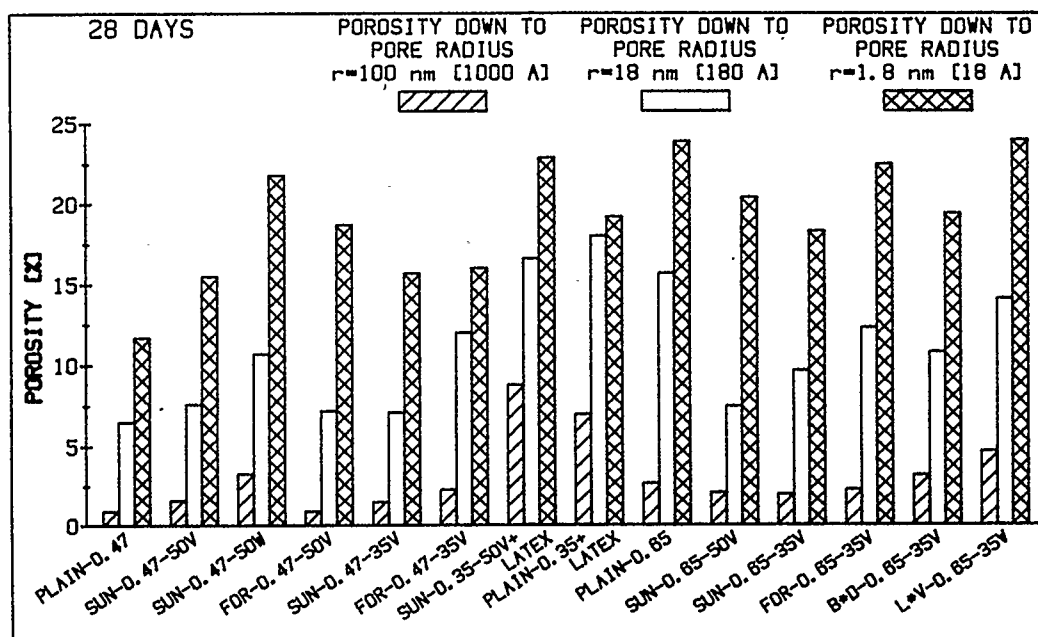


Fig. 6.13 Porosities down to certain pore radii at the age of 28 days

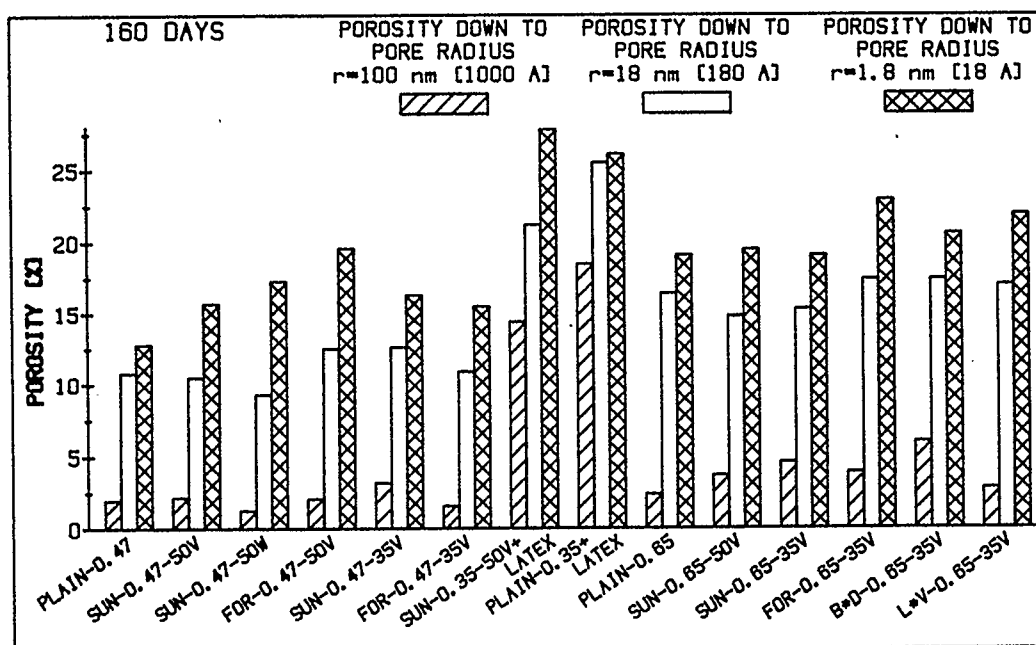


Fig. 6.14 Porosities down to certain pore radii at the age of 160 days

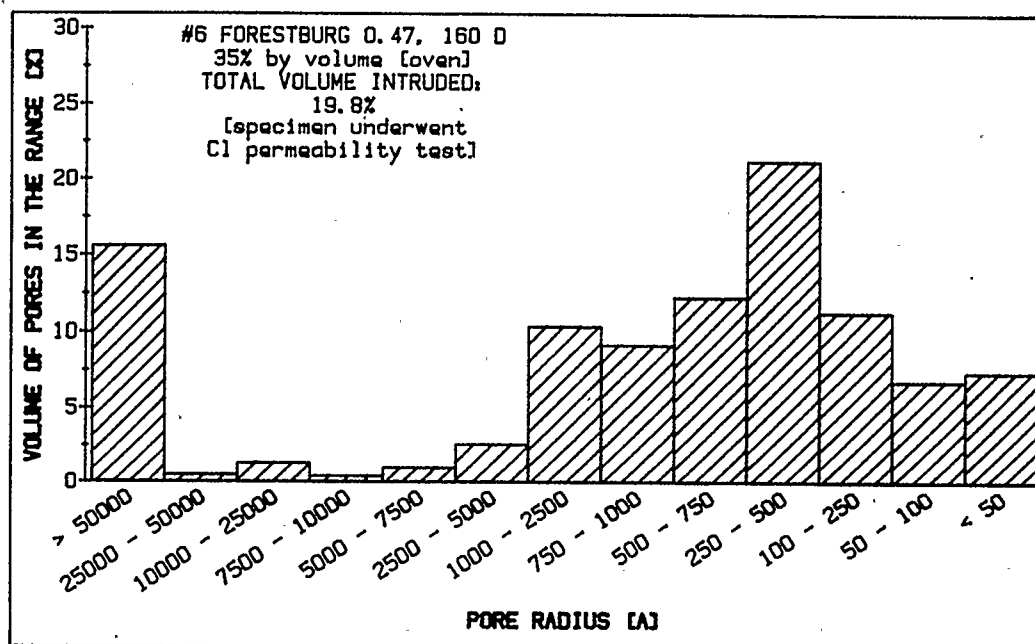
mortars without Latex Modifier were much smaller and were approximately the same for all mixes. The average value of the difference between porosities with and without these very large pores was 8% for blended mortars with $w/c = 0.47$, 10% for blended mortars with $w/c = 0.65$, and 34 and 57% for blended and plain mortars with latex.

Figures 6.13 and 6.14 display porosities down to pore radii $r = 100 \text{ nm}$ ($1000 \text{ \AA}$), $r = 18 \text{ nm}$ ($180 \text{ \AA}$) and $r = 1.8 \text{ nm}$ ($18 \text{ \AA}$) of all examined mortars as determined for the purpose of correlation with engineering properties. In latex mortars the volumes of large pores are included in these porosities. It will be shown in Chapter 7 that strength relates closely to the total porosity and thus low-pressure porosimetry results should be included.

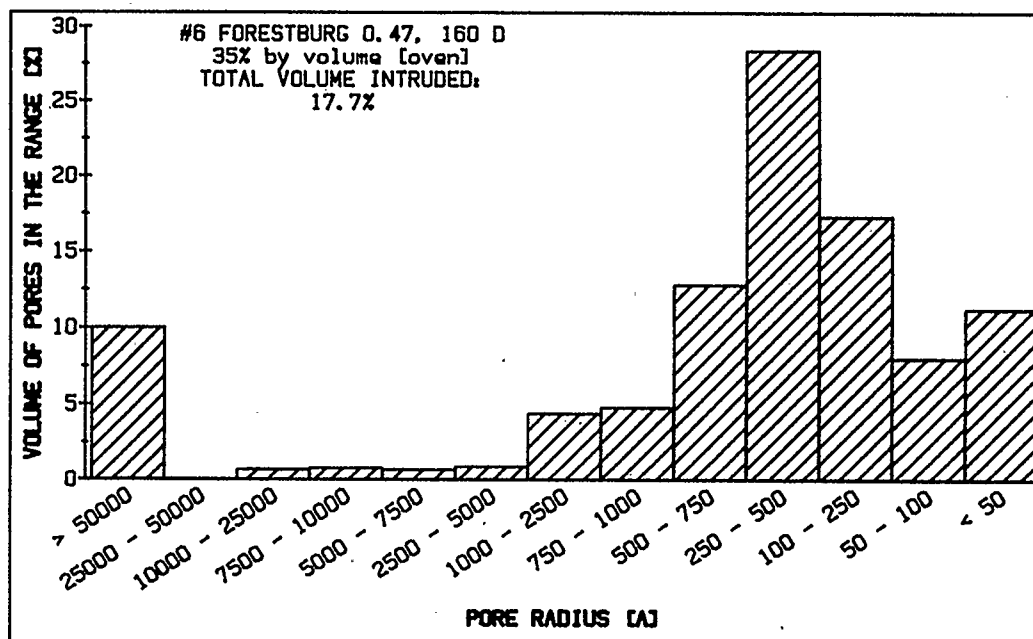
6.6 Other Microstructural Observations

It is reported by various workers (Richartz, 1969; Calleja, 1980; Midgley and Illston, 1984) that permeating chloride ions react with tricalcium aluminate (C_3A) left in unhydrated cement to form calcium monochloraluminate hydrate ($C_3A \cdot CaCl_2 \cdot 10H_2O$). Midgley and Illston (1984) also reported from mercury intrusion porosimetry results that chloride ion penetration into hardened cement paste (hcp) altered the pore size distribution; more pores in a finer pore size region were found. The total porosity did not show significant changes. Since a larger volume of smaller pores was present at comparable porosities, the permeability will be reduced.

The pore size distributions of two identical mortars examined in this work, one of them tested for chloride permeability, are shown in Figure 6.15. A coarser pore structure is observed for the specimen



a)



b)

Fig. 6.15 Pore size distribution of mortar (a) tested for Cl-permeability; (b) not tested for Cl-permeability

which underwent the Cl^- -permeability test.

X-ray diffraction was employed to confirm the presence of $\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ in the cement matrix; however, no trace of this mineral was detected.

Because the test is so rapid, the applied voltage cell test does not take into account the beneficial effect of reaction between C_3A and chloride ions (formation of calcium monochloraluminate hydrate and subsequent pore refinement) which may develop over a longer period of time. Therefore, the resistivity technique for the determination of chloride permeability simulates more severe conditions, especially in mixes without any ash replacement (blended mortars contain less cement; therefore, less C_3A is available for the reaction with the Cl^- -ion).

6.7 Conclusions

1. The pozzolanic reaction started as early as 7 to 28 days. Significant changes in CH content were recorded up to 120 days of age.
2. The two different water-cement ratios employed in mortars without latex (0.47 and 0.65) did not affect CH content values.
3. The higher the replacement of cement by fly ash (up to 50% by weight) the lower was the CH content in blended mortars.
4. The thermogravimetric technique involving dehydration of CH, can not be utilized for the assessment of CH content in latex mortars.
5. The solvent replacement technique preserves the original pore structure better than direct oven drying.
6. The pozzolanic reaction between CH and fly ash results in a finer

pore size distribution; the higher the replacement (up to 50% by weight) the higher the refinement of pore structure of the blended mortar.

7. The presence of latex in mortars has an opposite effect on the pore size distribution than the pozzolanic reaction; it results in a coarser pore structure with a significant increase of volume of pores in radii $> 5\ 000\ \text{nm}$ ($50\ 000\ \text{\AA}$).
8. Inclusion of low pressure porosimetry (vacuum to ambient pressure) yields a better indication of the pore size distribution of latex mortars.
9. The resistivity technique employed for the evaluation of chloride permeability does not take into account the beneficial effect of reaction between C_3A and chloride ions resulting in calcium mono-chloraluminate hydrate.

CHAPTER SEVEN

RELATIONSHIP BETWEEN ENGINEERING PROPERTIES AND MICROSTRUCTURAL CHARACTERISTICS

7.1 Introduction

Regression analyses were performed to see if correlations exist between engineering properties (i.e. compressive strength, water, oxygen and chloride permeabilities) and microstructural characteristics. From microstructural tests the following parameters were defined: total porosity, porosities down to a certain pore size, threshold radius, volume intruded at the threshold radius, maximum continuous pore radius and volume intruded at the maximum continuous pore radius. The definitions of the threshold and maximum continuous pore radii and the graphical techniques employed for their determination are presented in Chapter 6.

From other microstructural characteristics, calcium hydroxide content was correlated with engineering properties. The relationship between water permeability and specific surface, as investigated by Nyame and Illston (1981), was also examined. It was found that good correlations exist for most of the relationships between engineering properties and microstructural characteristics but for 160-days data only. For 28 days and combined 28 and 160-days data, the correlation coefficients were below the acceptable value which is $r = 0.632$ for the 95% confidence level.

7.2 Relationship between Compressive Strength and Porosity

Correlation of porosity with compressive strength has been investigated by many workers. The relationship was expressed by semi-empirical equations. For example:

$$\text{Bakshin} \quad \sigma = \sigma_0 (1 - P)^A \quad (7.1)$$

$$\text{Ryshkewitch} \quad \sigma = \sigma_0 \exp (-B \cdot P) \quad (7.2)$$

$$\text{Schiller} \quad \sigma = D \ln \frac{\sigma_0}{P} \quad (7.3)$$

$$\text{Tashiro \& Urashima} \quad \sigma = \sigma_0 + C \cdot P \quad (7.4)$$

where σ_0 is the compressive strength at zero porosity, P is the porosity and σ is the strength at porosity P . A , B , C and D are experimentally determined constants. Generally, all equations show good agreement with the experimental values; equation 7.2 shows good agreement at lower porosities and equation 7.3 at higher porosities.

Jambor (1973) reported that the strength is controlled not only by porosity but is related to the pore size distribution as well. In addition, strength may also be related to the type of bonding within the material, density, stress concentrations around pores, inhomogeneities due to applied stress and the duration of application of the imposed load (Ramachandran et al., 1981).

Obviously, it is difficult to include all these parameters. The agreement of experimental data to the relationships in equations 7.1 to 7.4 (Schiller, 1971; Roy and Gouda, 1973; Feldman and Beaudoin, 1976; and Tashiro and Urashima, 1984) show that an acceptable prediction of strength can be obtained from porosity.

Table 7.1 shows, among others, correlation coefficients between compressive strength and porosities down to 100 nm (1000 Å), 18 nm (180 Å) and total porosity as determined for the mortars examined in this work. The only significant correlation exists for the relationship between strength and total porosity (see Figure 7.1). The observation from this work leads to the conclusion that the compres-

Table 7.1 Correlation Coefficients for Relationships
between Engineering Properties and
Microstructural Characteristics

Volume Intruded at 100 nm (1000 Å)	
vs. Water Permeability	-0.771
Oxygen Permeability	-0.740
Chloride Permeability	0.668
Compressive Strength	-0.013
Volume Intruded at 18 nm (180 Å)	
vs. Water Permeability	-0.880
Oxygen Permeability	-0.882
Chloride Permeability	0.849
Compressive Strength	-0.394
Volume Intruded at 1.8 nm (18 Å) - i.e. Total Porosity	
vs. Water Permeability	-0.761
Oxygen Permeability	-0.606
Chloride Permeability	0.749
Compressive Strength	-0.688

Table 7.2 Correlation Coefficients for Relationships
between Permeabilities and other Micro-
structural Characteristics

Threshold Radius	
vs. Water Permeability	-0.616
Oxygen Permeability	-0.691
Chloride Permeability	0.641
Volume Intruded at the Threshold Radius	
vs. Water Permeability	-0.714
Oxygen Permeability	-0.675
Chloride Permeability	0.590
Maximum Continuous Pore Radius	
vs. Water Permeability	-0.609
Oxygen Permeability	-0.660
Chloride Permeability	0.666
Volume Intruded at the Maximum Continuous Pore Radius	
vs. Water Permeability	-0.392
Oxygen Permeability	-0.296
Chloride Permeability	0.396

sive strength depends on the total porosity and not on the volume of large pores only, contrary to the results of Roßler and Odler (1985). The present observation is in agreement with that of Lawrence et al., (1977). They reported that many studies show the strength development of hydrated Portland cement paste to be dependent on the total porosity and that changes in the microstructure of specimens, as observed by microscopy, do not influence strength significantly.

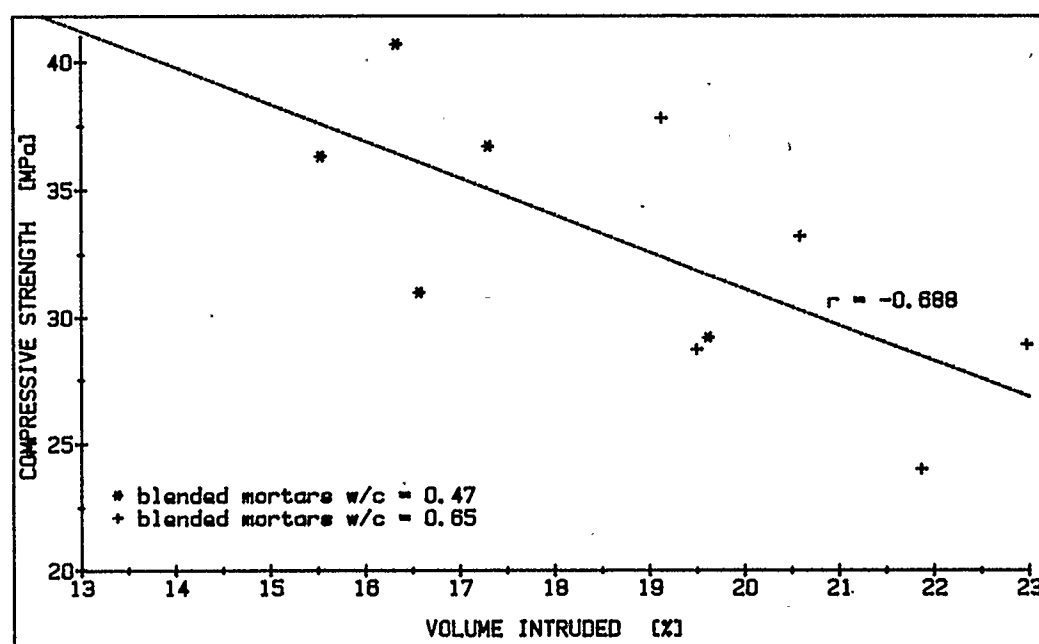


Figure 7.1 Relationship between total porosity and compressive strength

7.3 Relationship between Water, Oxygen and Chloride Permeabilities and Pore Size Distribution

The correlation coefficients in Table 7.1 display highest values for all three permeabilities determined in this work, when correlated with the porosities down to 18 nm (180 Å). The relationships are presented in Figures 7.2, 7.3 and 7.4. The correlation coefficients

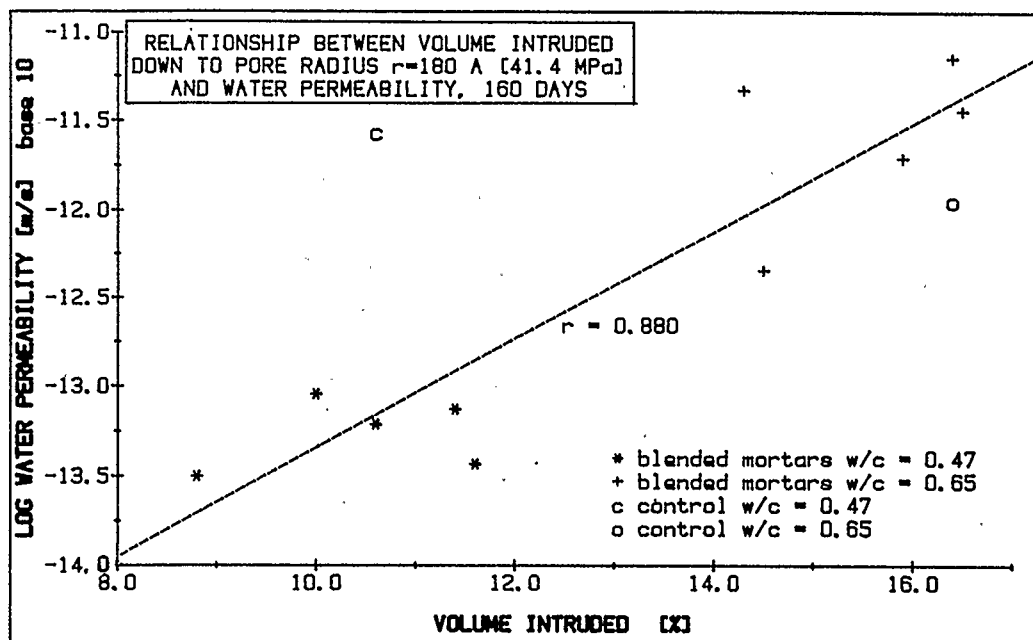


Fig. 7.2 Relationship between volume of pores larger than 18 nm and water permeability

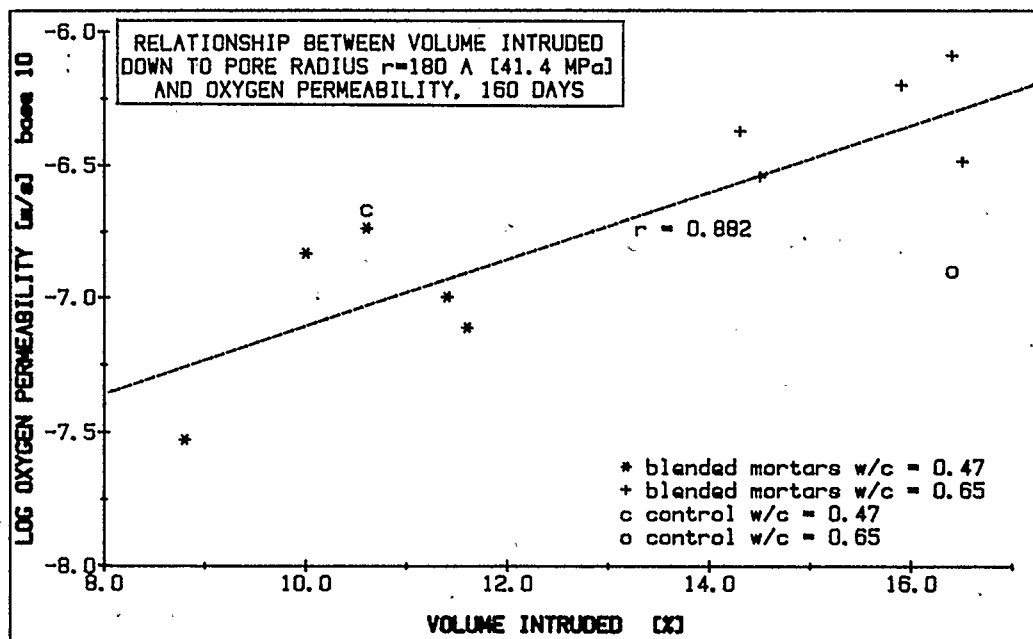


Fig. 7.3 Relationship between volume of pores larger than 18 nm and oxygen permeability

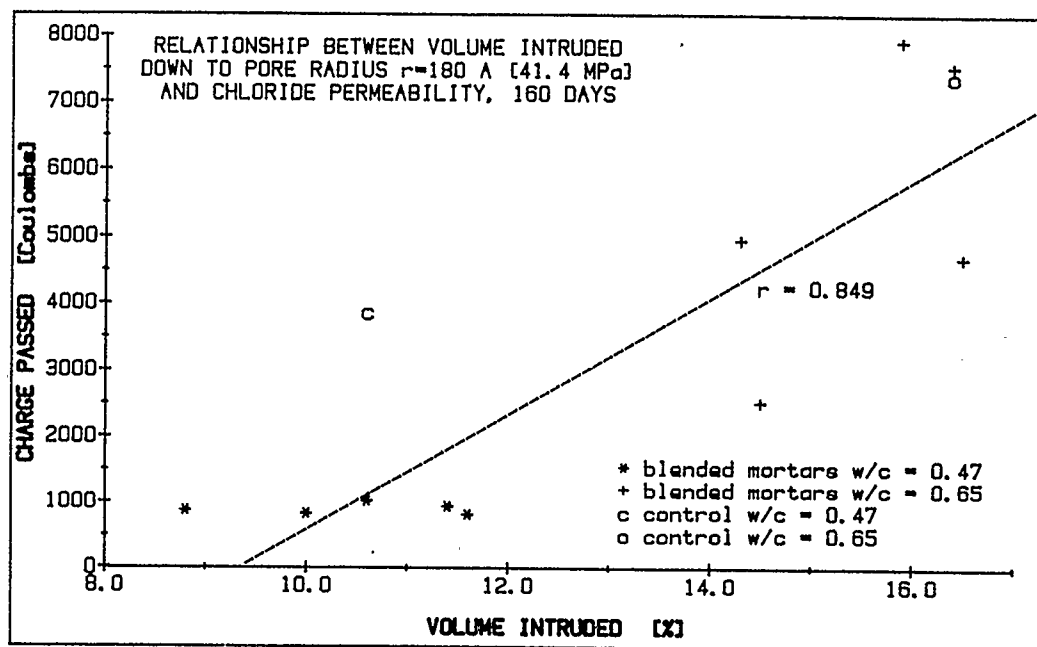


Fig. 7.4 Relationship between volume of pores larger than 18 nm and water permeability

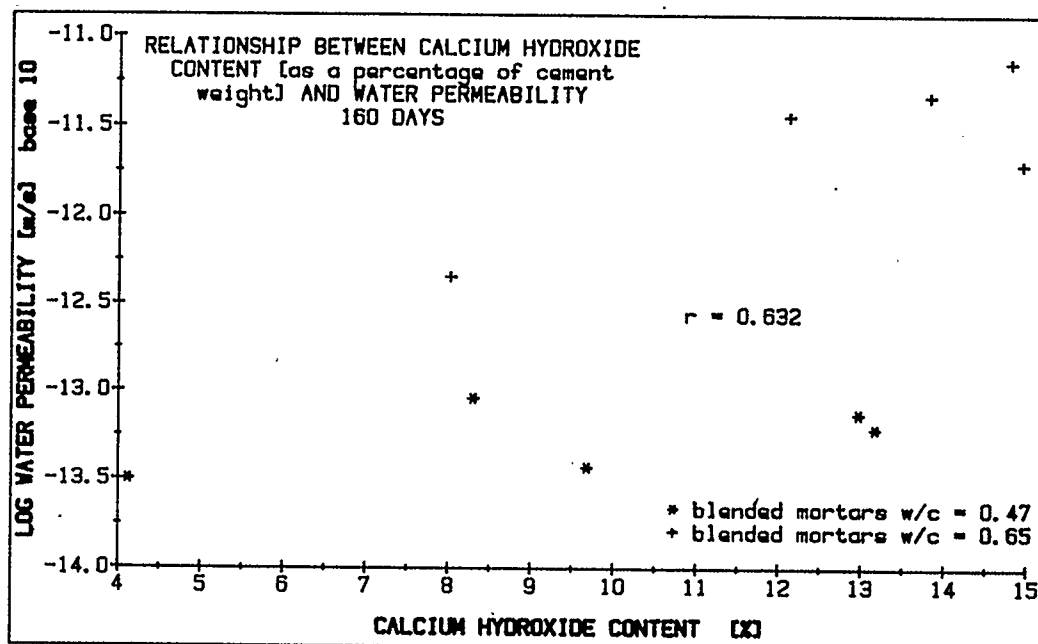


Fig. 7.5 Relationship between calcium hydroxide content and water permeability

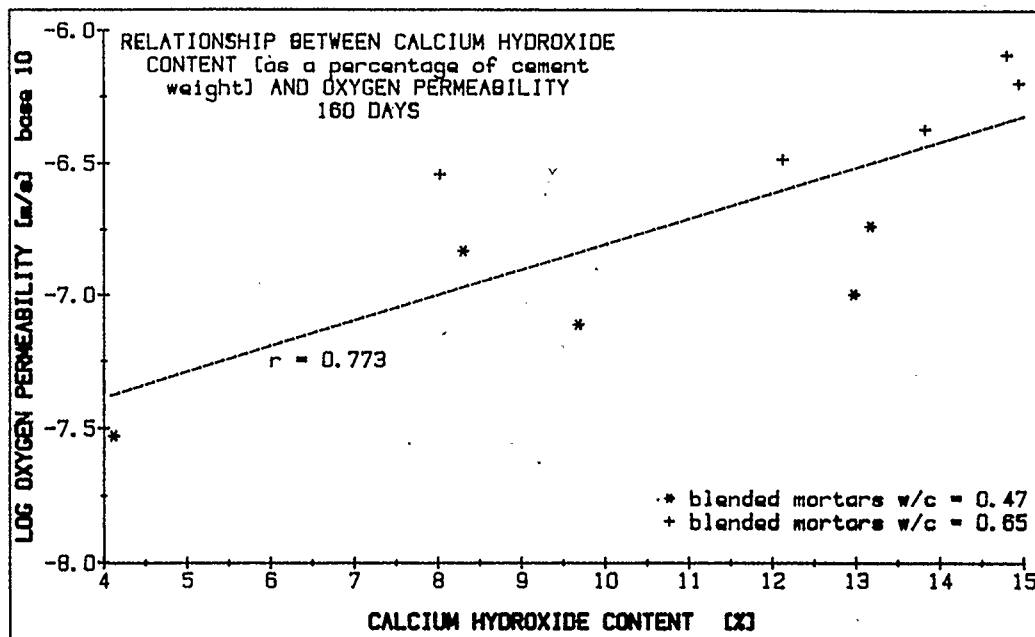


Fig. 7.6 Relationship between calcium hydroxide content and oxygen permeability

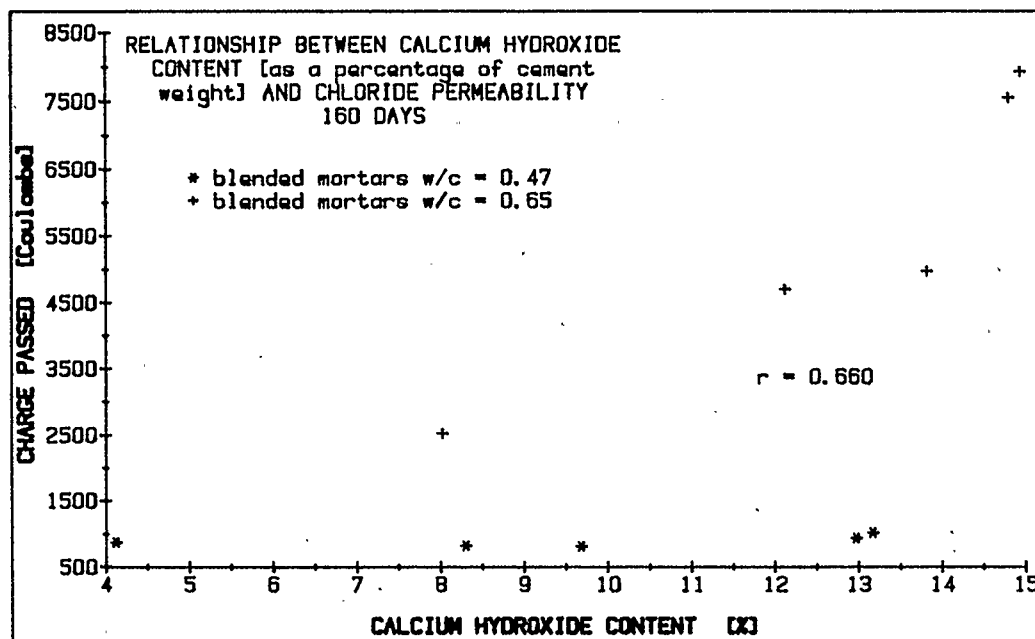


Fig. 7.7 Relationship between calcium hydroxide content and chloride permeability

for relationships between permeabilities and porosity down to 100 nm (1000 Å) or total porosity are lower.

From the regression analysis, it follows that the permeability of a mortar is not a simple function of its total porosity but depends mainly on the pore size distribution. Mortar which contains capillary porosity is more permeable than a mortar with the same total porosity but with higher proportion of gel pores and thus lower capillary porosity. Since only limited flow occurs in gel pores (see Chapters 2 and 6), it is clear that the main parameter which controls the permeability is capillary pores.

Microstructural characteristics such as threshold radius, maximum continuous pore radius and volumes intruded down to these pore radii (see Section 6.1) were also correlated with permeabilities. The values of the correlation coefficients are shown in Table 7.2. Generally, threshold radius (TR), volume intruded at the threshold radius (VTR) and maximum continuous pore radius (MCPR) correlated well with some permeabilities determined in this work. The value of correlation coefficient at the 95% confidence level should be $r \geq 0.632$ and, as shown in Table 7.2 for some relationships, the correlation coefficients are lower.

7.4 Correlation between Engineering Properties and Calcium Hydroxide Content

Relationships between calcium hydroxide content in blended mortars and water, oxygen and chloride permeabilities are presented in Figures 7.5, 7.6 and 7.7. Generally, as CH content decreases, C-S-H formed by the pozzolanic reaction fills and blocks large pores (on which permeability mainly depends) and thus the mortar becomes more

impermeable. Correlation is good for these relationships.

No correlation at the 95% significance level was found for the relationship between CH content and compressive strength.

7.5 Correlation between Water Permeability and Specific Surface

Nyame and Illston (1981) examined the relationship between water permeability and surface area of hardened cement paste. Specimens were oven dried and surface values were obtained from the mercury intrusion porosimetry examination of pores down to 3.7 nm ($37 \text{ \AA}$) radius. They observed that the water permeability at a given age increased with increasing surface area (see Figure 7.8).

In the present work, however, opposite results were obtained, i.e. water permeability decreased as specific surface increased. Figures 7.9 and 7.10 show the relationships for examined mortars in this work at the ages of 28 and 160 days respectively. As in the work of Nyame and Illston the specimens for these correlations were oven dried.

Although good correlations were obtained for the relationships between specific surface and water permeability, there are doubts whether the surface area values from mercury intrusion porosimetry, especially for oven dried blended mortars, represent the actual state. It was observed in this work that the specific surface values for oven dried specimens varied significantly (in some cases by 100% or more) from those for solvent replaced specimens. In Chapter 6, it was shown that the solvent replacement technique better preserves the specimen's microstructure than does oven drying. Therefore, the specific surface values from solvent replaced specimens, as determined by mercury porosimetry, will likely yield a better indication about the surface area. Nevertheless, it is the author's opinion that because of

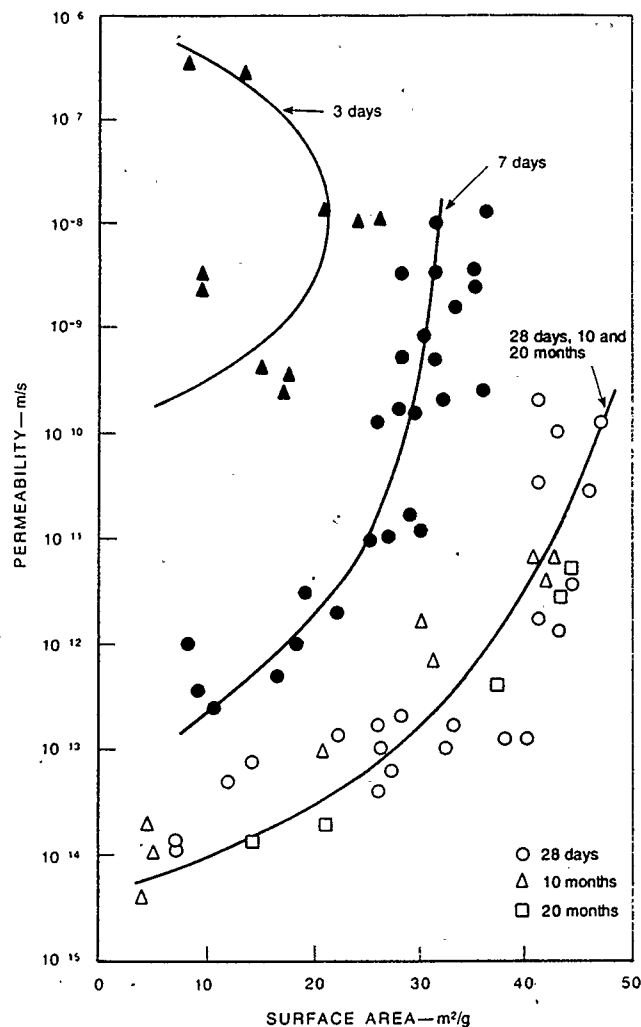


Figure 7.8 Relationship between water permeability and surface area of pores down to pore radius $r = 3.7 \text{ nm}$ (37 Å) (From Nyame & Illston, (1981))

considerable damage to the pore structure caused by mercury intrusion (see Chapter 4), mercury intrusion porosimetry is not the most suitable technique for the determination of specific surface.

7.6 Conclusions

The conclusions based upon the results of Chapter 7 are as follows:

1. Compressive strength depends on the total porosity. No

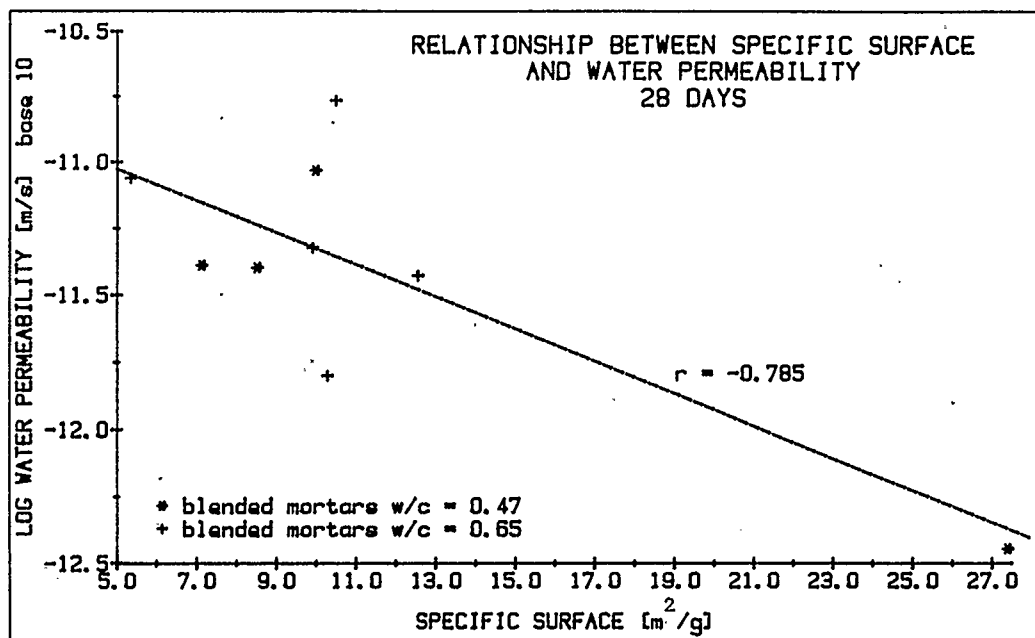


Fig. 7.9 Relationship between water permeability and surface area at the age of 28 days

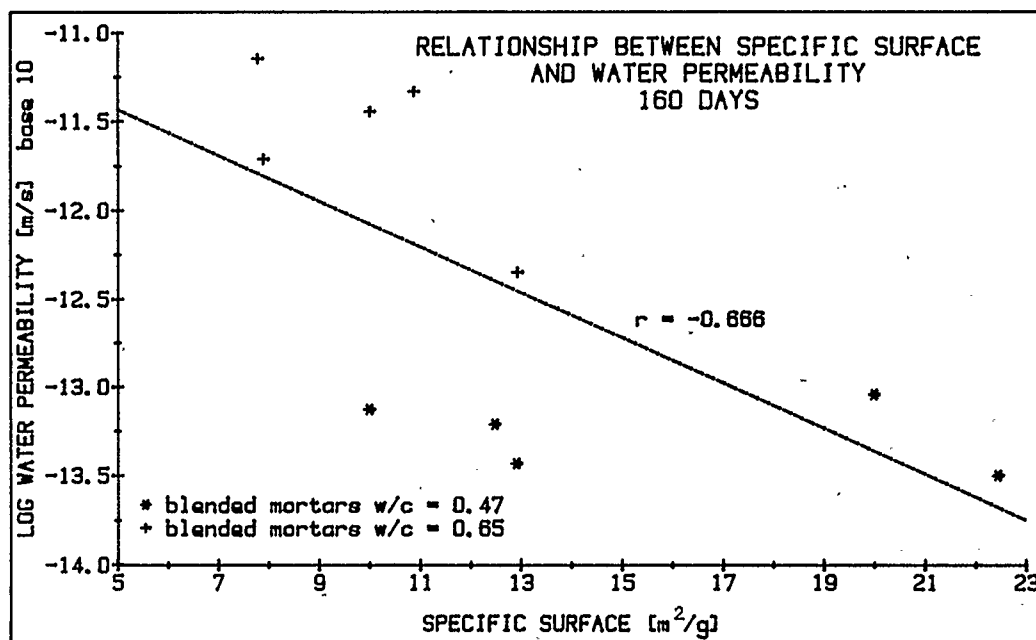


Fig. 7.10 Relationship between water permeability and surface area at the age of 160 days

correlations were observed for relationships between compressive strength and volumes of pores larger than 18 nm ($180 \text{ \AA}$) and 100 nm ($1000 \text{ \AA}$).

2. All permeabilities (i.e. water, oxygen and chloride) correlated best with the volume of pores down to 18 nm ($180 \text{ \AA}$).
3. Threshold radius, volume intruded at the threshold radius and maximum continuous pore radius are other microstructural characteristics from which an indication about permeability might be obtained; however, the correlations are not as significant, as mentioned in (2) above (see Table 7.1).
4. No correlations exist between volume intruded at maximum continuous pore radii and permeabilities.
5. Permeabilities of blended mortars decrease with CH content, i.e. as the pozzolanic reaction proceeds with age.
6. It was observed that the higher the surface area the greater the resistance to flow and therefore the lower the water permeability.

CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATION FOR FURTHER WORK

8.1 Conclusions

The following conclusions are drawn from this research project.

8.1.1 Engineering Properties

1. The compressive strength values of some blended mortars, although lower at early ages, were similar to or higher than those of plain mortars at the age of 160 days.
2. Mortars with latex modifier had only 50% of the strength of comparable mortars without latex. The lower strength of latex mortars partially resulted from the air-entraining property of latex modifier. The latex acting as an inner sealant may slow down or hinder pozzolanic and hydration reactions.
3. At the age of 160 days much lower water, oxygen and chloride permeabilities were observed for blended mortars with a water-cement ratio of 0.47 than for control mortars with the same w/c ratio. The permeabilities of blended mortars were generally higher than those of the control mix at earlier ages of 7 and 28 days.
4. Mortars containing latex displayed relatively high water and oxygen permeabilities; nevertheless, the same latex mortars showed the highest resistance to penetration by Cl⁻ ions.
5. The higher the replacement level of cement by fly ash, the lower was the permeabilities (water, oxygen and chloride) at later ages.

6. Mortars with a w/c ratio of 0.47 showed higher compressive strength and lower permeabilities than those with w/c = 0.65. Also, blended mortars with w/c = 0.65 did not benefit from the pozzolanic reaction as much as those with w/c = 0.47.
7. Good relationships exist between compressive strength and water permeability and between compressive strength and chloride permeability.

8.1.2 Microstructural Characteristics

1. The pore structure is better preserved by using the solvent replacement as a drying technique rather than by direct oven drying.
2. All mortars with partial cement replacement by fly ash show a finer pore size distribution than control mortars; the higher the replacement (up to 50% by weight) the more extensive the refinement. The finer pore size distribution of blended mortars results from the pozzolanic reaction between calcium hydroxide (CH) and fly ash.
3. The pozzolanic reaction started as early as 7 days. Increased rate of pozzolanic reaction was recorded mainly between 28 and 120 days of age.
4. Blended mortars with higher replacement level of cement by the fly ash displayed lower CH content (calculated as a percentage of cement weight).
5. The two water-cement ratios employed in mortars without latex did not affect CH content values.
6. Coarser pore size distributions (PSD) with a significant increase of volume of pores in radii $> 5000 \text{ nm}$ ($50\,000 \text{ \AA}$) were observed in

mortars with latex modifier. Therefore, latex has an opposite effect on the PSD than the pozzolanic reaction.

7. A rapid resistivity technique employed for the determination of chloride permeability is a severe test since it does not take into account the beneficial effect of the reaction between C_3A and Cl^- -ions which may develop over a longer period of time.

8.1.3 Relationship between Engineering Properties and Microstructural Characteristics

1. Compressive strength depends on the total porosity, i.e. volume of pores down to 1.8 nm (18 Å), as measured by mercury porosimetry.
2. The volume of pores larger than 18 nm (180 Å) correlated best with water, oxygen and chloride permeabilities.
3. Permeabilities of blended mortars decrease with the progress in pozzolanic reaction (i.e. as CH content decreases).

8.2 Recommendation for Further Research

Some suggestions concerning future tests are as follows:

1. The present study did not allow an in-depth investigation of such phenomenon as the extremely low permeability of latex mortars to chloride ions. Employment of other techniques (as recommended in Chapter 4) for the determination of CH content in latex mortars is required to support or reject the author's suggestions drawn from the permeability results of latex mortars in Chapter 5.
2. Further investigation of the air-entraining properties of latex modifiers.

3. The development of correction factors to use in bringing test results from mortars with various w/c ratios to a standard one (for example, 0.47).
4. Materials variables such as the effect of cement and fly ash composition on engineering properties need further study to be fully understood.
5. Development of an apparatus for field determination of permeabilities of existing structures.

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