Studies on the evaluation of permeability and corrosion resisting characteristics of Portland pozzolan concrete

Omar Saeed Baghabra Al-Amoudi

Civil Engineering

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Abstract

The aggressive service conditions of the Estern Saudi Arabia necessitate the production of quality concrete which is dense and impervious, so that it inhibits the penetration of chloride and sulfate salts which are uniquely effective in setting up corrosion of rebars and the chemical deterioration of hardened cement paste. Pozzolan is considered to be one of the potential admixtures which assists in the production of dense and impermeable concrete resulting in reduced sulfate attack and rebar corrosion.

This investigation was formulated to evaluate the effect of using pozzolan on the permeability, porosity and the general quality of concrete made with typical local aggregates consisting of finely graded beach/dune sands and crused limestone. The experimental program was designed to vary the pozzolan substitution from 0 to 40% and water cement ratio in the range of 0.35 to 0.55. The performance of pozzolans from four different sources was also evaluated.

The effects of hydration reaction of pozzolan on the properties of concrete was studied over a period of one year, by measuring water permeability, porosity, pulse-velocity and compressive strength. Accelerated corrosion tests were carried out in the laboratory to determine the effectiveness of pozzolan in inhibiting rebar corrosion. Exposure-site tests were carried out to evaluate the corrosion resistance characteristics of pozzolan concrete made with salt contaminated mixing water. The exposure-site samples were monitored to determine the time to cracking. Carbonation depth, weight loss of rebars, and pH measurements were carried out on these samples after 11 months of exposure in the field.

Results show that concrete incorporating 20% fly ash added as a replacement of cement reduces the porosity, permeability and improves the general quality of concrete. Pozzolan concretes show significantly better performance than straight portland cement concrete in terms of resistance against rebar corrosion. Pozzolan concrete contaminated with salts do not show any noticeable aggravation in the rebar corrosion process due to the presence of fly ash. Reaction between fly ash and calcium hydroxide [Ca(OH)] of the hydrated cement paste does not reduce the pH value below those observed for the no-fly ash concretes. Carbonation depths of about 1.0 cm were observed in a relatively short period of 11 months of concrete exposure. The best performance in terms of porosity, permeability and pulse-velocity, among the four pozzolans evaluated, was exhibited by French fly ash. These results indicate that pozzolan drawn from different sources may exhibit significantly different levels of performance necessitating careful evaluation and characterisation before actual use.

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by

Omar Saeed Baghabra Al-Amoudi

A Thesis Presented to the

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Al-Amoudi, Omar Saeed Baghabra, M.S.

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U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

University of Petroleum and Minerals

STUDIES ON THE EVALUATION OF PERMEABILITY AND CORROSION RESISTING CHARACTERISTICS OF PORTLAND POZZOLAN CONCRETE

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Dean, College of Graduate Studies

Date July 8, 1985

Department Chairman

THESIS COMMITTEE

Dr. Rasheeduzzafar
Chairman

Dr. Abbassi,A.F
Member

Dr. Maher A. Bader
Member

TO

MY PARENTS

a humble tribute

for the sacrifices

they made

to educate me

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ABSTRACT

The aggressive service conditions of the Eastern Saudi Arabia necessitate the production of quality concrete which is dense and impervious, so that it inhibits the penetration of chloride and sulfate salts which are uniquely effective in setting up corrosion of rebars and the chemical deterioration of hardened cement paste. Pozzolan is considered to be one of the potential admixtures which assists in the production of dense and impermeable concrete resulting in reduced sulfate attack and rebar corrosion.

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The best performance in terms of porosity, permeability and pulse-velocity, among the four pozzolans evaluated, was exhibited by French fly ash. These results indicate that pozzolan drawn from different sources may exhibit significantly different levels of performance necessitating careful evaluation and characterisation before actual use.

ملخــــص

تستلزم الظروف المناخية الصعبة بالمنطقة الشرقية للمملكة العربية السعودية ان تكون نوعية الخراسانة المستخدمة فى المبانى كثيفة ومنيعة لاتنفذ من خلالها املاح الكلور والكبريتات التى تعتبر العامل الرئيسى فى تاكل حديد التسليح والتلف الكيميائى للخراسانة . ويعتبر البوزولان من اهم المواد الاضافية التى تساعد على انتاج خراسانة كثيفة ومنيعة لما لها من خواص مختلفة ، ولذلك فهى تساعد على مقاومة املاح الكبريتات وتاكل حديد التسليح .

هذا وقد اجرى هذا البحث لتقييم النتائج المترتبة على استخدام مادة البوزولان على الخواص التالية : النفاذية ، المسامية والنوعية العامة للخرسانة المصنوعة من الحصى المحلى الذى يتكون من الرمل والحجر الجيرى . وخطط البرنامج على اساس تغيير نسبة البوزولان المضافة من صفر ٪ الى ٤٠٪ ونسبة الماء الى الاسمنت من ٠٫٣٥٪ الى ٠٫٥٥٪ اضافة الى تقييم الاداء لاربعة انواع مختلفة من البوزولان .

وقد تمت دراسة تاثير تميع مادة البوزولان على خواص الخراسانة لمدة عام كامل (٣٦٥ يوما) وذلك بقياس نفاذية الماء ، المسامية ، سرعة النبض اضافة الى قوة الضغط . واجريت اختبارات مخبرية متسارعة للتاكل لتحديد فعالية مادة البوزولان فى كبح تاكل الحديد . واجريت ايضا اختبارات ميدانية لتقييم خواص مقاومة التاكل للخراسانة المحتوية على البوزولان والتى اضيف اليها ماء ممزوج بالملح . هذا وقد تمت مراقبة تلك العينات الميدانية لتحديد وقت تشققها . واجريت اختبارات اخرى لتحديد عمق الكربنة ، فقد الوزن فى حديد التسليح و pH لتلك العينات الميدانية بعد احد عشر شهر من وضعها فى الموقع .

ودلت النتائج ان اضافة ٢٠ ٪ من الرماد المتطاير (البوزولان) عوضا عن الاسمنت قد قللت من المسامية والنفاذية وحسنت من الحالة العامة للخراسانة . واظهرت الاختبارات ان اداء الخراسانة البوزولانية افضل بكثير من الخراسانة العادية فى مقاومة تآكل حديد التسليح . ولم تشاهد اى زيادة ملحوظة فى تآكل حديد التسليح للخراسانة البوزولانية كنتيجة لاضافة الرماد المتطاير . وكانت معدلات pH كنتيجة لتفاعل الرماد المتطاير مع هيدروكسيد الكالسيوم لم تنقص عن معدلات الخراسانة التى لاتحتوى على الرماد المتطاير . وكان عمق الكربنة سنتمترا واحدا على و جه التقريب وذلك فى فترة الاحد عشر شهرا التى اشرنا اليها آنفا .

ثبت من تلك التجارب ان الاداء الافضل بالنسبة للانواع الاربعة المختلفة من البوزولان التى جرى تقييمها فى هذه الدراسة هو اداء الرماد الفرنسي المتطاير . وتدل هذه النتائج بوضوح ان الانواع المختلفة من البوزولان لها اداء مختلف ولذلك يجب تقييمها ودراستها بشكل كامل قبل استخدامها عمليا .

Chapter 1

INTRODUCTION

1.1 DURABILITY PROBLEM OF CONCRETE IN THE EASTERN PROVINCE

Deterioration of concrete structures in the Eastern Province of Saudi Arabia has been the subject of major concern and research for the past few years at the University of Petroleum and Minerals [1,2,3]. The contributing factors and their interactive effects have been catalogued in detail in these studies.

Condition surveys of concrete structures located in Eastern Province [1] show that the main causal factors for concrete deterioration, in decreasing order of importance are:

(i) corrosion of reinforcement,

(ii) sulfate attack and salt weathering and

(iii) cracking due to environmental effects and potential aggregate-cement reactivity.

Studies [1,3] have shown that corrosion of reinforcement is by far the most effectively operative causal factor causing concrete deterioration; the second most effective being the sulfate attack. Both of these factors in the Gulf conditions are visible manifestations of excessive salt inclusions in concrete through aggregates, mix water and subsequent ingress through cracks and pores. However, what is more significant is

the fact that the over all mechanisms of both dominant causal factors are extremely permeability oriented. Research by Okada and Miyagawa [4] has shown that the rate of deterioration is heavily dependent on the diffusion of oxygen into the concrete to the cathodic region. Carbonation which is greatly facilitated in porous and permeable concretes drastically reduces the alkalinity of the concrete and creates conditions conducive to rebar corrosion. Further, the presence of moisture in the pores of hardened cement paste is an essential pre-requisite as an electrolyte for the progress and continuation of electrochemical corrosion process in concrete. Sulfate attack in concrete also progresses only in the presence of moisture. Also, only permeable concrete will allow the subsequent ingress of chlorides to the concrete-rebar interface and would enable the destruction of the passivating gamma iron oxide film on the rebar surface.

The discussion of the preceeding paragraph entails that concrete in the Gulf region contains seeds of potential deterioration due to the presence of chloride and sulfate salts. However, whether these potential deteriorations would actually materialize in terms of rebar corrosion and sulfate attack would depend mainly on the ability of concrete to keep moisture, carbon dioxide and oxygen from penetrating into its texture. This in effect amounts to saying that the permeability of concrete is the most important property determining its long-term durability in aggressive environment. This necessitates that mix design techniques in the Gulf conditions be formulated to yeild dense and impervious concrete.

1.2 CONCRETE MIX DESIGN CRITERIA FOR THE GULF AREA

In order to produce dense and durable concrete the mix design criteria should be formulated to include the following considerations:

(a) mixes should be so formulated, in terms of grading, water-cement ratio and cement content that the resulting concrete is dense and impervious. This inhibits the penetration of chlorides, oxygen, carbon dioxide and sulfate salt solution necessary for rebar corrosion and sulfate attack.

(b) mixes should evolve as little heat of hydration as possible to eliminate severe differential thermal gradients which cause early age cracking.

(c) use of admixtures which reduce salt attack, inhibit rebar corrosion and assist in the production of dense and water-tight concrete.

1.3 USE OF POZZOLAN FOR THE PRODUCTION OF DURABLE CONCRETE

Whereas several possible approaches have been suggested to achieve the desirable attributes outlined in the above section, one possible solution is to replace straight cement mixes by pozzolan-cement concretes. The inclusion of pozzolanic material is known to reduce heat of hydration, increase stability and mobility of plastic mix and results

in a dense sulfate resistant hardened concrete.

1.3.1 Pozzolanic Materials

With the advent of air entrainment as an effective means of improving workability and alleviating bleeding, pozzolans are the only surviving category of mineral admixtures. This is so because unlike the other mineral admixtures, they provide several decisive beneficial effects in the manufacture of high quality concrete.

The term "Pozzolan" is employed to designate a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide (a product of hydration of portland cement) at ordinary temperatures to form compounds possessing cementitious properties. Calcium hydroxide is liberated during the hydration of portland cement, and pozzolans combine with this liberated calcium hydroxide to form stable cementitious compounds which contribute strength and water tightness [5].

The amounts of pozzolan used in concrete has varied from 5 percent or less of the total cementitious material, when employed solely for the purpose of improving workability, to between 15 and 40 percent, when utilized for its pozzolanic properties resulting in several beneficial effects. In the United States, the amount used generally ranges between 15 and 35 percent by weight of total cementitious material. In Italy, where pozzolans interground with portland cement are used extensively,

specifications are formulated to optimize the quantum of inclusion on the basis of a complete consumation of free lime in cements with the silicates and aluminates thereby utilizing more completely the cementitious properties of the pozzolans.

Pozzolans are classified into two major groups:

(i) raw or calcined natural, and

(ii) artificial

Natural pozzolans include such materials as some diatomaceous earths, opaline cherts and shales, tuffs, and volcanic ashes or pumicites. Each may or may not require calcination, depending upon its clay content or grinding or both in order to be suitable for use as pozzolans.

Artificial pozzolans include the fine fly ash which is a by-product of the burning of pulverised coal in power plants. It is removed by mechanical collectors or electrostatic precipitators as fine particles from the combustion gases before they are discharged into the atmosphere. The particles are typically spherical, ranging in diameter from 0.000002 to 0.0002 mm. Electrostatic precipitators capture the preferable, finer-sized particles that escape mechanical collectors . The chemical composition of fly ash is determined by the mineral matter in the coal. There are two classifications of [5] fly ash in ASTM C618: Class F fly ash produced from burning anthracite or bituminous coal and Class C fly ash produced from lignite or subbituminous coal. Major national organizations generally use ASTM C618 Class F requirements as the basis for their specifications for fly ash used in concrete, and

most state transportation departments cite it as well, except that they use a lower limit on loss on ignition, usually 6 percent but sometimes as low as 3 percent. Information presented here is based mainly but not exclusively on experience with Class F, with which the major published reports deal. The basic chemical requirements for fly ash are shown in Table 1.1.

The American Society for Testing Materials, several federal agencies such as the Bureau of Reclamation and the Corps of Engineers as well as some state agencies such as the California Department of Water Resources have established specifications for pozzolans in terms of chemical limitations and physical requirements. A typical specification format is reproduced in Tables 1.2 and 1.3.

1.3.2 Advantages of Pozzolan Addition to Concrete

Use of pozzolan is reported to reduce the water demand and bleeding in fresh concrete, improve workability resulting in better placement and compaction characteristics, decrease the size and number of large voids in hydrated cement paste, lower the amount and degree of orientation of crystalline calcium hydroxide as well as micro-cracking in the transition phase and improve the impermeability of portland cement concrete [6]. In addition to these attributes, portland-pozzolan concretes generate less heat of hydration and show significantly higher resistance to sulfate attack and alkali-aggregate expansion and cracking.

At early ages, pozzolan used as a replacement for portland cement, serves only as an inert component and is therefore similar to reduction in cement content. At later ages, it contributes to the formation of cementitious components but it does so in a manner which does not change the relative proportions of the usual hydrate materials. Finally, it converts some of the calcium hydroxide to less reactive calcium silicates and aluminates through the pozzolanic reaction. The removal of free calcium hydroxide by reactive combination with pozzolans was shown by Lea [7] to progress as shown in Figure 1.1. This figure shows the quantity of free calcium hydroxide liberated by plain and pozzolan concretes. It is generally considered that in concrete, this process leads to long-term gains in water tightness, strength and resistance to aggressive environment [8].

1.3.3 Permeability Characteristics of Pozzolan Concrete

Porosity and permeability of concrete are controlled by a number of variables which include the physical and chemical properties of the ingredients, i.e. size, distribution, and chemical composition ...etc. of the cement, aggregate and mixing water used, and the procedure and techniques followed during the proportioning, mixing, casting and curing stages of the concrete. These variables will affect air content, pore size, pore continuity and the permeability [9]. These are discussed in detail in the next chapter.

Addition of finely divided pozzolanic material such as fly ash has been reported to have a markedly beneficial effect in producing dense and low

permeability concretes [10,11]. Finely divided fly ash initially fills the interstices between the hydrated cement grains and reduces the porosity [12]. Secondly, it reacts with coarse calcium hydroxide crystals and fixes them in the structure in the form of gel-like calcium silicate hydrate. Calcium silicate hydrate tends to fill the pore spaces in the concrete and by its formation the amount of lime that can be leached out of the concrete structure is significantly reduced.

Although the exact mechanism of permeability reduction through pozzolanic action is not understood to date, there are several broad features of the densification process which have been highlighted by several researches. Mehta [6] has shown that at various stages of the curing process the strength and permeability are strong functions not of the total porosity of the hydrated paste, but of the volume of large voids (>100 µm). Subsequently; Manmohan and Mehta [13] have shown that additions of pozzolanic materials such as rice husk ash, fly ash and granulated blast furnace slag to cement had resulted in the transformation of large pores into fine pores thereby causing pore refinement. It is most likely [14] that the pore refinement occurs due to the conversion of $Ca(OH)_2$ by the pozzolanic silica into a C-S-H phase. This secondary C-S-H phase, although less dense than the primary C-S-H formed in straight hydrated portland cements, neverthless effectively fills up large voids in the hydrated portland-pozzolan cement system. The reaction between pozzolanic silica and lime, therefore, has far reaching effect on reducing the permeability of the concrete made with pozzolan blended cements. The mechanism of pore refinement [6] has been hypothesized as shown in Figure 1.2.

It has been reported [10] that a seven to ten fold reduction in permeability can be achieved by the proper replacement of fly ash to concrete.

1.4 NEED FOR THIS STUDY

Foregoing discussions indicate that the addition of pozzolan is beneficial in refining the pore structure of the portland-pozzolan concrete thus; making it more dense and impermeable. Permeability of concrete is mainly governed by the permeability of the cement paste, although permeability of aggregate may also contribute to the overall permeability of concrete, especially when the aggregate is of low quality. Aggregate in the Gulf being weak, porous and absorptive may contribute significantly in modifying the permeability characteristics of concrete. Hence, it would be of considerable interest to develop data on portland-pozzolan concretes made with local aggregates in terms of the permeability, strength and durability characteristics of such concretes.

In addition to the aforesaid several beneficial aspects of portland-pozzolan concretes, there is also a concern among concrete technologists to the effect that the reaction between pozzolan and calcium hydroxide would consume the lime, thereby reducing significantly the component of hydration within the concrete which provides the alkaline environment to the hardened cement paste; this way the pozzolanic reaction would at best reduce the reserve basisity in concrete or at worst may reduce the alkalinity below the level which is

considered protective to steel against corrosion. Since corrosion of reinforcement constitutes the most serious form of concrete deterioration in this region, this aspect should therefore be fully investigated before the use of pozzolans could be recommended in the Gulf states.

1.5 OBJECTIVES OF THIS STUDY

The objectives of this study are to investigate the effect of cement replacement by pozzolan on the general quality, porosity, permeability and corrosion resisting characteristics of portland-cement concretes.

The specific objectives of the test program are:

(i) to develop data on general quality, porosity, permeability, ultimate strength and corrosion resisting characteristics of portland-cement concrete made with various water-cement ratios (0.35, 0.385, 0.45, 0.50 and 0.55),

(ii) to evaluate the performance of three different pozzolans with regard to afore-mentioned characteristics, and

(iii) to evaluate the corrosion resistance characteristics of pozzolan concrete made with salt contaminated mixing water.

The following parameters have been included in this study:

(i) Cement replacement by pozzolan: 0, 10, 20, 30 and 40 %

(ii) Water-cement ratio: 0.35, 0.385, 0.45, 0.5 and 0.55

(iii) Pozzolan from four sources.

An overview of the experimental program is shown in Figures 1.3, 1.4 and 1.5.

Data developed in this investigation in conjunction with results obtained in a previous investigation [15] carried out at UPM will be useful in developing specifications for use of pozzolans in Eastern Saudi Arabia.

TABLE 1.1: Basic Chemical Requirement for Fly Ash

ASTM 618	Class F	Class C
Silicon dioxide (SiO_2) + aluminum oxide (Al_2O_3) + ferric oxide (Fe_2O_3), percent, not less than	70.0	50.0
Sulfur trioxide (SO_3), percent, not more than	5.0	5.0
Moisture content, percent, not more than	3.0	3.0
Loss on ignition, percent, not more than	12.0	6.0

TABLE 1.2: Typical Chemical Requirements for Pozzolans

Item	Bureau of Reclamation and Corps of Engineers		ASTM Specification C 618	
	Natural Pozzolan	Fly Ash	Natural Pozzolan	Fly Ash
Silicone Dioxide (SiO_2) + aluminum oxide (Al_2O_3) + ferrite oxide (Fe_2O_3), not less than	70.0	70.0	70.0	70.0
Magnesium oxide (MgO), not more than	5.0	5.0	5.0	....
Sulfur trioxide (SO_3), not more than	4.0	4.0	4.0	5.0
Loss on ignition, not more than	8.0	6.0	10.0	12.0
Moisture content, not more than	3.0	3.0	3.0	3.0
Exchangeable alkalies as Na_2O, not more than	1.5	1.5	....	1.5

TABLE 1.3: Typical Physical Requirements for Pozzolans

Item	Bureau of Reclamation and Corps of Engineers		ASTM Specification C 618	
	Natural Type N	Fly Ash	Natural Type N	Fly Ash
Fineness : Specific surface , Blaine air permeability cm^2/cm^3 , not more than	12,000	6,500	12,000	6,500
Material retained on No. 325 mesh sieve , percent, not more than	....	....	20	34
Compressive strength : With portland cement , percent of control , 28 days, not less than, MPa	75	85	75	85
With lime, 7 days, psi	900	900	800	800
Increase in drying shrinkage of mortar bar, percent shrinkage of pozzolan bar minus percent shrinkage of control bar , not more than	0.03	0.03	0.03	0.03
Water requirement, percent not more than	115	105	115	105
Reduction of reactive expansion at 14 days percent, not more than	75	....	75	....
Mortar expansion at 14 days , percent not more than	0.020	0.020	0.020	0.020

Cont'd. TABLE 1.3

Soundness, autoclave expansion , percent not more than	0.50	0.50	0.50	0.50

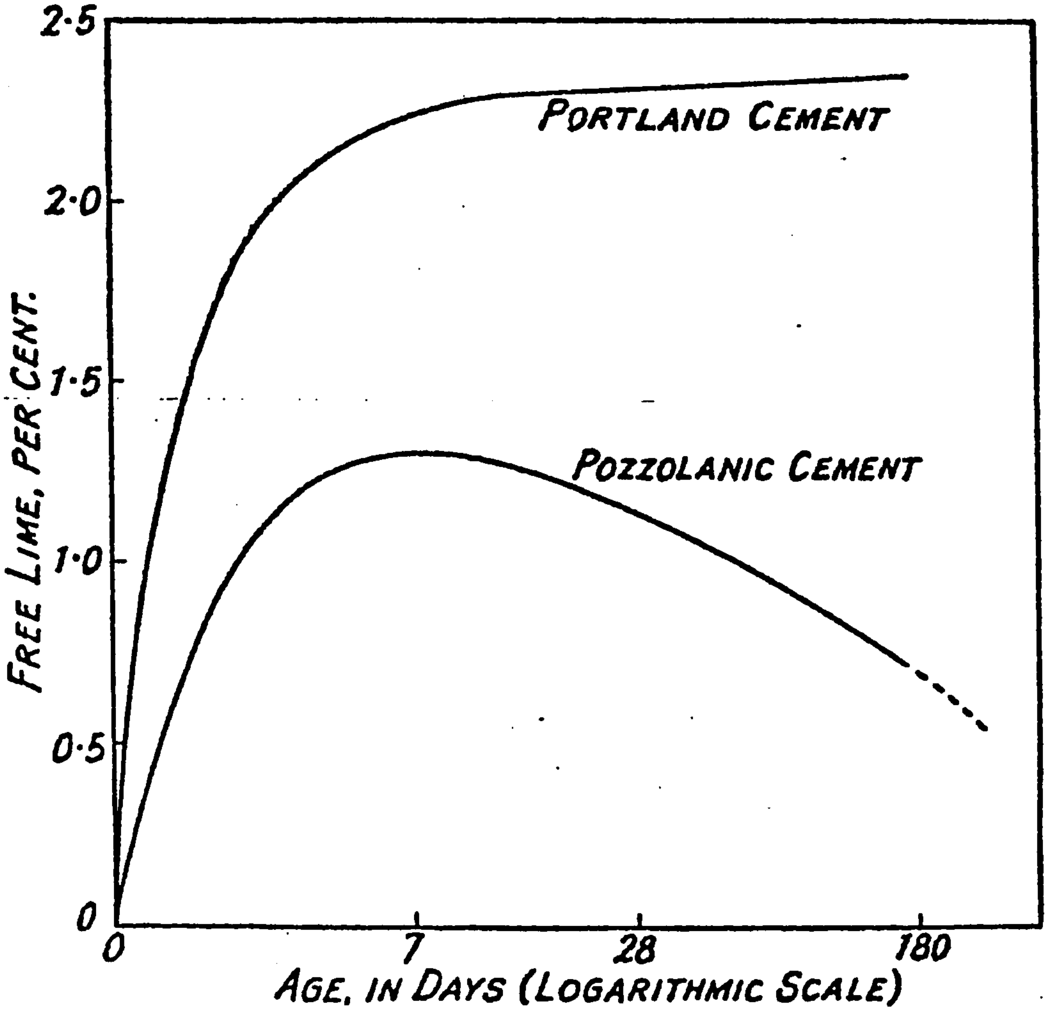

Figure 1.1 Relation between Age and Free Calcium Hydroxide liberated by Cement

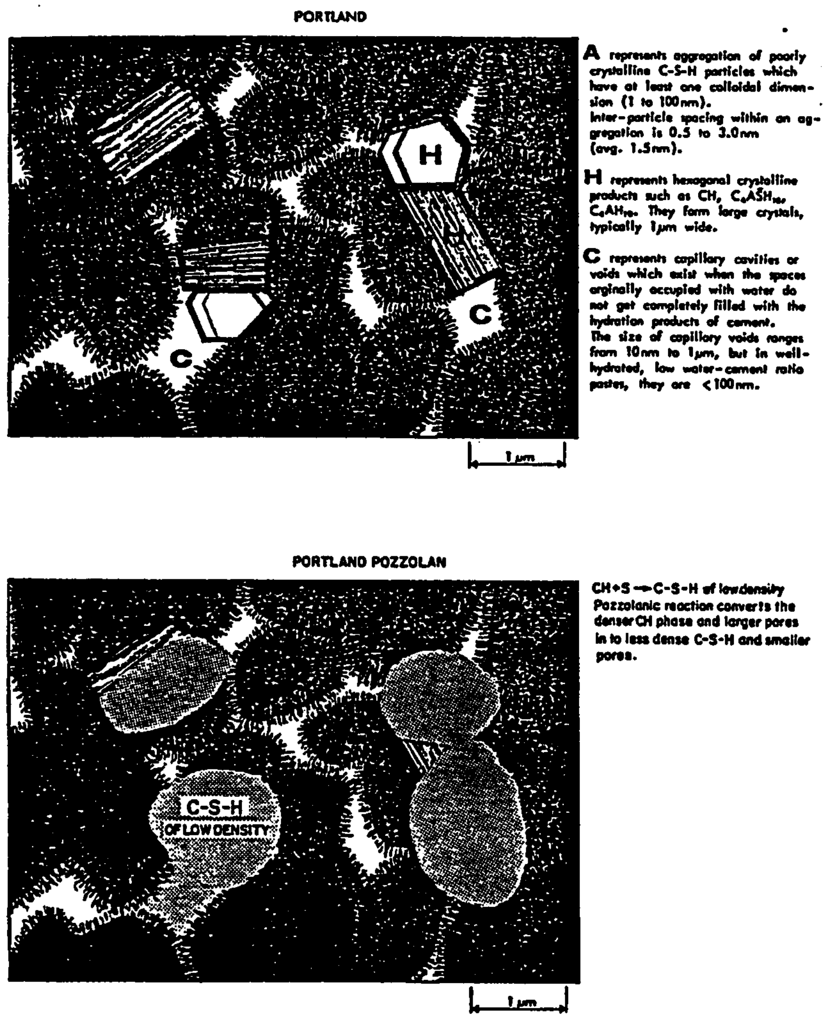

Figure 1.2 Schematic Diagram of Pore Refinement in Cements

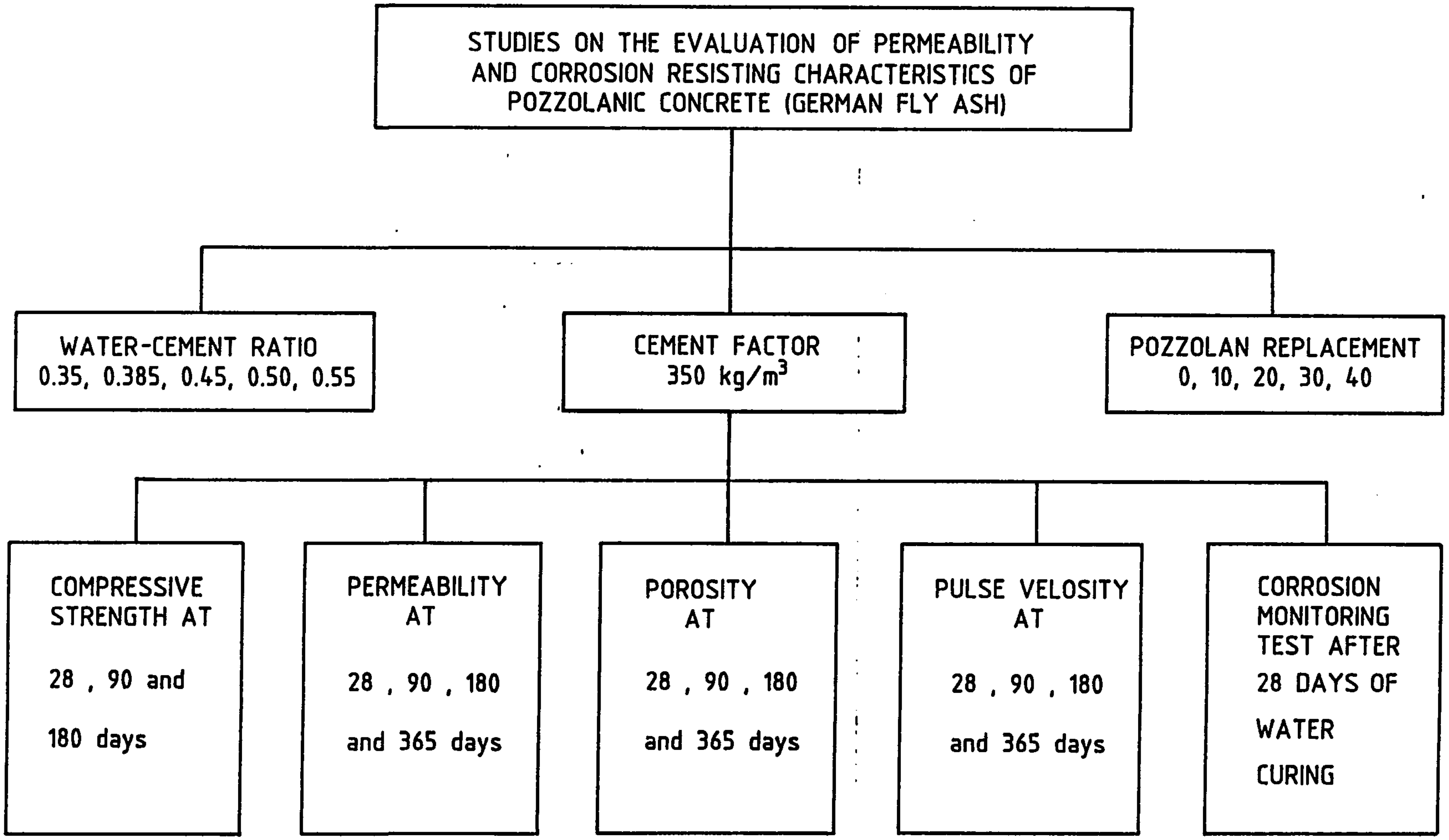

Figure 1.3 An Overview of the Experimental Program

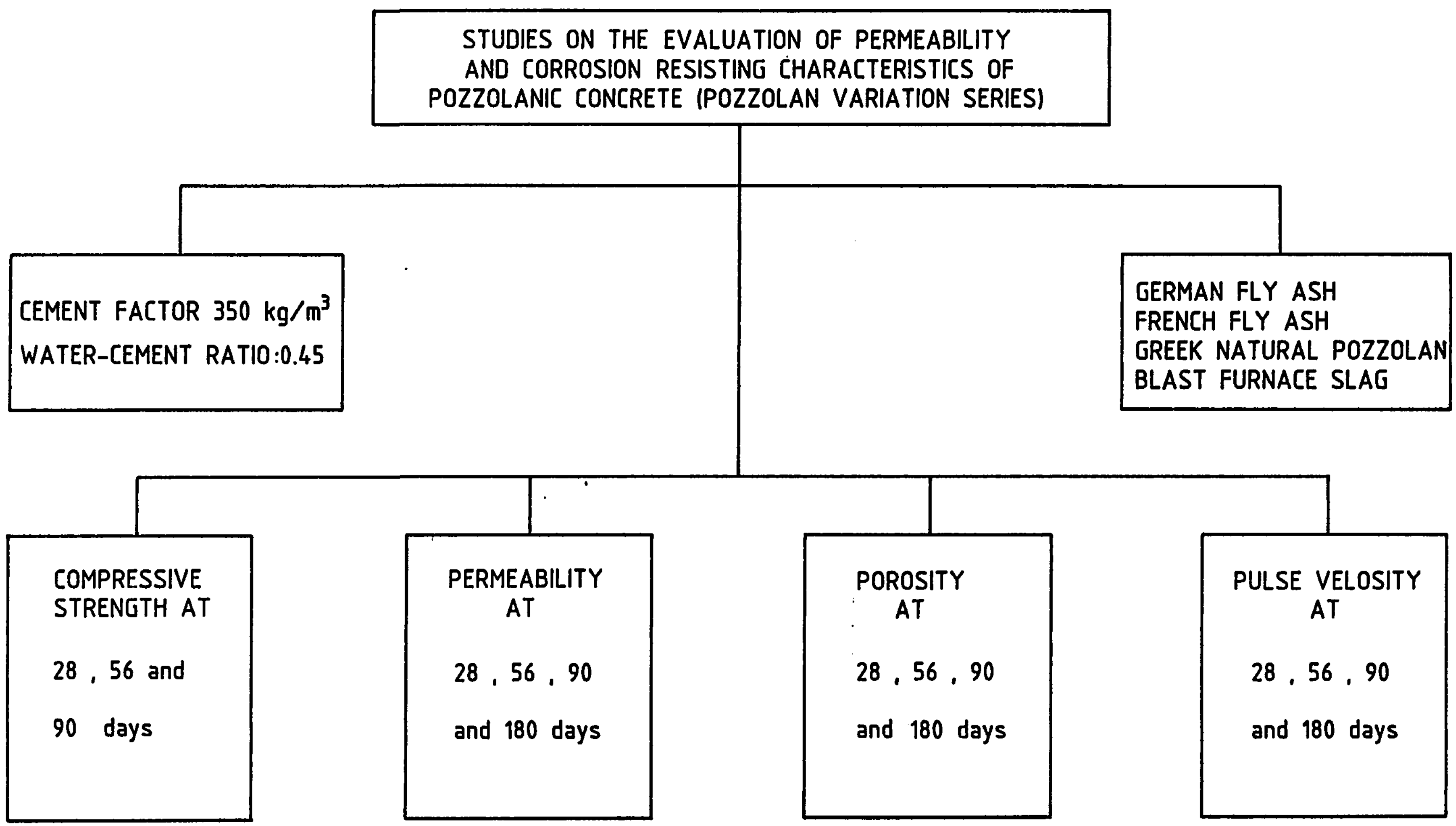

Figure 1.4 An Overview of the Experimental Program (Pozzolan Variation Series)

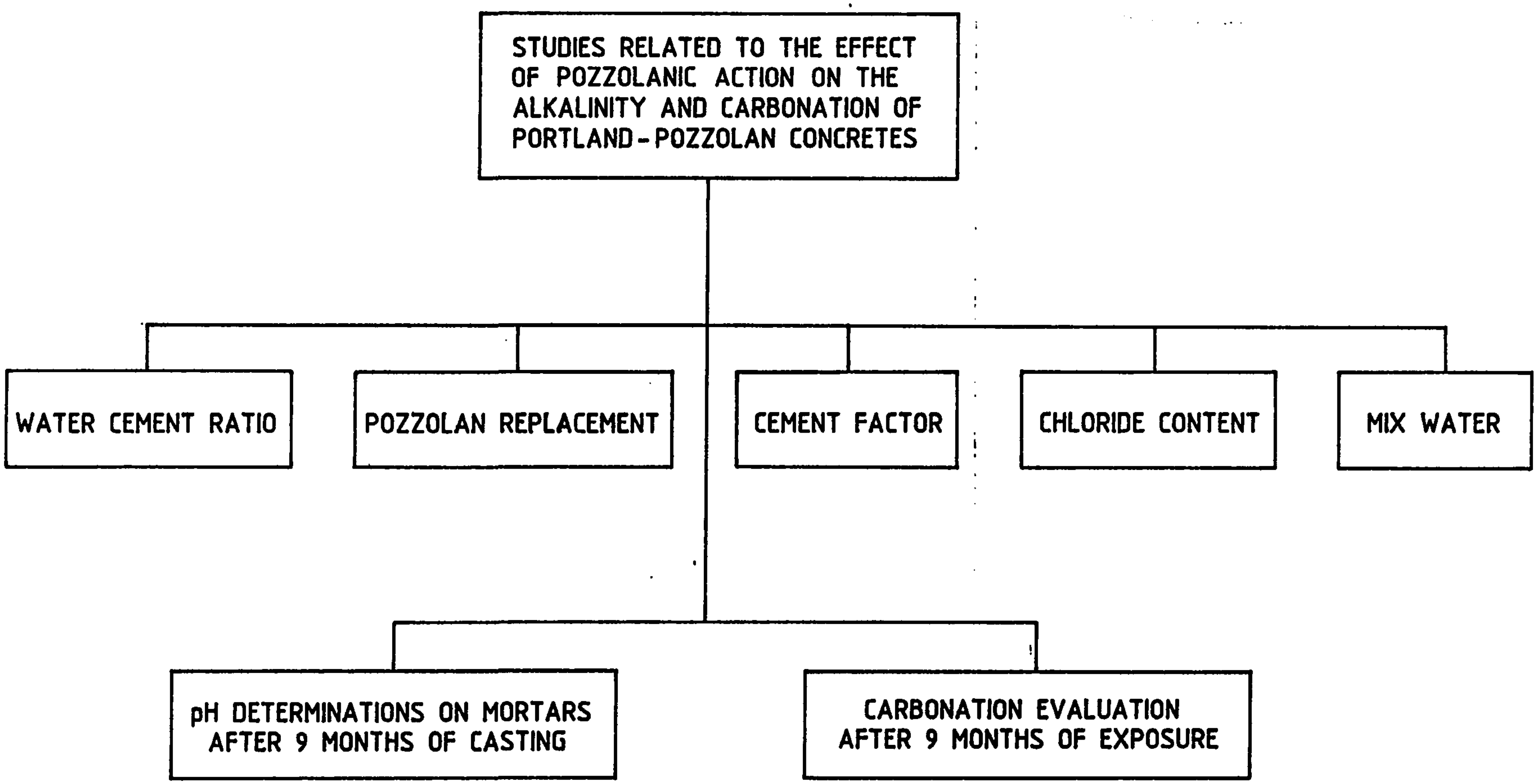

Figure 1.5 An Overview of the Experimental Program to determine the Effect of Carbonation

Chapter 2

PERMEABILITY OF CONCRETE AND ITS TESTING

There is almost complete unanimity in identifying concrete permeability as the pre-eminent criterion governing its durability performance in aggressive environments. As pointed out in the preceding chapter the mechanisms of both the dominant causal factors (rebar corrosion and sulfate attack) generating deterioration in Gulf environment are extremely permeability oriented. It follows that in the Gulf conditions, concrete should be sufficiently dense and impervious for high durability performance. For concrete free of microcracking, its permeability will be governed by the permeability of the hardened paste. However, the paste permeability is not a simple function of its porosity but is governed by the pore size distribution. Unfortunately, there is little data on the permeable pore space characteristics of concrete and on its applied engineering interpretations to establish a direct correlation between this significant parameter and the durability characteristics.

There are three broad groups of factors which directly affect the permeability of concrete:

(i) Nature and proportioning of constituent materials

(ii) Methods of preparing and curing concrete

(iii) Factors related with age and testing conditions.

Figure 2.1 shows a listing of these factors and their detailed break-up. Some of the relatively more important factors are discussed in detail in the following sections.

2.1 CONSTITUENT MATERIALS

2.1.1 Coarse Aggregate

Aggregates used in concrete are relatively impermeable and hence permeability of concrete is primarily a function of the permeability of cement paste. However, there are certain aspects of aggregate characteristics and their dispersion in relation to paste which affect concrete permeability characteristics.

2.1.1.1 Aggregate Size

By restraining shrinkage of the cement paste, either due to reduction in relative humidity or temperature, aggregate tends to induce microcracking at the aggregate-cement interface. Larger pieces of aggregate cause more microcracking because they provide more local restraint to shrinkage. Studies at the U.S. Bureau of Reclamation [16] showed that, at a given water-cement ratio, the coefficient of permeability of concrete increased considerably with increasing size of aggregate. The recommended concrete practices for sea structures, therefore, limit the maximum aggregate size or require greater depth of cover when aggregate size is increased. Conversely, when cover thickness is restricted due to any reasons, the aggregate size must be reduced. Recent guidelines suggest that the cover be 1.5 to 2 times the maximum size of aggregate.

2.1.1.2 Aggregate Shape

Use of elongated and flaky aggregates noticeably increase the permeability by trapping sizeable mobile bleed water and air bubbles under their flat surfaces producing under-aggregate fissures and zones which are very porous.

2.1.1.3 Aggregate Type

Aggregates composed mainly of coarse-grained silicate minerals such as quartz and feldspar are known to produce weaker bond with cement paste than calcareous rocks such as limestone and dolomite. The weak bonds are easily broken due to normal temperature and humidity changes, thereby causing considerable microcracking. There is evidence that, given similar concrete quality, reinforced concrete structures containing limestone aggregate show less damage due to corrosion of reinforcement than the structures containing quartzitic aggregate. Similarly, it is believed that excellent durability of reinforced lighweight concrete in the marine environment is mainly due to good bond between the aggregate and cement paste. Differential thermal expansion and stiffness characteristics between the cement paste and aggregate contribute to microcracking at the interface.

2.1.1.4 Voids Between Aggregates

The amount of sand-cement paste in the concrete mix should always be sufficient and of such consistency as to fill the voids between aggregate particles. The amount of cement-sand paste required depends on the amount and gradation of aggregates. Lack of paste also results

in particle interference causing a reduction in workability which could cause problems in compaction, thereby resulting in a relatively porous concrete. Figure 2.2 shows how a lack of sufficient fine aggregates can affect the pore structure of the concrete; the cement-sand mortar does not completely fill the spaces between the aggregate particles and this results in the presence of voids within the texture of concrete. If such voids are located close to a reinforcing bar, heavy localized corrosion of steel will take place in the vicinity of the void. The internal structure of a typically dense concrete is shown in Figure 2.3.

2.1.2 Fine Aggregate

The sand to be used in making concrete should be clean and free of silt, clay or dust. The slurry formed by silt and clay forms an undesirable coating over sand particles and inhibits strong bond between sand particles and the cement paste. If a graded fine aggregate is used, there should be sufficient fines present in sand to fill the voids between the larger particles.

2.2 PROPORTIONING OF MIXES

Figures 2.4 and 2.5 show the relationship between water-cement ratio and the permeability of the hardened cement paste and concrete made with different aggregate sizes. It is seen from these Figures that below a certain water-cement ratio, the permeabilities of hardened cement paste and concrete are reduced to extremely low values; this is because with low water-cement ratios, the pores in the cement gel become progressively smaller in size thereby making the paths of linked pores

segmented and discontinuous. As aggressive ions such as Cl^- and SO_4^{--}, commute through concrete by bulk flow and concentration diffusion, it is rational to assume that reduction in permeability by the segmentation of paths of linked pores will block the flow of such ions within the concrete mass and will enhance the time necessary for either sulfate attack or the onset of corrosion. With present knowledge, it is difficult to precisely quantify the water-cement ratio for segmentation, but on the basis of whatever data exist, it is regarded to lie between 0.4 and 0.45.

Another concept of considerable significance affecting concrete permeability is the binary aggregate proportioning. The use of local fine sands even with a continuous coarse aggregate gradation results in situation where the workability of concrete is significantly sensitive to the volume fraction of sand in the total aggregate content. The importance of workability cannot be overemphasized for obtaining impermeable concrete. It ensures stability of the mix with freedom from bleeding and segregation as well as ensure full compaction; all three measures are needed to obtain a low permeability concrete of high quality. Research carried out at UPM [17] shows that binary aggregate proportioning should be optimized for highest workability. Excess sand increases the surface area effect and reduces the workability; for undersanded mixes, the particle interference has the similar effect of reducing workability. Oversanded mixes are found to require either a higher water-cement ratio or a higher cement factor to achieve the required workability, whereas undersanded mixes are found to have a strong tendency toward harshness and segregation. A correct

proportioning of sand and coarse aggregate is, therefore, an essential mix design paramenter to obtain minimum permeability.

2.3 METHODS OF PREPARING AND CURING CONCRETE

Mixing, transportation, placement, compaction and curing of concrete are the important steps which significantly affect permeability. Mixing should ensure proper and uniform blending. Adequate mixing and compaction would ensure the filling of voids between aggregates by cement paste which is a necessary process to obtain low permeability. The required mixing time varies with the size of mixer and also depends to a certain extent on the type of mixer. Current specifications reqiure a minimum mixing time of one minute for common mixers having a capacity of one cubic yard or less, and an additional 15 seconds for each additional 0.5 cubic yard or fraction thereof.

Transportation, placement and compaction in the forms should be done in such a manner as to positively avoid seggregation and excessive bleeding. Segregation of concrete can cause "honey comb" regions especially around the bars resulting in a porous concrete. Subsequent limited vibration of wet concrete can remove honey combing to a certain extent. Over vibration, however, has its own side effects and should be avoided.

Careless finishing of concrete surfaces also has an important effect on the permeability of surface and near-surface layers which may facilitate the penetration of water and other aggressive medium.

Curing is one of the most important factors affecting concrete permeability. Figure 2.6 shows the effect of curing time on the permeability of concrete and the data of these presentations make the significance of effective curing abundantly clear.

2.4 PERMEABILITY OF HARDENED CEMENT PASTE AND CONCRETE

2.4.1 Hardened Cement Paste

Studies carried out by Powers et al. [18] show that the permeability of mature hardened cement paste to water at 50 psi range from 1×10^{-13} to 1×10^{-19} cm/sec for water-cement ratios ranging from 0.3 to 0.7. Permeabilities were also found to be a strong function of the period of hydration, the variation for a paste of 0.70 water-cement ratio being from 4×10^{-8} cm/sec at 5 days to 0.6×10^{-10} cm/sec ultimately. Powers and co-workers also evaluated paste permeabilities in comparison to various rocks commonly used as parent material for the coarse aggregate. The results showed that hardened cement pastes of water-cement ratios in the range of 0.38 to 0.71 have permeabilities which are of the same order of magnitude as those encountered in the commonly used concrete aggregate material. It was found that although the total porosities of cement pastes were higher than those of rocks, permeabilities were equivalent.

Sorensen et al. and Glover and co-workers [19,20] evaluated permeabilities of cement pastes in terms of water vapor transmission through the pastes. Sorensen [19] found values ranging from 4×10^{-8} cm/sec for very dry specimen conditions (RH = 10%) to 1×10^{-8} cm/sec

for values close to saturation. Glover [20] found water vapor diffusion coefficients for a paste of water-cement ratio of 0.28 to vary in the range of 15 x 10^{-8} cm^2/sec at 2 days to 8 x 10^{-8} cm^2/sec at 28 days, remaining almost constant up to 90 days.

The movement of ions through hardened cement paste as indicative of their permeabilities has also been studied by Berman [21] and Kondo [22]. Berman studied the diffusion of chloride, flouride and chromate solutions into hardened cement pastes (water-cement ratio of 0.40 and 0.50, age 28 days). Results show a significantly greater penetration of sodium chloride than any other salts tested. His data also show that dissolved ions penetrate the paste more rapidly than water. Similar studies by Kondo on pastes of 0.40 water-cement ratio cured for 28 days show the diffusion coefficient of chloride ion to be greater than that of the associated cation. His results made him to conclude that "hardened cement paste seemed to behave as an electro-positive semi-permeable membrane". For Sodium chloride solution at 20° C, the diffusion coefficient for chloride ion was 6 x 10^{-8} cm^2/sec.

2.4.2 Concrete

Most of the earlier studies on the permeability of concrete were conducted in the form of flow of bulk water through concrete under relatively large pressure heads.

The earliest comprehensive study on the permeability of concrete was conducted by Glanville [23] in 1926 on concrete specimens made with varying mix proportions cured upto one year and subjected to

permeability testing under a water pressure of 100 psi. Results showed reduction in permeability with decreasing water-cement ratio and increasing age. Permeability ranged from 0.19 ft/day (6.7×10^{-5} cm/sec) at 7 days to less than 8.5×10^{-3} ft/day (3.0×10^{-6} cm/sec) at 1 year. Effects of aggregate gradings were found to be of a minor nature.

In the studies carried out at the Portland Cement Assocition by McMillan and Lyse [24] pressurized water was applied on 6 in. diameter x 2 in. thick specimens. Results at 24 hours showed that permeability decreased from about 2.7×10^{-7} cm/sec at a water-cement ratio of 0.8 to values too small to measure below water-cement ratio of about 0.50.

The most widely quoted and referenced work amongst the earlier studies is that due to Reuttgers, Vidal and Wing at the U.S. Bureau of Reclamation [25]. Concrete specimens upto 18 x 18 in. in size were subjected to water pressures of 400 psi. In addition to the usual increase in permeability with water-cement ratio, the investigators found an increase of 30 times when the maximum size of the aggregate was increased from 0.25 in. to 9 in. The authors attribute this to a greater probability of voids occuring beneath larger aggregate particles. However, it is possible that the increased permeability may be due to two additional reasons:

> <u>firstly</u>, larger aggregate provides more local restraint to shrinkage thereby causing an enhanced microcracking due to more shrinkage restraint.

secondly, flow might have occured through the limestone aggregates used and therefore, total flow would increase in proportion to the aggregate content, which would be greater as the maximum aggregate size was increased.

Cook [26] carried out another series of tests on concrete permeability under high water pressure of 200 psi applied to lean mass concrete. Specimens with cement contents ranging from 188 to 282 lb/yd^3 with water-cement ratio from 0.50 to 0.86 were tested at 3 and 12 months age. Permeabilities at 3 months ranged from 1.5×10^{-8} cm/sec for water-cement ratio of 0.86 to 6×10^{-9} cm/sec for water-cement ratio of 0.50.

Permeation of water into concrete under high pressure heads is only one of the several techniques to evaluate concrete permeability characteristics. This type of permeability data may not be directly applicable to the needs of the construction industry. In this area what may be more directly relevant are the concrete permeability data obtained on the basis of water vapor transmission (WVT) or absorption based on capillary flow testing. Early tests by Wiley and Coulsen [27], although devised as a rapid test for water permeability, were actually a measure of capillary flow and vapor transmission through the concrete pipe sections used. The peremeability coefficients obtained using these techniques were of the order of 3 to 40×10^{-8} cm/sec. These values were 100 to 1000 times higher than the values obtained by Ruettgers, Vidal, and Wing [25] at the U.S. Bureau of Reclamation using water pressure technique in the case of mixes ranging in water-cement ratio

from 0.53 to 1.1. These results strongly suggest that capillary forces can be significantly more effective in rapidly moving water through concrete than pressures upto 400 psi used by Reuttgers, Vidal and Wing. Barre [28] also evaluated permeability of concrete using water vapor transmission and found the values ranging from 4.66 x 10^{-9} gm/cm^2.sec at water-cement ratio of 0.46 to 8.19 x 10^{-9} gm/cm^2.sec at water-cement ratio of 0.82. A relatively recent work in this area has been reported by the U.S. Naval Civil Engineering Laboratory [29]. Concrete discs of 4 inch diameter and 1.5 inch thick were used with a differential relative humidity situation prevailling on opposite faces of the disc specimens. These experiments indicate that the water vapor transmission increased with water-cement ratio, decreased with relative humidity and was also reduced by the addition of sodium chloride to the concrete mix.

The movement of chloride ions through concrete has also been used as a relative index of its permeability to aggressive medium. Three investigations which may be of considerable relevance and interest have been carried out by Monfore and Ost [30], Clear [31] and Collepardi and Marcialis [32]. Monfore and Ost [30] monitored chloride levels in 2 x 4 inch concrete cylinders exposed on one face to 23% and 8% $CaCl_2.2H_2O$ solutions. The results indicated that after 12 months of ponding, chloride levels were significant at 1 inch depth for concretes made with water-cement ratios of 0.40 and above. At the 2-inch depth chloride levels were at baseline levels after 12 months of ponding if water-cement ratio was at 0.44 or less. Clear [31] has investigated chloride penetration into especial low void concretes in comparison to the conventional portland cement concrete. His data indicate that

chloride penetration into properly prepared especial low void concretes such as latex modified concrete, polymer impregnated concrete, concrete made with "Iowa Method" was significantly lesser than in conventional concrete. Collepardi and Marcialis [32], using techniques similar to that of Monfore, calculated chloride diffusion coefficients from the rate of penetration of the chloride front through the concrete cylinders. Values determined were 1.7×10^{-8} cm^2/sec for portland cement concrete of water-cement ratio 0.50 (vibrated) and 3.3×10^{-8} cm^2/sec for water-cement ratio of 0.60 (non-vibrated). Pozzolanic cements exhibited somewhat lower diffusion coefficients.

2.5 PERMEABILITY TESTING OF CONCRETE

The type of concrete permeability testing techniques which have relevence to this research may be broadly stated as follows:

Water Permeability

- High Water Heads
- Variable Head
- Initial Surface Absorption Test (ISAT)
- Water Injection

Air Permeability

- High Pressure Air
- Pressure Decline
- Vacuum Methods

2.5.1 Water Permeability

2.5.1.1 High Water Heads

In this technique water is made to flow into and through specimen under pressure. Pressure regulators can be varied to supply pressures upto 450 psi without much difficulty. Specimen containers are especially designed to ensure water-tightness. A typical apparatus and technique in this category are those developed by the U.S. Bureau of Reclamation [16]. This technique works well with conventional concretes, although long times (upto 25 days) are necessary to achieve constant flow conditions.

Murata [33] has devised a more rapid test based on calculation of the water diffusion coefficient through a concrete specimen (6 inch in diameter and 6 inch long). A water head (dye being added to the water) of from 142 psi to 287 psi is applied to the specimen for 48 hours, the specimen being subsequently fractured and the average depth of penetration calculated from planimeter measurements of the area of penetration of the dye. From the experimental data, diffusion coefficient is calculated.

2.5.1.2 Variable Head Technique

In the variable-head technique [34], the rate of passage of water through a specimen is monitored by the fall of the water level in a manometer connected to the specimen under test.

Saturation of the specimen is essential prior to testing to eliminate the effect of variable capillary force developed in the specimen as a

result of the varying degrees of stauration. The test prócedure is significantly slow and time consuming.

2.5.1.3 Initial Surface Absorption Test (ISAT)

This technique [35] recognizes that high pressure permeability testing does not realistically simulte the actual rate of permeation of deleterious agents into concrete surfaces. The test apparatus consists of a gasketted cap which is clamped to the concrete specimen surface. Water is poured into the inlet until the outlet runs clear. A capillary tube is then affixed to the outlet tube, an initial reading is taken at 10 min, 30 min, 1 hr, and 2 hr. The test is fully described in BS 1881 part 5. Clearly, the results predict the quality of the surface layer of concrete but fail to provide an indication of the interior material.

2.5.1.4 Water Injection

This technique developed at the British Building Research Establishment (BRE) responds to the limitation of the Initial Surface Absorption Test which provides information only on the durability quality of surface layers of the concrete. Water injection test can be used to evaluate the permeability of concrete at any depth below the surface. The procedure consists of drilling a hole 30 mm deep and 5.5 mm diameter into the concrete, sealing the hole with a silicone rubber plug, ensuring an air tight seal by means of a hypodermic needle placed through the silicone plug. The rate of fall of water is then monitored in a capillary after injecting water by means of the hypodermic syringe into the small cavity in the concrete.

The results of this technique have a significant scatter indicating substantial aggregate effects. Data also show a significant moisture content effect especially at higher water-cement ratios.

2.5.2 Air Permeability

2.5.2.1 Air Flow under Pressure

Air permeameters which have been designed to cover a wide range of applied pressure essentially consist of the following components:

(i) Suitable specimen holder to ensure flow in the longitudinal direction

(ii) Stable gas supply source

(iii) Precision pressure gauges

(iv) Accurate flow meter on the downstream side.

ASTM C577-68 [36] describes equipment and techniques used for the determination of air permeabilities on refractory materials at 240 mm Hg pressure on 2 inch specimens. These techniques are directly applicable to concrete specimens also.

2.5.2.2 Pressure Decline Technique

Air permeability measurements may also be made by monitoring the pressure drop in a vessel sealed by the specimen itself to the outside atmosphere. The method is termed constant-volume technique [37].

A simpler and more rapid test called the "variable volume-decay-rate" method comprises a system in which air is caused to permeate from the atmosphere through the specimen into a container by draining water from the container. The technique incorporates an indeterminate effect caused by the loss of head due to the restricted outflow of liquid from the container. Drennan [38], however, has proposed corrections for head loss effect.

2.5.2.3 Vacuum Methods

Whiteway [39] devised an apparatus which utilizes negative pressure for air permeability determination of concrete. The system is comprised of three 100 cm^3 bulbs connected through the test piece to a vacuum pump. The drop in pressure was monitored by a manometer equipped with electrical contacts which were arranged to allow timing of the interval between any two selected pressure levels. This elapsed time constituted the measure of the permeability.

The British Building Research Establishment [40] has also developed a device using vacuum in the evaluation of concrete permeability. The hole and sealant similar to those described in the water injection method were used in conjunction with a 3-way stopcock to allow air to be withdrawn from the concrete until a vacuum of 112 mm Hg is created. The pump is then cut off and the time required for the pressure to rise to 150 mm Hg is recorded. This time is taken as a relative measure of the air permeability of the concrete. The results obtained by this method were found to be a strong function of the moisture content of concrete.

2.6 WATER VAPOR TRANSMISSION

ASTM C355-64 [41] details a Standard Test Method using water vapor transmission technique for the permeability testing of materials upto 1.25 inch thick. The test specimen is in the form of a flat plate. It is sealed into a wide, shallow pan containing either a desiccant or water. The rate of change of weight of the entire apparatus contained in a controlled atmosphere with time is taken as a measure of the water vapor transmission.

In order to obtain reproducible results, specimens should be brought to some uniform moisture state prior to the initiation of the test. For concretes, an oven-dry state may be considered as a test initiation state. Morrison et al. [42] have developed a variation on the desiccant method using a water reservoir instead of a controlled atmosphere on the opposite specimen face.

2.7 ION DIFFUSION

Ion diffusion may be a relevant measure of concrete permeability as it is very probable that chlorides commute into concrete through ionic diffusion. The process, however, is likely to be complicated by chemical reactions with hardened cement paste constituents. Electrokinetic effects due to interactions within the gel pores are also likely to affect the rate of ion diffusion within the concrete matrix.

Although very little direct work has been done related to concrete permeability determination, works on ionic diffusion through porous

substance by Northrop and Anson [43], Garrels [44], and Spinks et al. [45] provide significant useful lead for applications to concrete permeability evaluations.

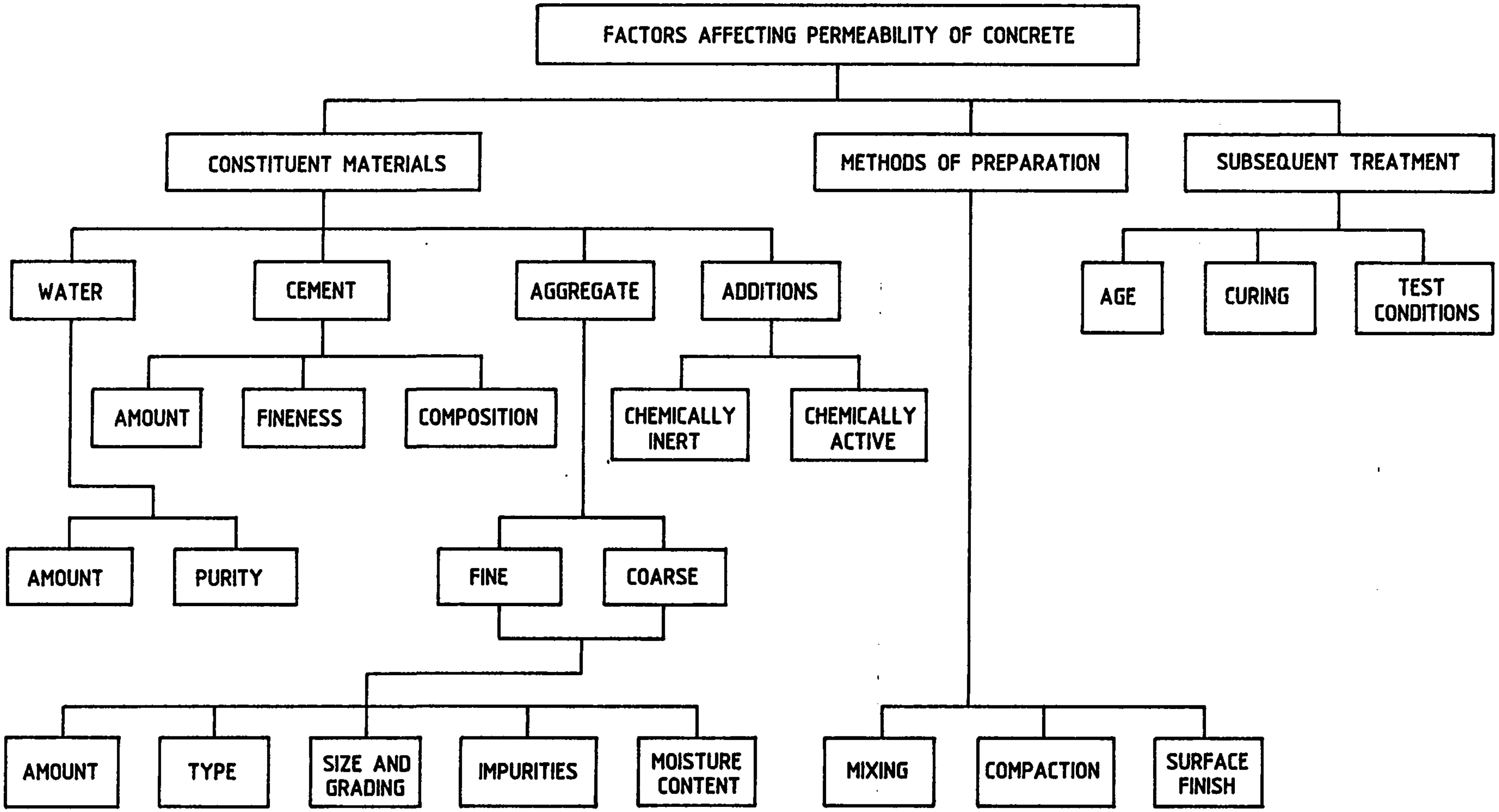

Figure 2.1 Factors Affecting Permeability of Concrete

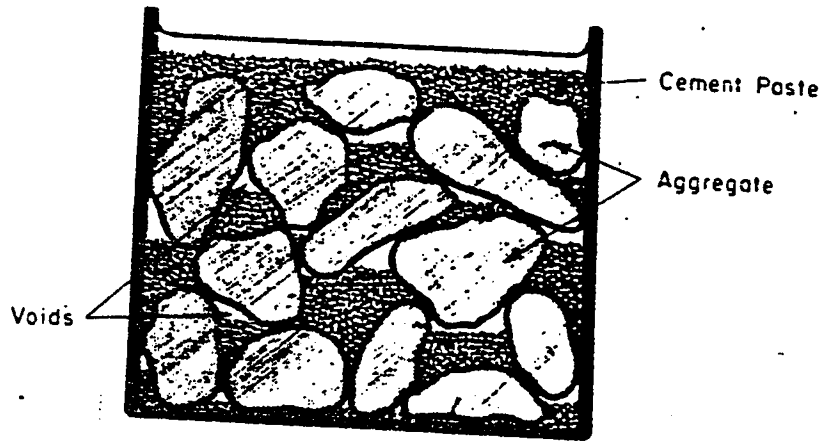

Figure 2.2 Voids in Concrete due to Improper Gradation

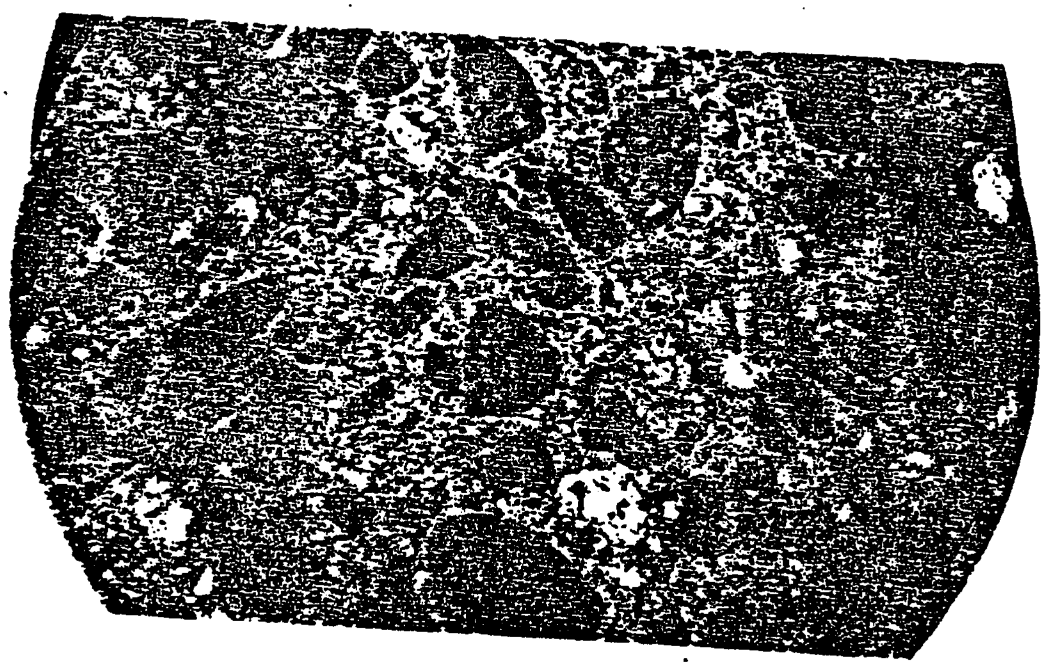

Figure 2.3 Internal Structure of Dense Concrete

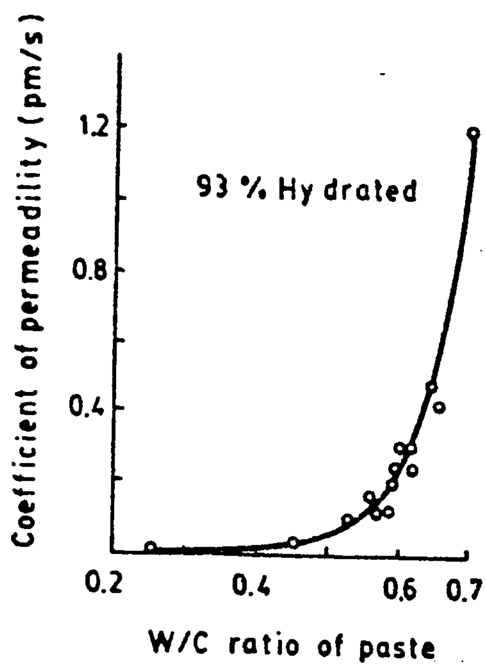

Figure 2.4 Permeability of Mature Cement Paste as influenced by Water-cement Ratio

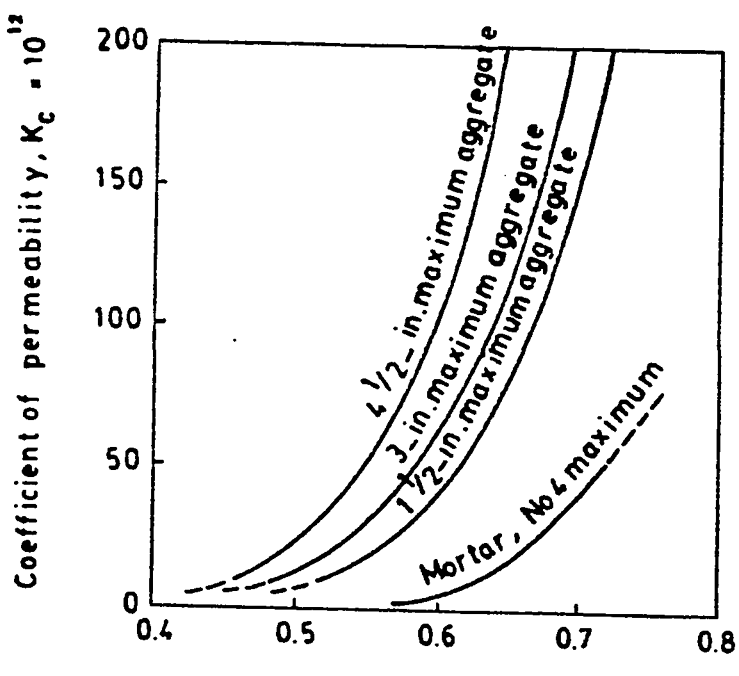

Figure 2.5 Permeability of Concretes as influenced by Water-cement Ratio

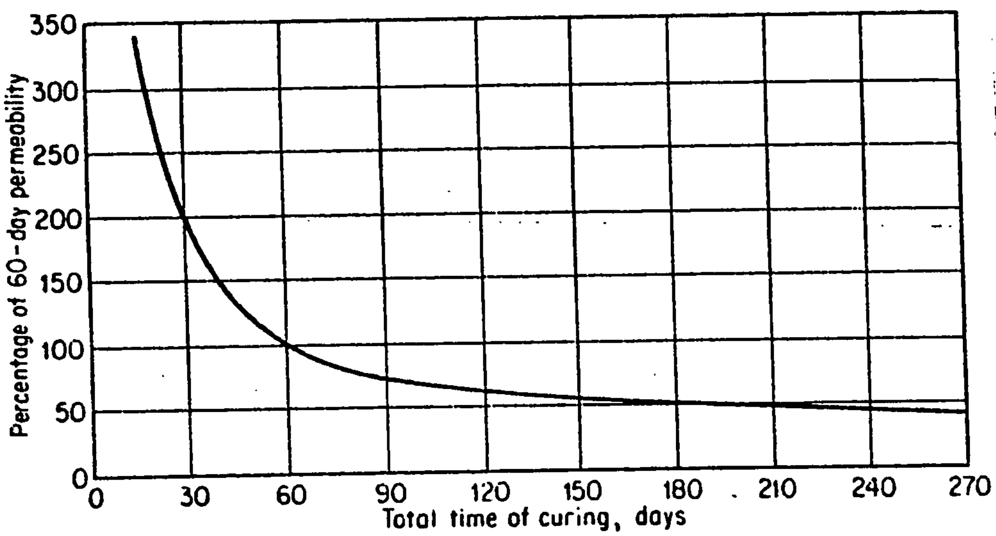

Figure 2.6 Effect of Curing Period on Permeability of Concrete

Chapter 3

METHODOLOGY OF RESEARCH

This chapter outlines the test methods used in this investigation. Wherever possible, standard ASTM or BS test methods have been adopted. In order to achieve the objectives of this test program 28 concrete mixes totalling to 674 specimens were cast for laboratory testing. Twenty one (21) mixes were cast for exposure-site evaluation of corrosion performance of pozzolan-portland cement which had a range of chloride salt content inducted in the mixing water.

3.1 CONCRETE MIXES

Concrete mixes were designed in accordance with the absolute volume method. Proportioning of the materials was carried out on weight basis. The following parameters were kept invariant for all the mixes :

1) Coarse to fine aggregate ratio : 2 : 1

2) Cement factor : 350 kg/m^3 (590 lb/yd^3)

Specific gravity and absorption of coarse and fine aggregates were determined in accordance with ASTM standard tests C127 and C128, respectively. Effective water/cement ratio was calculated incorporating 30 minutes absorption determined according to the method proposed by Newman [46].

3.2 MIXING PROCESS

The constituents were mixed in a half bag electrically operated revolving drum type concrete mixer. The coarse aggregate, used was washed free of dust with sweet water and dried at about 110°C for a period of 20 to 24 hours. Fine aggregate was only air dried. The aggregates were air cooled before use. The constituents were mixed for a period of 3 to 6 minutes from the time the water was added.

3.3 CASTING AND CURING

Different specimen sizes were used in carrying out various tests planned in this investigation. Table 3.1 shows the sizes of specimens used in this investigation. The moulds were filled in accordance with the method outlined in ASTM test method (C192) for laboratory preparation of concrete specimens. The moulds were vibrated on a vibrating table at a rate of 3600 vibrations per second until complete consolidation was assumed to have occured when a thin film of mortar appeared on the concrete surface. After casting, the specimens were air dried for about 24 hours then demoulded and stored in water at room temperature (about 25°C).

3.4 PULSE VELOCITY

Pulse-velocity was determined according to ASTM C597-71 by using PUNDIT pulse-velocity equipment, as shown in Figure 3.1. In this technique a transducer is affixed on one face of the sample which propagates ultrasonic pulses through the concrete to be received by a second transducer affixed on the opposite face. The time taken by the wave to

travel the measured path of concrete is indicated on a digital display. The path length divided by the time gives the pulse-velocity, which measures the general quality and the relative denseness of the concrete. A schematic diagram of the pulse-velocity apparatus used in this investigation is shown in Figure 3.2. Transducers of 82 kHz frequency were used in the pulse-velocity measurements. Lubricating grease was applied to the junction of the sample and the transducers to ensure a good coupling of the transducers with the concrete surface.

3.5 COMPRESSIVE STRENGTH

Compressive strength was determined on 100 mm cubes according to ASTM C39-80 on ELE Mark XII digital compressive testing machine. A load rate of 133 kN/min. was kept invariant in all the tests.

3.6 POROSITY MEASUREMENTS

Porosity was deterimined using Helium Gas Expansion-Boyle's law Porosimeter. The results of helium gas porosimetery are considered to be more accurate because: (1) the small helium molecules will penetrate the very minute submicroscopic capillary pores (0.000008-0.013mm), (2) the low mass of the helium atom allows it to have a high diffusivity into the matrix of concrete characterized by the dispersion of submicroscopic capillary and gel pores, and (3) the adsorption of helium is minimal.

In the helium porosimeter, helium gas at a regulated pressure (100 psi) is passed into a reference cell of known volume and the resulting

pressure is recorded. By inducing the gas again in a sample and recording the pressure, its volume can be calculated using Boyle's law. The dial gauge of this equipment is calibrated to read the volume directly.

The sample to be tested is placed in a core holder, 25 mm diameter and 50 mm length. Before the actual sample is placed in the core holder it is packed with solid steel discs and the line volume (V_1) is calculated. The steel discs are then replaced with the sample and helium gas is pumped in to fill the pores and the dial guage reading (V_2) is recorded. Pore volume is equal to ($V_2 - V_1$). The apparatus is shown in Figure 3.3.

The bulk volume of the sample is calculated either by accurately measuring its dimensions or by using mercury displacement method.

Porosity is then calculated using the relation:

$$\text{Porosity (\%)} = (\text{ Pore volume / Bulk volume }) \times 100$$

In this study, 25 x 50 mm cylindrical specimens cored from 150 mm cubes were used. Four specimens cored from different parts of the cubes were tested for each measurement. The cored samples were dried in an oven at 110°C for 24 hours to drive out entrapped air and moisture before they were tested for porosity. In all about 416 cylinderical specimens were tested for porosimetric measurements. Typical cored specimens for porosimetry measurements are shown in Figure 3.4.

3.7 PERMEABILITY MEASUREMENTS

Concrete permeability determination either in laboratory or in the field has met with little success, and even in the controlled conditions it is a very difficult test to perform and interpret. A typical permeability test is more expensive, time consuming, and tedious compared with some other substitute type of tests that measure the relative absorption or surface absorptive characteristics of the specimens.

3.7.1 Description of the Permeability Apparatus

The apparatus adopted for this test is shown in Figure 3.5. It is similar to those developed by Lindsay [47] and Tyler and Erlin [48]. The apparatus consists essentially of: (i) a water-tight pressure vessel (Figure 3.5), into which a 70 mm diameter and 100 mm long test specimen is placed, (ii) a hand pump for applying the hydraulic pressure, (iii) high quality pressure gauges for measuring hydraulic head, and (iv) a graduated glass cylinder for measuring the amount of water pumped into the pressure vessel, and consequently into the test specimen. The accuracy of the graduated glass cylinder is up to 0.10 ml. The pressure chamber is just large enough to accomodate the specimen, thus keeping the volume not occupied by the specimen to a minimum. Water flows by gravity from the graduated glass cylinder into the hand pump. Every attempt was made to keep all fittings leak proof, includig the top vessel. Test apparatus was fabricated at UPM workshop.

3.7.2 Test Procedure

Test specimens were cored from 100 mm cubes. Typical cored specimens

are shown in Figure 3.6.

After coring, the specimens were cleaned and kept at room temperature for about 24 hours to enable them to achieve a stable uniform state of surface moisture content. Each specimen was weighed to obtain the dry weight (Wd) and placed in the vessel chamber in water for about 15 minutes to allow it to absorb water. This time was enough to fix the apparatus and make it ready for the test. Water was pumped into the system from the graduated cylinder. Air was always removed from the system before the hydraulic pressure was applied. This is ensured by opening the exit valve V_1 and by observing the dripping of water from the outlet of the system. Valve V_1 is then closed and the water is then pumped again until the pressure gauge shows slight increase in hydraulic pressure. Valve V_1 is opened once again to allow water under pressure to drive out any air remaining in the system. Valve V_1 is then closed and water is pumped until the gauge records the required pressure of 1000 psi; thereupon the entrance valve V_2 is closed to prevent any leaking of water back to the hand pump. After 5 minutes the gauge pressure is recorded, and the entrance valve V_2 is reopened and water is pumped again till the 1000 psi hydraulic pressure is restored. At this stage, water level in the graduated glass cylinder is recorded; when deducted from the original level this gives the volume of water absorbed by the specimen during the first 5 minutes of the test. Ten minutes later, the gauge pressure is recorded and valve V_2 is reopened, water is re-pumped and water level in the cylinder is recorded. This process is repeated at 10 minutes intervals until the water absorption readings become stable at 0.10 ml or the hydraulic pressure drop is small (less

than 100 psi). The test is then concluded and the exit valve V_1 is opened to release the pressure, and the specimen withdrawn from the pressure chamber. The specimen is thoroughly cleaned with absorbent paper to remove any free water on the surface. The specimen is then weighed to give the weight of the fully saturated sample (Ws). The weight of the total water absorbed during the 15 minutes initial immersion of pre-test soaking and the water forced into the specimen under pressure during the whole period of the test is then obtained and is equal to (Ws-Wd). Thereafter, the weight of water at the start of the test due to the 15 minute immersion and the initial 1000 psi pressure applied (zero time water weight) is calculated by deducting from the total absorbed water (Ws-Wd) minus the cumulative water forced into the specimen under pressure during the whole test. Consequently, from these data, the water forced into the specimen after 5, 15, 25...etc. minutes after the initiation of the test is obtained by adding to water at zero time the corresponding value of the water forced at that time into the specimen. This data of water absorbed vs. time (in minutes) is plotted to get the relative permeability characteristics of different concrete mixes.

3.8 ACCELERATED CORROSION MONITORING

Prismatic samples 100 x 62.5 x 300 mm with a 12 mm diameter steel bar embedded in the centre of the sample were used to monitor the chloride attack. The concrete sample had an effective cover of 25 mm at the bottom. After 28 days of water curing, three prismatic specimens representing similar mix constituents were immersed in a five percent

sodium chloride solution. The quantity of solution and its level were so adjusted that the specimens were 150 mm in the solution (Figure 3.7). The concentration was monitored and adjusted on weekly basis. The negative terminal of a high impedance voltmeter was connected to the rebar and the positive terminal was hooked to a Standard Calomel half-cell reference electrode (ASTM C876-80). The corrosion activity was monitored each week by noting the potential with reference to the Calomel half-cell. In this test, potentials more positive than -270 mV represent a passive state of corrosion whereas potentials more negative than -270 mV represent an active state of corrosion.

3.9 CORROSION MONITORING AT EXPOSURE SITE

A concern often expressed by concrete technologists is in terms of the effect of the reaction of pozzolans with calcium hydroxide on the alkalinity of the concrete environment. It is argued that consumption of calcium hydroxide by pozzolans may adversely affect the alkalinity of concrete thereby creating conditions conducive to accelerated rebar corrosion. Some evidence suggests that inclusion of salt in a concrete mix especially reduces the reserve basisity and results in significantly rapid corrosion.

A test series was therefore planned to investigate this aspect of the performance of portlant-pozzolan cements. In this series the mixes were characterized by the same compositional parameters as outlined in Section 3.1. In addition, the following parameters were included in the program:

Cement replacement by fly ash : 0, 20 and 40%

Quantity of chlorides inducted: 1, 2, 4, 8 and 16 lb/yd^3

in mixing water

Other types of mixing water used : UPM saline tap water and Dhahran beach sea water

In all 21 mixes incorporating 65 prismatic specimens were made in this series. The specimen was 50 x 50 x 150 mm in size and had a centrally embedded 12 mm bar with a cover of about 25 mm on the sides, top and bottom. The specimens were positioned on the exposure-site in June 1984 as shown in Figure 3.8.

The degree of corrosion on the specimens was monitored using two techniques:

(i) Recording the time to cracking of concrete along the bar from the date of exposure.

(ii) Monitoring the loss in the weight of the bar after the removal of the corrosion products.

Time to the appearance of the first crack in the exposure-site specimens was monitored through regular visual observations of these specimens with a magnifying glass. As soon as a crack appeared, which was of hairline width to start with, it was recorded on a schedule sheet. The crack widths were also recorded after 330 days of exposure. Figure 3.9 shows two typical cracked specimens.

Weight loss provides information about total metal loss due to corrosion and pitting. To determine the loss of metal, the bars were extracted from the specimens (Figure 3.10) and the products of corrosion were removed by cleaning the bars (Figure 3.11) with Clarke's solution. Clarke's solution is inhibited hydrochloric acid and is known for being inactive in terms of attacking the base material. The bar and pits were scrubbed with a stiff bristle brush and the bar was again dipped in Clarke's solution which ensured the removal of all loose corrosion product material from the bar surface and the pits. The bar was thereafter weighed on a precision balance. The loss in weight was determined as follows:

$$\text{Weight loss (\%)} = \frac{\text{(pre-exposure weight - post exposure weight)}}{\text{pre-exposure weight}} \times 100$$

3.10 DETERMINATION OF pH VALUES OF PORTLAND-POZZOLAN CONCRETES

In order to evaluate the pH values of the hardened cement paste after reaction with fly ash which continued for a period of 300 days during the exposure of the specimens at the exposure-site, the 50 x 50 x 150 mm prismatic specimens containing the single central bar were sliced as shown in Figure 3.12. These slices were then crushed to make composite granular material consisting of coarse aggregate and the mortar powder. The coarse aggregate was seperated and the mortar was further crushed and finely ground. The fine mortar powder was then spread in a circular configuration on a glass plate and divided into eight equal radial segments. The mortar powder samples were then randomly selected from these segments for the pH determination.

The pH determinations were carried out on extracts of the hydrated cement powder. The randomly selected specimens of the fine mortar powder were mixed with distilled water in a ratio of 1:1 by weight. A rigorous mixing was carried out for 30 minutes and then the mixture was left for about one hour; thereafter the liquid phase was filtered off. The pH was then determined on this filtered liquid phase using a caliberated pH meter (Figure 3.13).

3.11 DETERMINATION OF CARBONATION DEPTH

The carbonation reaction in concrete is characterized by the conversion of calcium hydroxide into calcium carbonate by the atmospheric carbondioxide on $Ca(OH)_2$, which is present in hardened cement paste as a product of hydration. The depth of carbonated layer in a concrete component can be assessed by several different methods. X-ray or chemical analysis of suitable samples collected from different depths to determine their content of calcium hydroxide and calcium carbonate may be made in the laboratory. For the purpose of assessing the potential hazard of corrosion of embedded metal, adequate indication of the extent of carbonation is generally provided by the simple procedure of observing the resulting reduction of alkalinity by spraying appropriate freshly-broken surfaces of the concrete samples with solutions of suitable acid-base indicator compounds possessing different colours according to the alkalinity or pH value. However, tests with these indicator compounds only distinguish between the zones where the alkalinity or pH value of the environment has been maintained at a high level and the zones where the alkalinity has become reduced to a pH value in the region of 10, or lower, by carbonation.

For testing the depth of carbonation with indicator solution, any of the indicator compounds alizarin yellow (colour change from yellow to orange red in highly alkaline solution), thymolphthaline (from colourless to blue in highly alkaline solution), or phenolphthaline (from colourless to purple red in highly alkaline solution) may be used. The colour changes produced on concrete surfaces by phenolphthaline indicator solution are usually more distinct than those produced by the other two indicators, and hence phenolphathaline indicator is most commonly used.

In this study, the exposure-site specimens after 300 days of exposure were sliced on a sawing machine. This made the sliced surface exactly perpendicular to the exposed face. Using a spraying bottle, the phenolphthaline indicator solution was sprayed on the freshly sliced surface. As illustrated in Figure 3.14, a purple-red colouration is obtained almost immediately in the unaffected interior of the sample where the concrete is still highly alkaline due to the presence of calcium hydroxide. No colouration is observed in the outer most surface, where the alkalinity of the concrete environment has become reduced by penetration of atmospheric carbon dioxide.

Measurements of the depths were made at the points along each of the four sides of the exposed surface and were recorded in a tabular form.

3.12 MATERIALS USED

3.12.1 Aggregates

Coarse and fine aggregates acquired from Saudi Arabian Vulcan (SAVL), Jubail have been used in this research program. The specific gravity and 24-hour absorption data for coarse aggregate are shown in Table 3.2. Table 3.3 shows the same characteristics for the fine aggregate. The gradings of coarse and fine aggregate are shown in Figures 3.15 and 3.16, respectively.

3.12.2 Cement

Saudi Bahraini Type-V cement was used in all the mixes. The chemical composition of this cement is shown in Table 3.4.

3.12.3 Pozzolans

The following natural and artificial pozzolans and pre-blended cements were used in the test program.

1) German fly ash

2) French fly ash

3) Greek natural pozzolan

4) blast furnace slag cement

Chemical composition of these pozzolans is shown in Tables 3.5 and 3.6.

3.12.4 Water

Soft water from the UPM facility was used in the casting of concrete samples. The chemical analysis of the sweet water is shown in Table 3.7. The chemical analysis of the other types of water used in this investigation is shown in Table 3.8.

TABLE 3.1: Type and Number of Specimens Tested in This Investigation

Test	Specimen Type	Dimensions (mm)	Specimens Tested
Compression	Cubes	100	330
Pulse-Velocity	Cubes	100	386
Porosity	Cylinders	25 x 50	416
Permeability	Cylinders	70 x 100	277
Corrosion (Lab. Testing)	Prisms	62.5 x 100 x 300	75
Corrosion (Field testing)	Prisms	50 x 50 x 150	65
Total Number of Specimens			1549

TABLE 3.2: Specific Gravity and Absorption of Coarse Aggregate *

Weight of oven dry specimen	2956.50 gm
Weight of saturated surface dry in air	3024.50 gm
Weight of saturated surface dry in water	1832.60 gm
Bulk specific gravity	2.48
Bulk specific gravity (SSD)	2.54
Apparent specific gravity	2.63
Absorption	2.30 %

* Test Method: ASTM C127-80

TABLE 3.3: Specific Gravity and Absorption of Fine Aggregate *

Weight of saturated surface dry sample	669.6 gm
Weight of oven dry specimen	665.8 gm
Weight of pycnometer filled with water	1413.81 gm
Weight of pycnometer filled with specimen and water to calibration mark	1829.40 gm
Bulk specific gravity	2.62
Bulk specific gravity (SSD)	2.64
Apparent specific gravity	2.66
Absorption	0.57 %

* Test Method: ASTM C128-80

TABLE 3.4: Chemical Composition of Cement

Constituent	(% by Weight)
Silicone Dioxide (SiO_2)	22.3
Aluminium Oxide (Al_2O_3)	3.55
Ferric Oxide (Fe_2O_3)	3.63
Magnesium Oxide (MgO)	2.10
Sulfur Trioxide (SO_3)	1.93
Calcium Oxide (CaO)	64.6
Sodium Oxide (Na_2O)	0.10
Pottasium Oxide (Ka_2O)	0.21
Titanium Dioxide (TiO_2)	0.29
Loss on Ignition	1.22
Insoluble Residue	0.59
Total Sulfur	0.90
Tricalcium Aluminate (C_3A)	3.27
Tetracalcium Aluminoferrite (C_4AF)	11.04
Tricalcium Silicate (C_3S)	58.97

TABLE 3.5: Chemical Composition of Pozzolans

Cosntituent % by Weight	Fly Ash (German)	Fly Ash (French)	Fly Ash (Greek)
Silicone Dioxide (SiO_2)	60.5	47.9	37.9
Aluminium Oxide (Al_2O_3)	23.0	27.5	9.49
Ferric Oxide (Fe_2O_3)	7.52	6.23	3.61
Calcium Oxide (CaO)	2.08	2.05	27.8
Magnesium Oxide (MgO)	1.00	1.80	1.56
Sulfur Trioxide (SO_3)	0.26	0.38	1.61
Loss on Ignition	1.38	6.88	11.2

TABLE 3.6: Chemical Composition of Blast Furnace Slag Cement

Constituent	(% by Weight)
Silicone Dioxide (SiO_2)	27.7
Aluminium Oxide (Al_2O_3)	12.80
Ferric Oxide (Fe_2O_3)	1.17
Magnesium Oxide (MgO)	8.28
Sulfur Trioxide (SO_3)	3.06
Calcium Oxide (CaO)	44.0
Sodium Oxide (Na_2O)	0.49
Pottasium Oxide (Ka_2O)	0.75
Loss on Ignition	0.90

TABLE 3.7: Chemical Analysis of Sweet Water

pH	7.2
Total dissolved solids (mg / l)	674
Conductivity (µmhos / cm)	1025
Turbidity NTU	0.5
Alkalinity , bicarbonate as $CaCO_3$ (mg / l)	192
Alkalinity , carbonate as $CaCO_3$ (mg / l)	Nill
Alkalinity , hydroxide as $CaCO_3$ (mg / l)	Nill
Chloride as Cl^- (mg / l)	141
Sulfate as SO_4^{--} (mg / l)	42.5
Hardness , total as $CaCO_3$ (mg / l)	59
Hardness , calcium as $CaCO_3$ (mg / l)	31.3
Hardness , magnesium as $CaCO_3$ (mg / l)	27.7
Sodium & Pottasium (mg / l)	144

TABLE 3.8: Chemical Analysis of Different Types of Water Used in This Investigation

Cosntituent % by Weight	Sweet Water	UPM Saline Tap Water	UPM Beach Water
Total Solids , in (mg/l)	659 689	3,275 3,200	62,632 62,234
Conductivity , (μ mhos / cm)	1,000 1,050	4,800 4,700	104,000 103,000
Chloride as Cl^- , in (mg/l)	143 138.5	1,179 1,128	50,397 49,976
Sulfate as SO_4^{--} , in (mg/l)	50 35	450 440	3,400 3,300

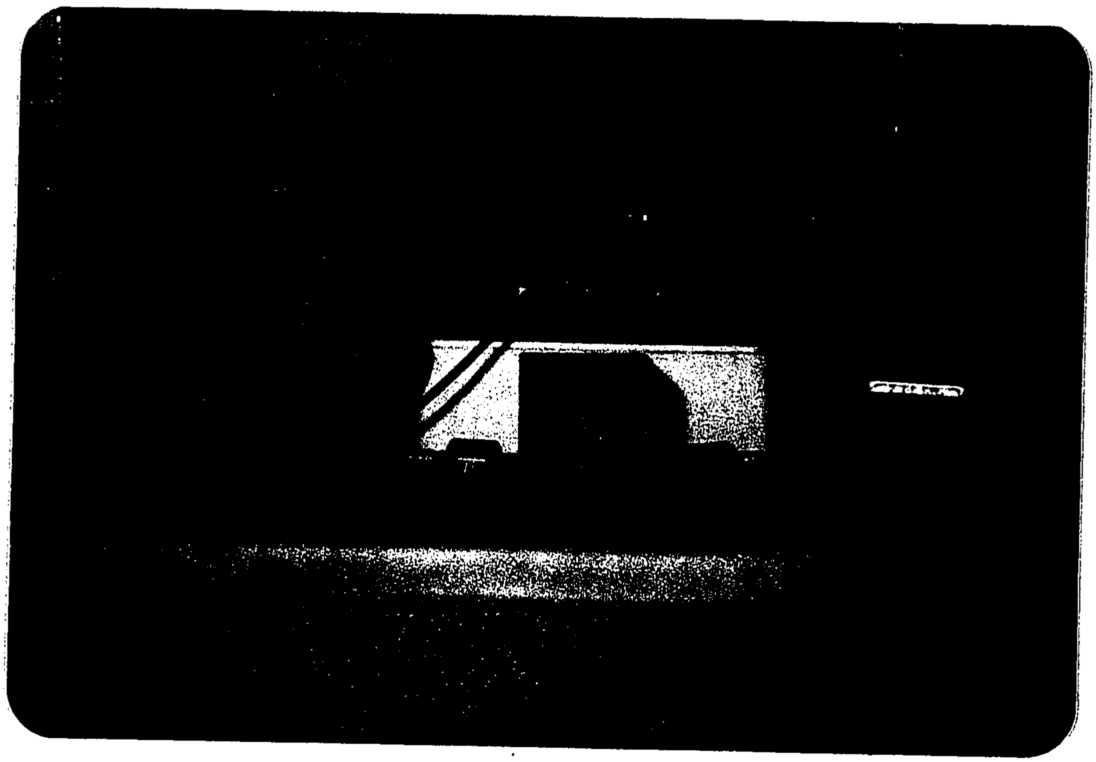

Figure 3.1 Pulse-Velocity Apparatus

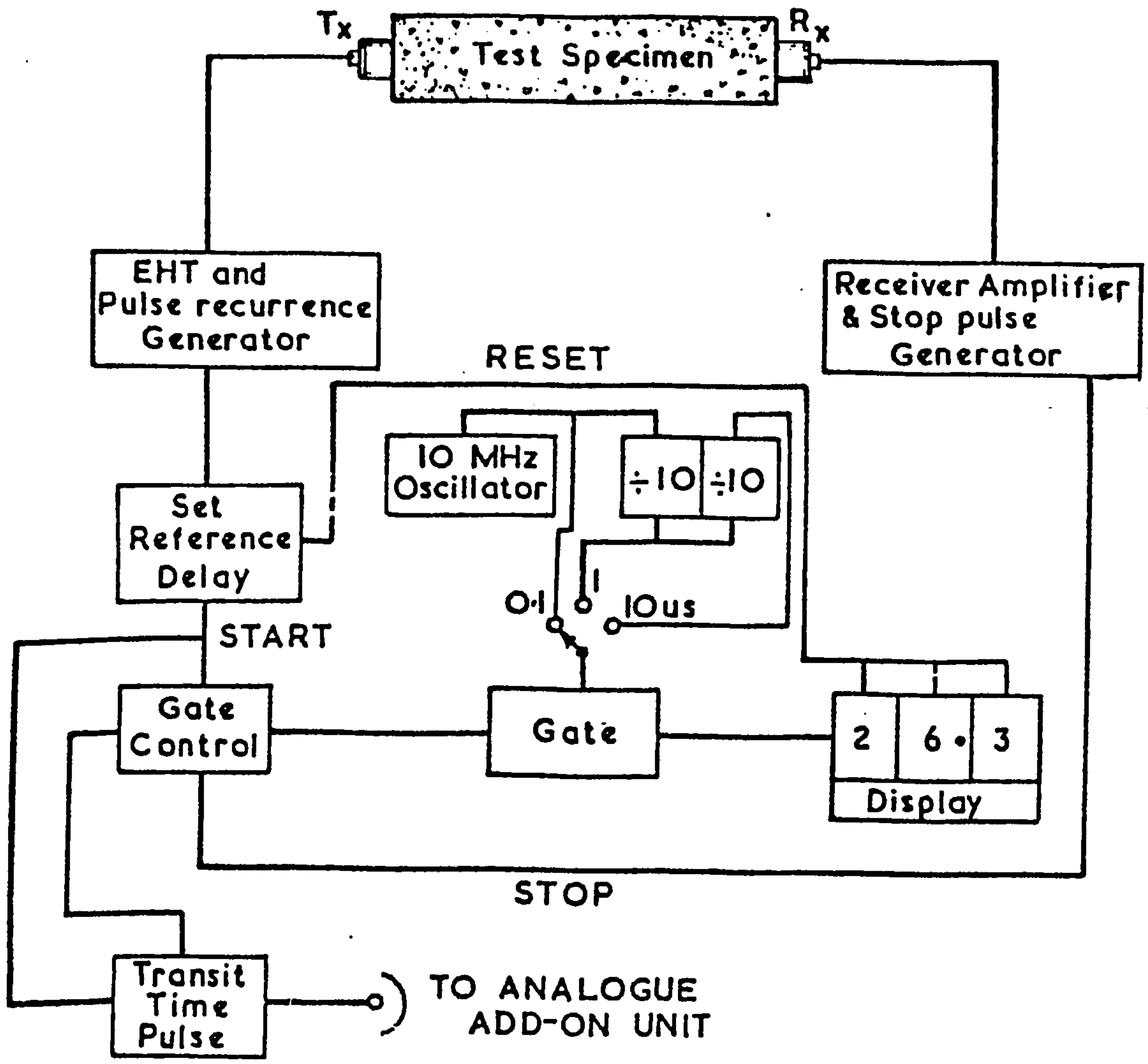

Figure 3.2 Schematic Diagram of the Pulse-Velocity Apparatus

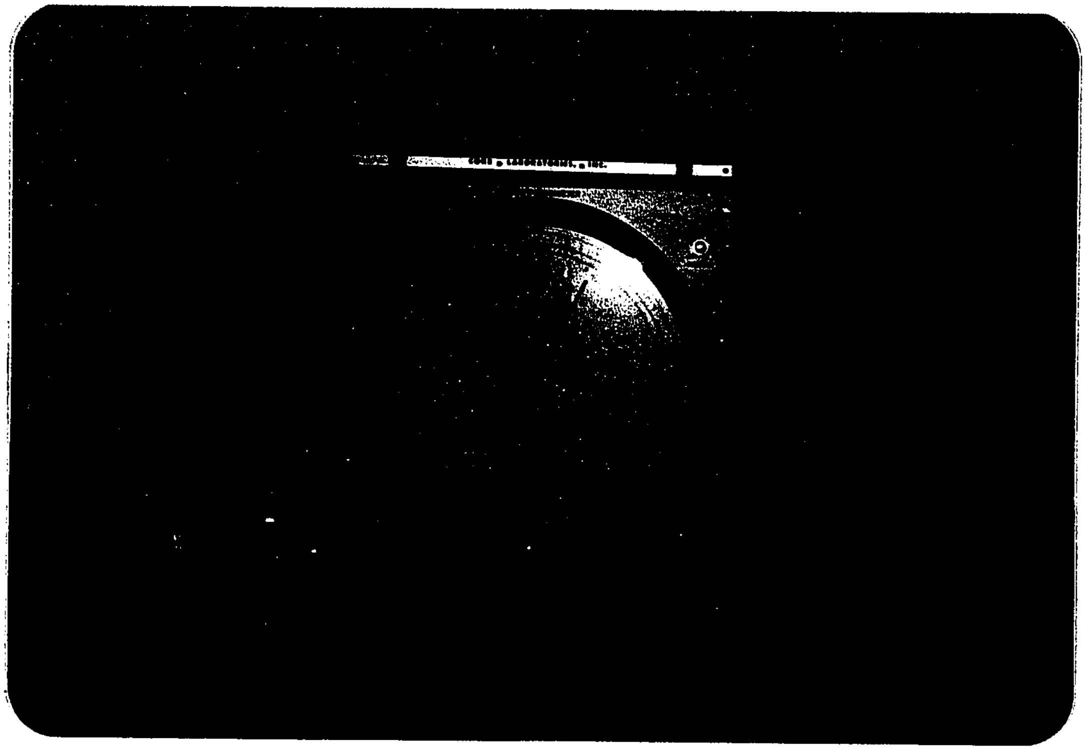

Figure 3.3 Apparatus used to Measure the Porosity

Figure 3.4 Specimens used for the Porosity Measurement

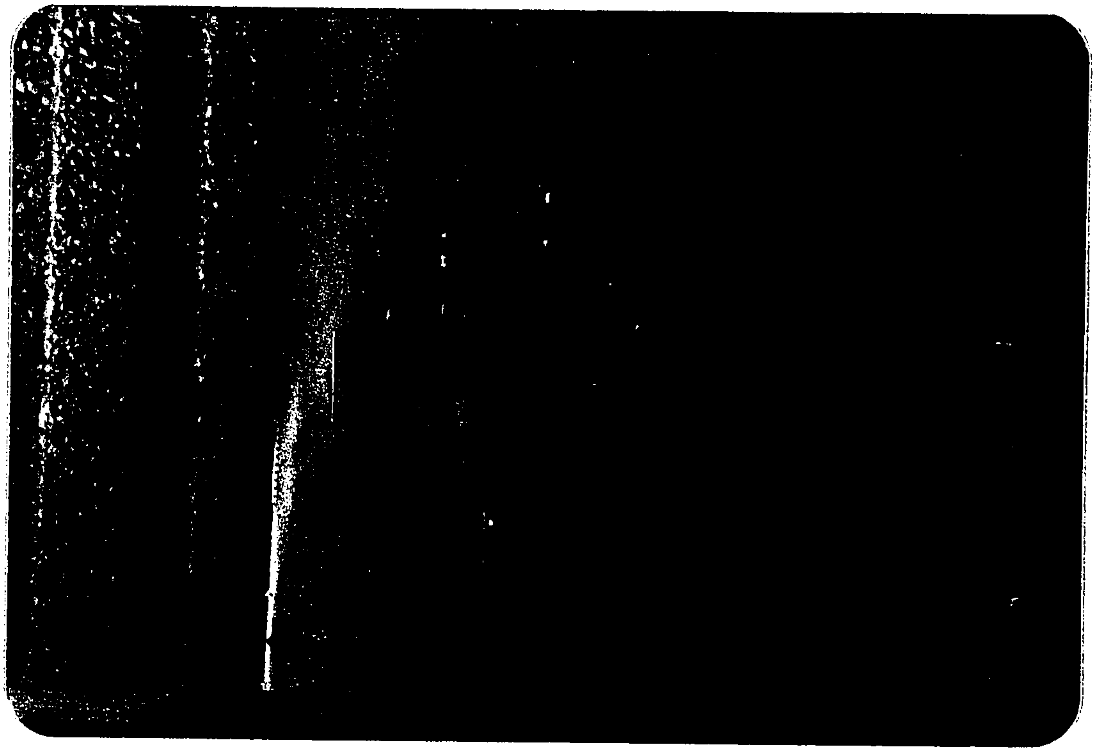

Figure 3.5 Apparatus used to Measure the Permeability

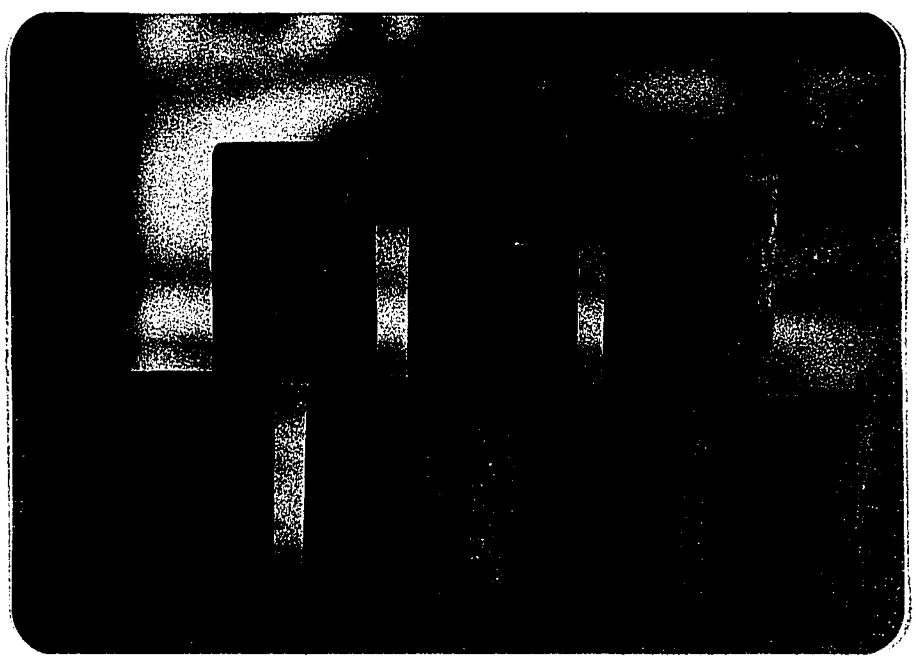

Figure 3.6 Specimens used for the Permeability Measurements

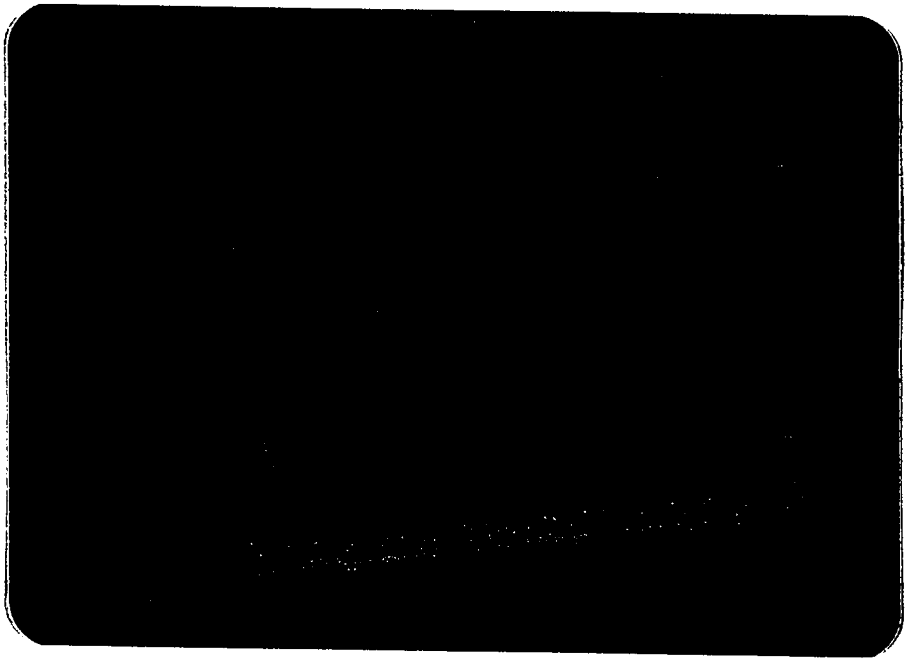

Figure 3.7 Laboratory Corrosion Monitoring Setup

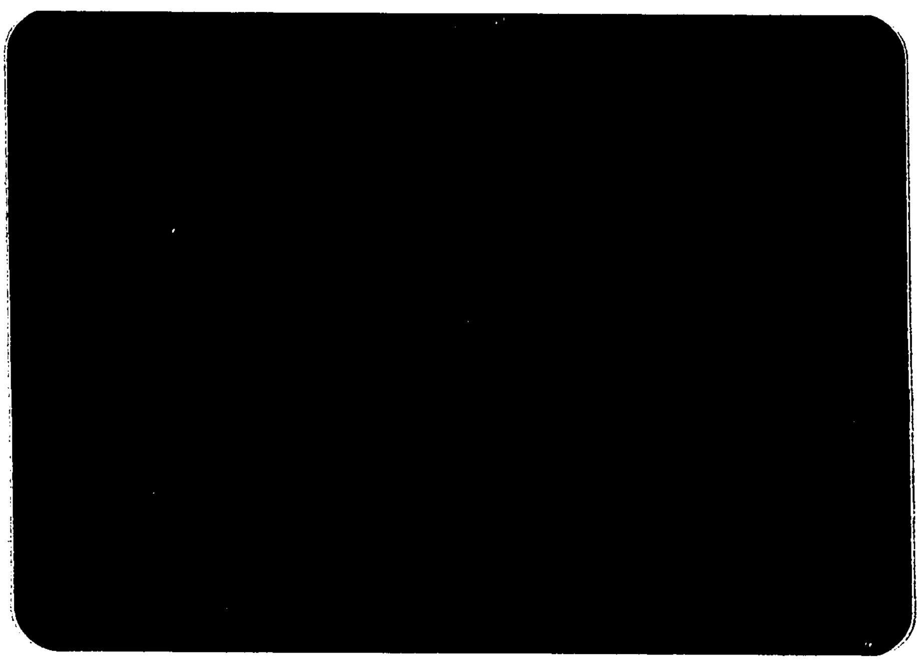

Figure 3.8 Corrosion Monitoring Samples at Exposure - Site

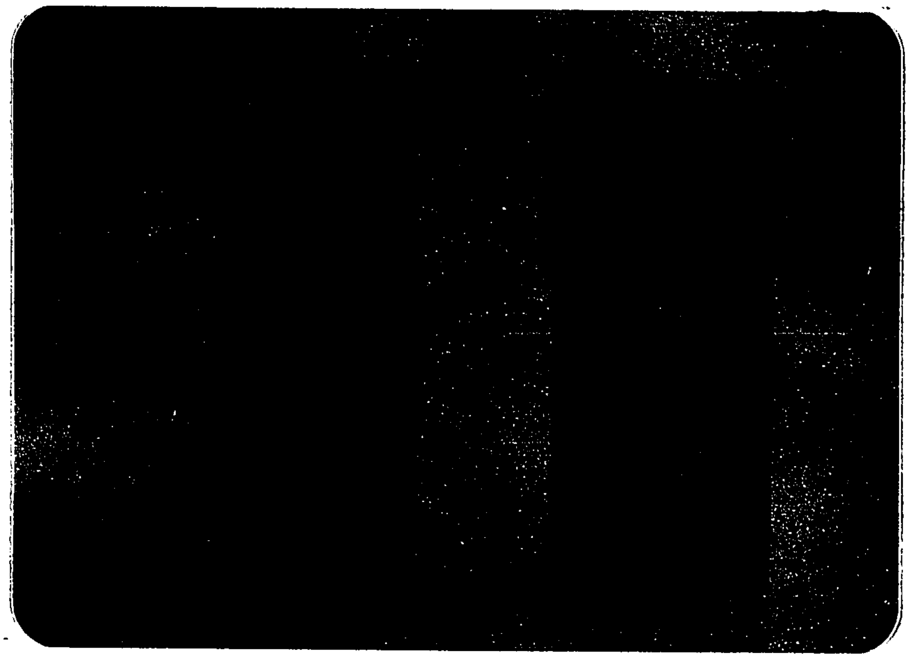

Figure 3.9 Two Typical Exposure - Site Cracked Specimens

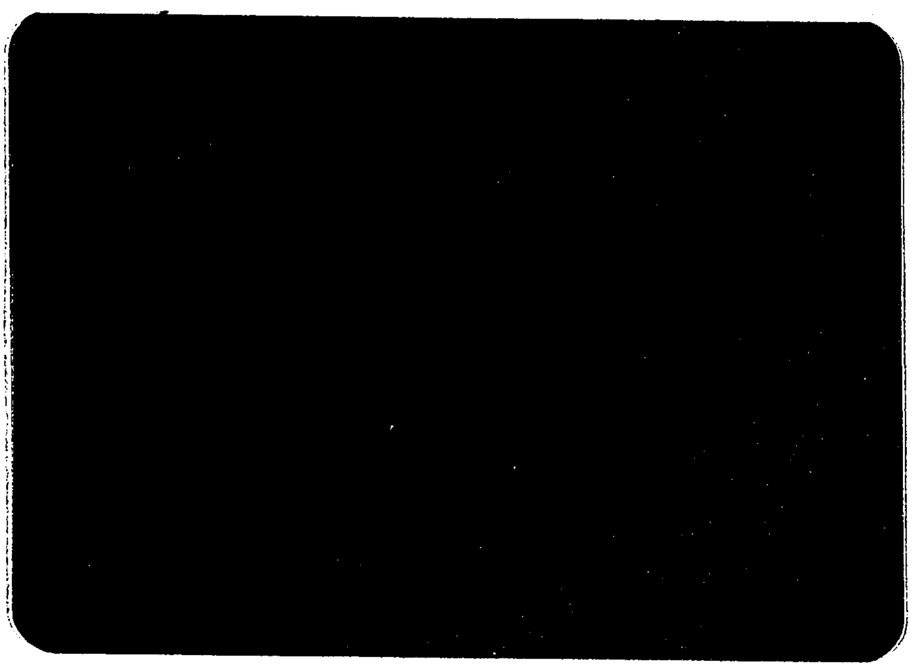

Figure 3.10 Reinforcing Bar Specimen Extracted from Exposure - Site Samples (before cleaning)

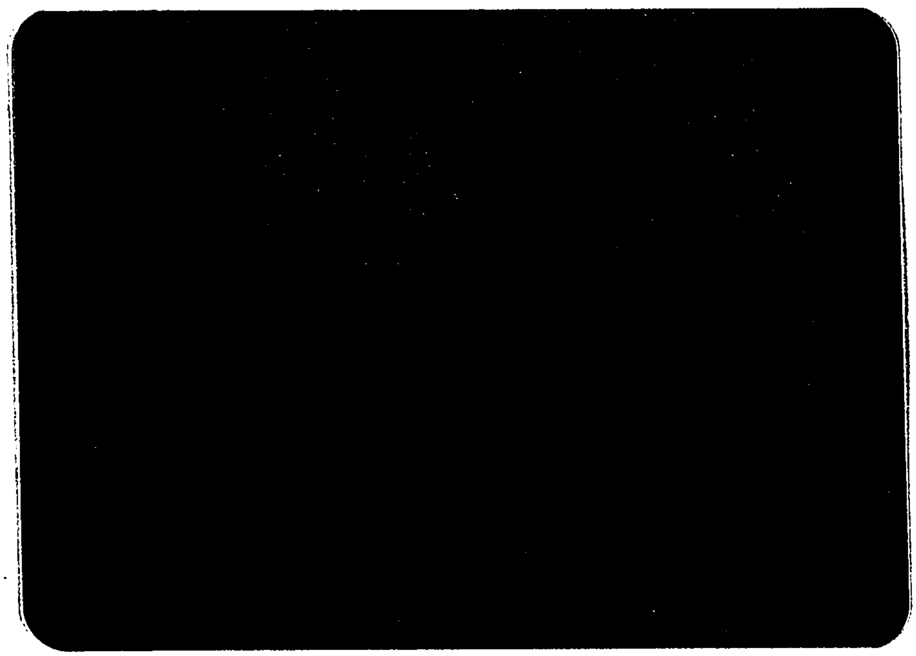

Figure 3.11 Reinforcing Bar Specimen extracted from Exposure - Site Samples (after cleaning)

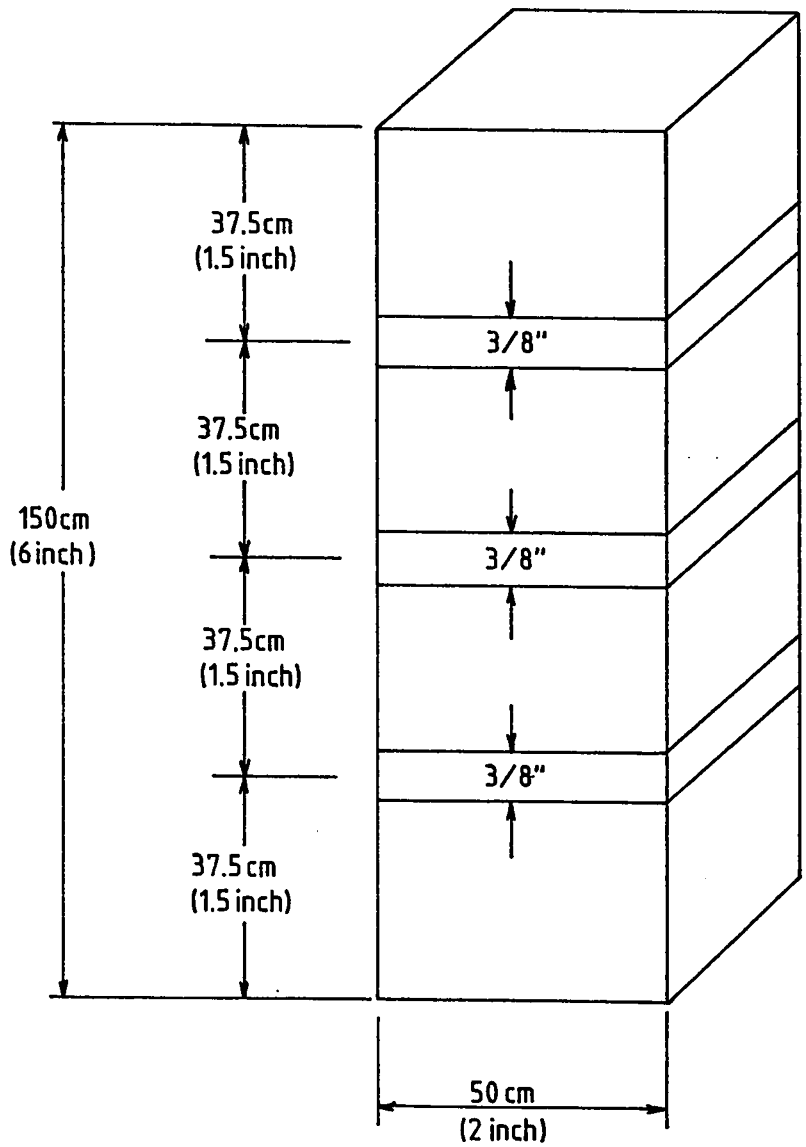

Figure 3.12 Slicing Plan of Exposure - Site Samples

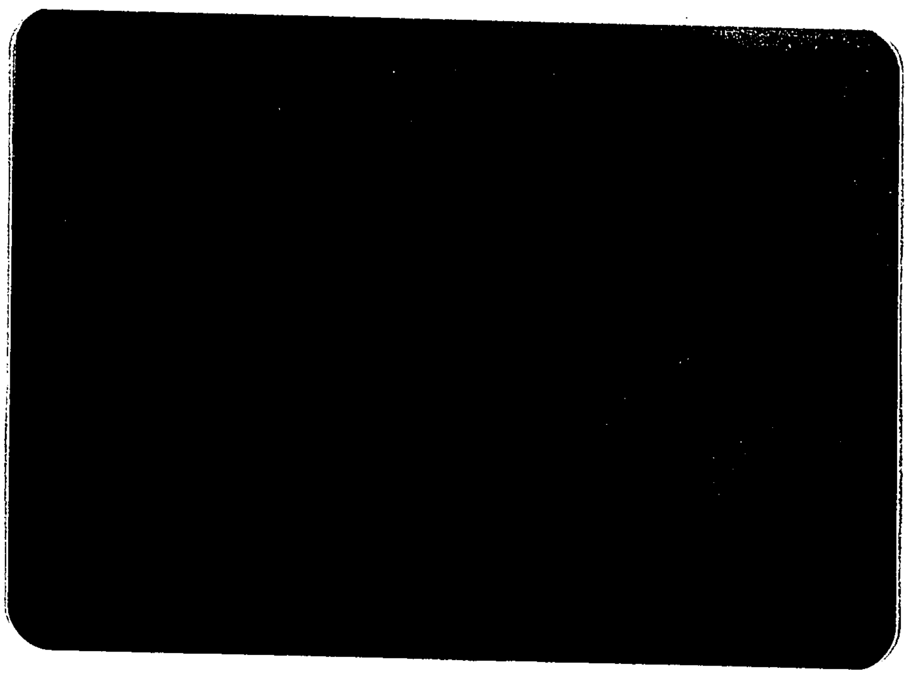

Figure 3.13 pH Meter used to determine the pH Values of the Exposure - Site Specimens

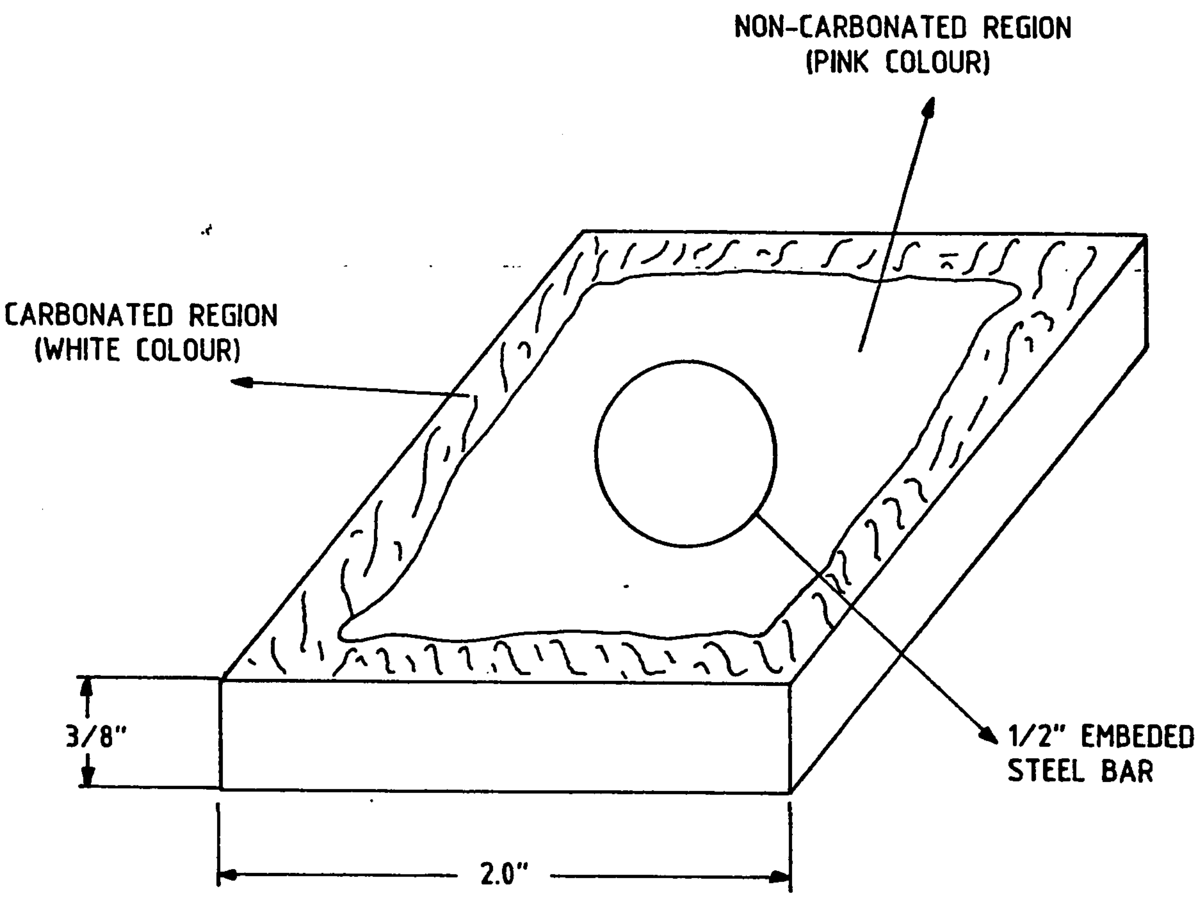

Figure 3.14 Exposure - Site Samples tested for Carbonation Depth

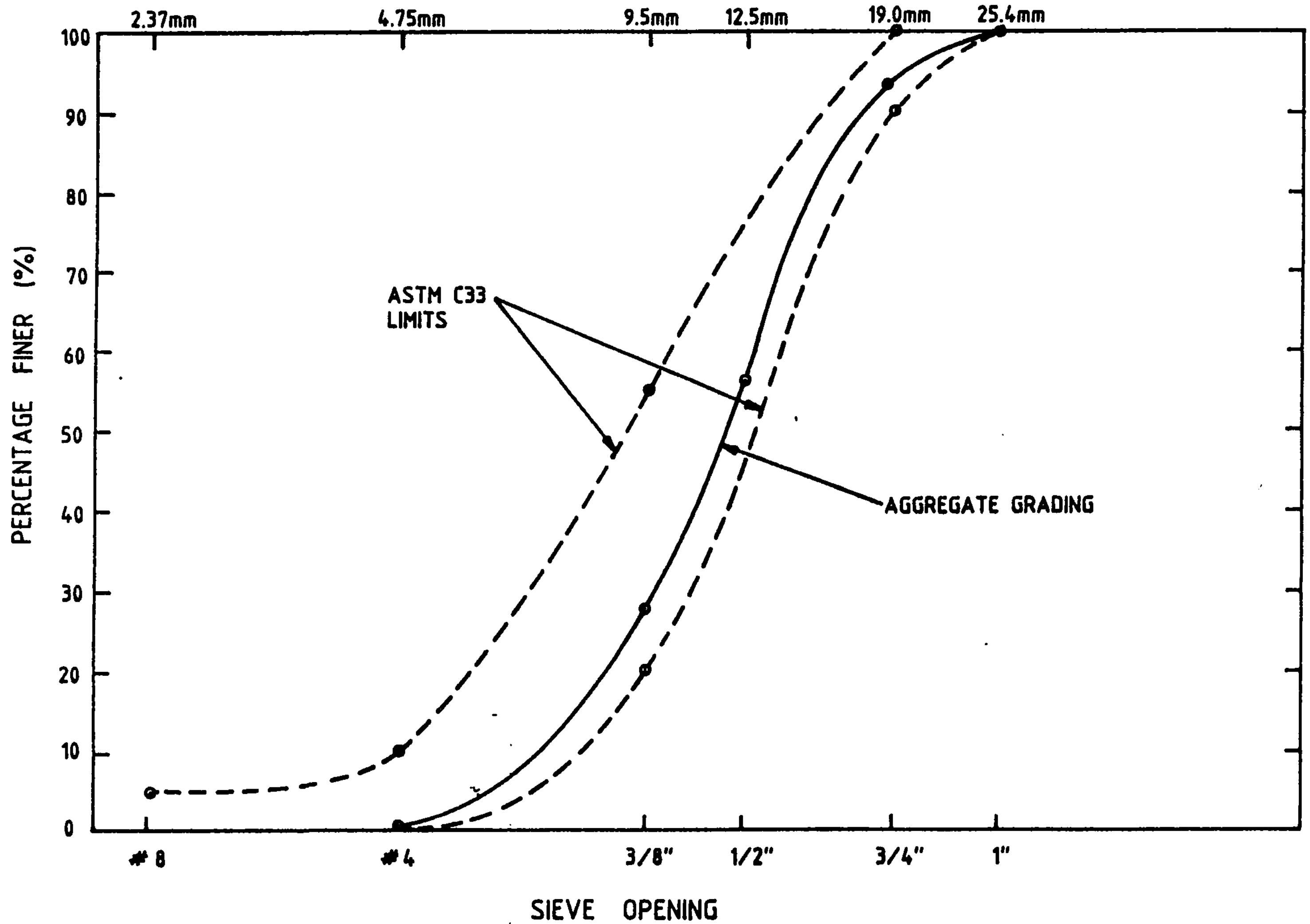

Figure 3.15 Grading of Coarse Aggregate

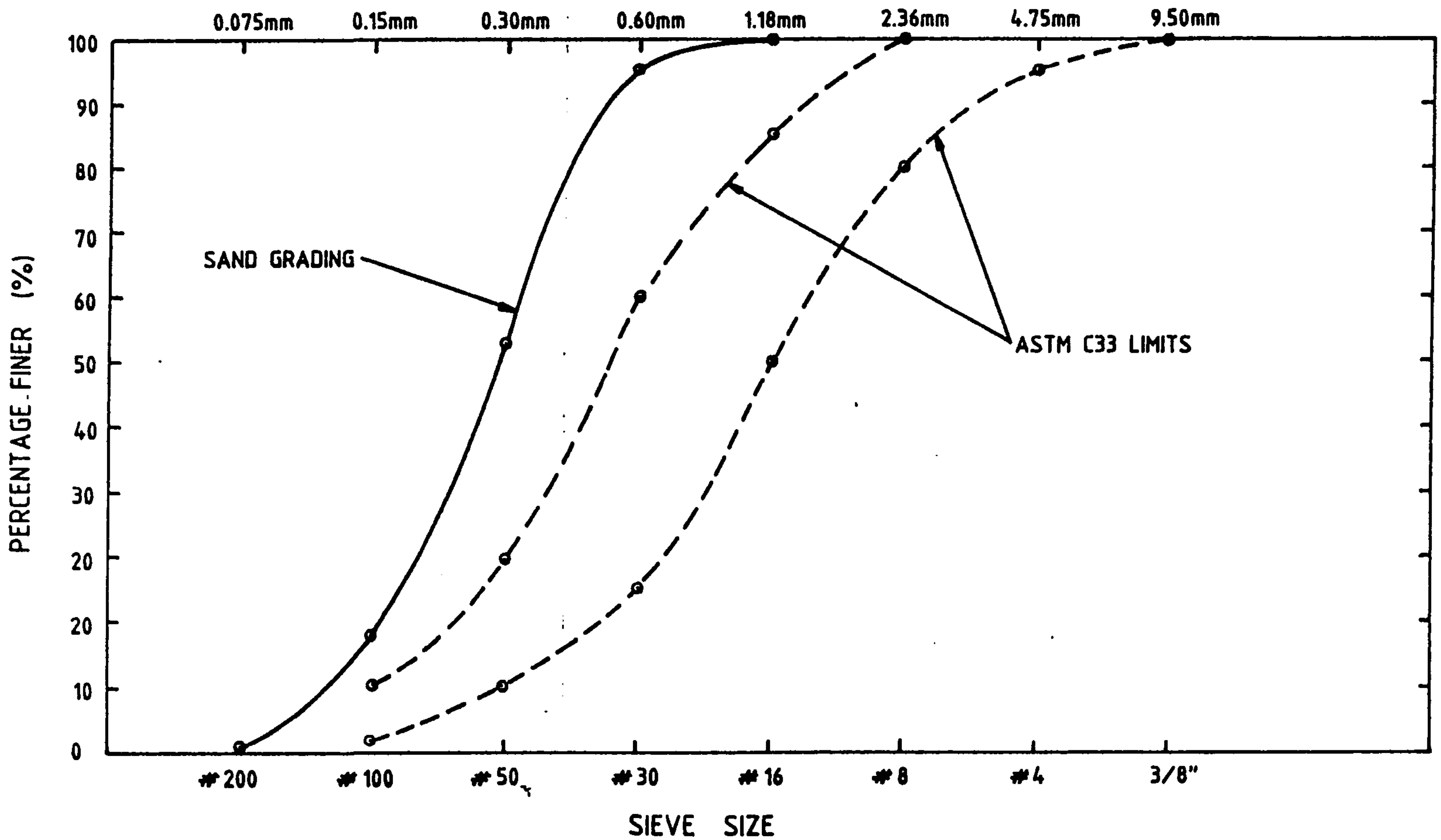

Figure 3.16 Grading of Fine Aggregate

Chapter 4

RESULTS

4.1 INTRODUCTION

The results of this investigation are presented in Figures 4.1 through 4.34. Broadly speaking, the data developed fall in three categories:

(i) permeability and porosity characteristics of portland-pozzolan concretes,

(ii) strength of portland-pozzolan concretes, and

(iii) durability performance of portland-pozzolan concretes against rebar corrosion which has been ascertained to be the number one durability problem in the Gulf region.

The data on porosity are presented in Table 4.1 and are shown graphically in Figures 4.1 through 4.7 and that of permeability are shown in Table 4.2 and Figures 4.8 through 4.16. Table 4.3 and Figures 4.17 through 4.23 show the pulse-velocity data. These data pertain to three techniques used to evaluate the permeability and general quality of portland-pozzolan concrete in comparison with the straight portland cement concrete. Helium porosimetry, pulse-velocity technique and water-permeability measurements under high pressure have been used to evaluate the degree of impermeability or water tightness imparted to concretes of different water-cement ratios by blending fly ash pozzolan with portland cement in various proportions. Strength data for

porland-pozzolan concretes have been developed upto a period of 180 days. These data are presented in Table 4.4 and Figures 4.24 through 4.30.

Attempts have been made to develop the performance data against corrosion on the basis of accelerated laboratory and exposure-site corrosion tests as explained in Sections 3.8 and 3.9. The results of accelerated rebar corrosion testing with fly ash replacement ranging from 0 to 40% are presented in Figures 4.31 through 4.34. For the exposure-site specimens results related to corrosion monitoring, pH determination and depth of carbonation are shown in Tables 4.5 through 4.8

4.2 RESULTS RELATED TO POROSITY, PERMEABILITY AND GENERAL QUALITY OF PORTLAND-POZZLAN CONCRETES

4.2.1 Porosity Characteristics

Figures 4.1 through 4.5 show the effect of age and cement replacement by fly ash on the porosity of reference and portland-pozzolan concretes. These data relate to cement replacement by fly ash in the range of 0 to 40% and porosity measurements upto the age of one year. The specimens tested had a cementitious phase (cement or cement plus fly ash) content of 350 kg/m^3 and water-cement ratios of 0.35, 0.385, 0.45, 0.50 and 0.55.

The effect of water-cement ratio on porosity for plain and

portland-pozzolan concrete specimens with 20% cement replacement is shown in Figure 4.6.

Figure 4.7 shows the porosity characteristics of concretes made with four cements; namely German fly ash, French fly ash, Greek natural pozzolan, and blast furnace slag cement.

4.2.2 Permeability Measurements

Figures 4.8 through 4.12 show the effect of age and cement replacement by fly ash on the permeability characteristics of reference and portland-pozzolan concretes. As in the case of porosity data, the permeability measurements were obtained on portland-pozzolan concrete specimens made with cement replacement by fly ash in the range of 0 to 40%. Permeability data were obtained at ages of 28, 90, 180 and 365 days. The data shown in Figures 4.8 through 4.12 have been compiled by evaluating the total amount of water absorbed in the specimen during the permeability tests described in Section 3.7. Each point on the curves in Figures 4.8 through 4.12 is an average of 2 or 3 permeability measurements. The typical permeability curves obtained as a result of high pressure permeability measurements are shown in Figures 4.13 through 4.14 for water-cement ratio of 0.35 (10% cement replacement by fly ash) and water-cement ratio of 0.55 (20% cement replacement by fly ash). Each figure incorporates four curves corresponding to ages of 28, 90, 180 and 365 days.

These curves were developed for about 280 specimens corresponding to

five water-cement ratios, four cement replacements, four ages and usually two to three specimens for each test to obtain an average value for that test.

The effect of water-cement ratio on permeability of plain and portland-pozzolan specimens with 20% cement replacement is shown in Figure 4.15.

Figure 4.16 shows the permeability characteristics of concretes made with German fly ash, French fly ash, Greek natural pozzolans and blast furnace slag cement.

4.2.3 Pulse-Velocity Measurements

Figures 4.17 through 4.21 show the effect of age and cement replacement by fly ash on the pulse-velocity measurements of reference and portland-pozzolan concretes. As in the case of porosity and permeability measurements, pulse-velocity data have been developed for specimens with cement replacement by fly ash in the range of 0 to 40%. Measurements were made at ages of 28, 90, 180 and 365 days. The specimens had a cementitious phase of 350 kg/m^3 and water-cement ratios of 0.35, 0.385, 0.45, 0.50 and 0.55. The effect of water-cement ratio on pulse-velocity observations for plain and 20% fly ash concretes is shown in Figure 4.22.

Figure 4.23 shows the pulse-velocity data for concretes made with German fly ash, French fly ash, Greek natural pozzolan and blast furnace slag cement.

4.3 RESULTS RELATED TO THE STRENGTH OF PORTLAND-POZZOLAN CONCRETES

Figures 4.24 through 4.28 show the strength development characteristics of portland-pozzolan concretes in comparison to the straight cement concrete for a period of six months. The portland-pozzolan concrete specimens were made with cement replacements by fly ash of 10, 20, 30 and 40%. The cementitious phase content was kept constant at 350 kg/m^3. The water-cement ratios used were 0.35, 0.385, 0.45, 0.50 and 0.55. The effect of water-cement ratio on compressive strength is shown in Figure 4.29. Figure 4.30 shows the strength characteristics of concretes made with German fly ash, French fly ash, Greek natural pozzolan and blast furnace slag.

4.4 RESULTS RELATED TO THE DURABILITY PERFORMANCE OF PORTLAND-POZZOLAN CONCRETE AGAINST REBAR CORROSION

Figures 4.31 through 4.34 show the half cell potentials of rebars embedded centrally in plain and portland-pozzolan concrete specimens for a period of more than 400 days. These specimens were subjected to an accelerated corrosion inducing environment of chloride salt solution as explained in Section 3.8.

For the exposure-site specimens, corrosion monitoring was carried out in terms of the time to cracking, crack width and weight loss of metal. The cracking data are shown in Table 4.5 whereas the weight loss data are shown in Table 4.6. Figure 4.35 shows a typical assortment of specimens showing different extent of cracking.

The pH data developed following the technique described in Section 3.10 are detailed in Table 4.7. Table 4.8 shows the depth of carbonation data developed on the exposure-site specimens. Figures 4.36 and 4.37 show typical specimens investigated for depth of carbonation determinations.

TABLE 4.1: Data on Porosity of Plain and Pozzolan Concrete

Water to Cement Ratio	Cement Replaced by Pozzolan	Average Porosity (%) at			
		28 days	90 days	180 days	365 days
0.35	0 %	10.704	10.025	9.443	9.207
0.35	10 %	11.10	9.215	8.30	8.10
0.35	20 %	11.326	8.687	7.50	7.335
0.35	30 %	11.50	9.00	7.858	7.707
0.35	40 %	12.089	9.80	8.70	8.45
0.385	0 %	11.00	10.30	9.80	9.55
0.385	10 %	11.40	9.90	8.90	8.401
0.385	20 %	11.663	9.30	8.102	7.70
0.385	30 %	11.929	9.645	8.50	8.032
0.385	40 %	12.783	10.48	9.40	8.80
0.45	0 %	11.818	10.90	10.45	10.10
0.45	10 %	12.30	10.65	9.60	9.10
0.45	20 %	12.51	10.097	8.90	8.40
0.45	30 %	13.00	10.45	9.20	8.762
0.45	40 %	13.272	11.189	10.045	9.50
0.50	0 %	12.80	11.525	11.00	10.795
0.50	10 %	13.013	11.253	10.492	10.20
0.50	20 %	13.480	10.853	9.85	9.55
0.50	30 %	14.00	11.343	10.256	9.90
0.50	40 %	14.358	11.90	10.771	10.382
0.55	0 %	13.808	12.598	12.015	11.800
0.55	10 %	14.032	12.325	11.441	10.906
0.55	20 %	14.40	12.089	10.80	10.20
0.55	30 %	15.00	12.41	11.10	10.55
0.55	40 %	15.344	13.039	11.80	11.290

TABLE 4.2: Data on Permeability of Plain and Pozzolan Concrete

Water to Cement Ratio	Cement Replaced by Pozzolan	Average Permeability (ml) at			
		28 days	90 days	180 days	365 days
0.35	0 %	19.52	15.71	14.00	12.80
0.35	10 %	22.22	13.80	10.20	8.70
0.35	20 %	22.72	12.90	9.000	7.60
0.35	30 %	23.91	14.90	11.20	9.41
0.35	40 %	25.02	16.10	12.30	10.30
0.385	0 %	21.88	16.80	14.68	13.50
0.385	10 %	23.99	14.94	11.10	9.80
0.385	20 %	24.82	14.00	9.90	8.70
0.385	30 %	25.76	15.95	12.00	10.50
0.385	40 %	27.81	17.20	13.10	11.40
0.45	0 %	23.60	18.08	15.80	14.50
0.45	10 %	24.41	15.90	12.20	11.25
0.45	20 %	24.90	15.68	11.40	10.10
0.45	30 %	25.80	17.05	12.96	11.85
0.45	40 %	26.58	18.40	14.00	12.50
0.50	0 %	24.60	21.00	18.19	15.60
0.50	10 %	26.63	20.00	14.40	12.00
0.50	20 %	27.43	19.20	13.30	11.00
0.50	30 %	27.79	20.60	15.20	12.50
0.50	40 %	29.02	21.65	16.50	13.60
0.55	0 %	26.55	22.84	18.40	16.90
0.55	10 %	28.19	22.40	15.80	12.60
0.55	20 %	28.59	21.60	14.80	11.70
0.55	30 %	29.50	23.20	16.50	13.10
0.55	40 %	30.31	24.20	17.70	14.50

TABLE 4.3: Data on Pulse-Velocity of Plain and Pozzolan Concrete

Water to Cement Ratio	Cement Replaced by Pozzolan	Average Pulse-Velocity (m/s) at			
		28 days	90 days	180 days	365 days
0.35	0 %	4892	4994	5110	5174
0.35	10 %	4813	4956	5105	5197
0.35	20 %	4733	4925	5112	5217
0.35	30 %	4704	4890	5050	5131
0.35	40 %	4626	4830	5005	5093
0.385	0 %	4794	4908	5005	5060
0.385	10 %	4740	4865	4995	5070
0.385	20 %	4697	4854	5007	5093
0.385	30 %	4644	4823	4955	5030
0.385	40 %	4593	4770	4910	5000
0.45	0 %	4672	4823	4930	4967
0.45	10 %	4614	4805	4920	4975
0.45	20 %	4559	4775	4932	4995
0.45	30 %	4516	4748	4880	4940
0.45	40 %	4461	4697	4850	4920
0.50	0 %	4620	4780	4878	4933
0.50	10 %	4577	4755	4873	4940
0.50	20 %	4540	4735	4880	4956
0.50	30 %	4507	4711	4838	4902
0.50	40 %	4492	4680	4804	4885
0.55	0 %	4522	4704	4850	4920
0.55	10 %	4496	4682	4845	4926
0.55	20 %	4463	4653	4855	4942
0.55	30 %	4456	4618	4800	4885
0.55	40 %	4450	4590	4765	4867

TABLE 4.4: Data on Compressive Strength of Plain and Pozzolan Concrete

Water to Cement Ratio	Cement Replaced by Pozzolan	Average Compressive Strenght (psi) at		
		28 days	90 days	180 days
0.35	0 %	8185 (56.43)	9035 (62.29)	9189 (63.36)
0.35	10 %	7735 (53.33)	8550 (58.95)	8800 (60.67)
0.35	20 %	6947 (47.90)	7900 (54.47)	8350 (57.57)
0.35	30 %	6274 (43.26)	7412 (51.10)	7840 (54.06)
0.35	40 %	5693 (39.25)	6950 (47.92)	7400 (51.02)
0.385	0 %	7601 (52.41)	8400 (57.92)	8660 (59.71)
0.385	10 %	7348 (50.66)	8098 (55.82)	8360 (57.64)
0.385	20 %	6795 (46.85)	7600 (52.40)	7950 (54.81)
0.385	30 %	6214 (42.84)	7150 (49.30)	7503 (51.73)
0.385	40 %	5649 (38.95)	6600 (45.51)	7023 (48.42)
0.45	0 %	6922 (47.73)	7750 (53.43)	8086 (55.75)
0.45	10 %	6291 (43.38)	7250 (49.99)	7756 (53.48)
0.45	20 %	5519 (38.05)	6800 (46.88)	7350 (50.68)
0.45	30 %	4851 (33.45)	6320 (43.58)	6900 (47.57)
0.45	40 %	4337 (29.90)	5850 (40.33)	6519 (44.95)
0.50	0 %	6049 (41.71)	7128 (49.15)	7588 (52.32)
0.50	10 %	5200 (35.85)	6500 (44.82)	7100 (48.95)
0.50	20 %	4600 (31.72)	6013 (41.46)	6600 (45.51)
0.50	30 %	4250 (29.30)	5650 (38.96)	6250 (43.09)
0.50	40 %	3949 (27.23)	5339 (36.81)	6023 (41.53)
0.55	0 %	5085 (35.06)	6100 (42.06)	6500 (44.82)
0.55	10 %	4805 (33.13)	5800 (39.99)	6200 (42.75)
0.55	20 %	4200 (28.96)	5255 (36.23)	5878 (40.53)
0.55	30 %	3920 (27.03)	4900 (33.78)	5600 (38.61)
0.55	40 %	3000 (20.68)	4000 (27.58)	4655 (32.10)

Note: Numbers in parenthesis are equivalent values in MPa
1.0 psi = 0.0068948 MPa

TABLE 4.5 : Data on Cracking Status of the Exposure-Site Samples

Sample No.	Pozzolan (%)	Chloride content lb/yd³	Cracking Status: Cracked, C / Uncracked, U	Cracking Status: Observed date of Cracking	Cracking Status: Average crack width (mm)
2	0	1	U		
3	0	1	U		
4	0	1	U		
6	20	1	U		
7	20	1	U		
8	20	1	U		
10	40	1	U		
11	40	1	U		
13	0	2	U		
14	0	2	U		
16	20	2	U		
17	20	2	U		
19	40	2	U		
20	40	2	U		
22	0	4	U		
23	0	4	U		
25	20	4	U		
26	20	4	U		
28	40	4	U		
29	40	4	U		
31	0	Tap water	U		
32	0	Tap water	U		

Cont'd. TABLE 4.5

34 35	20 20	Tap water Tap water	U U		
37 38	40 40	Tap water Tap water	U U		
40 41	0 0	8 8	U U		
43 44	20 20	8 8	U U		
46 47	40 40	8 8	U U		
49 50	0 0	16 16	C C	April 1, 1985 April 21,1985	0.20 0.40
52 53	20 20	16 16	C C	March 24,1985 April 1, 1985	0.35 0.18
54 56	40 40	16 16	C C	March 20,1985 March 24,1985	2.00 2.10
58 59	0 0	Sea water Sea water	U U		
61 62	20 20	Sea water Sea water	U U		
64 65	40 40	Sea water Sea water	U C	 March 24,1985	 0.43

TABLE 4.6 : Data on Weight Loss of Rebars of the Exposure-Site Samples

Sample No.	Pozzolan (percent)	Chloride content (lb/yd^3)	Percent Loss in Weight
1	0	1	11.12
5	20	1	8.50
9	40	1	9.36
12	0	2	9.97
15	20	2	8.62
18	40	2	17.78
21	0	4	12.64
24	20	4	6.96
27	40	4	7.99
30	0	Saline tap water	3.81
33	20	Saline tap water	10.97
36	40	Saline tap water	12.45
39	0	8	10.71
42	20	8	12.74
45	40	8	11.23
48	0	16	17.70
51	20	16	12.39
55	40	16	12.14
57	0	Sea water	8.53
60	20	Sea water	9.72
63	40	Sea water	8.43

TABLE 4.7 : Data on pH Values of the Exposure-site Samples

Sample No.	Pozzolan (percent)	Chloride content (lb/yd^3)	pH Value
1	0	1	12.70
5	20	1	12.30
9	40	1	12.22
12	0	2	12.35
15	20	2	12.30
18	40	2	12.40
21	0	4	12.25
24	20	4	12.30
27	40	4	12.30
30	0	Saline tap water	12.25
33	20	Saline tap water	12.40
36	40	Saline tap water	12.70
39	0	8	12.75
42	20	8	12.35
45	40	8	12.25
48	0	16	12.35
51	20	16	12.40
55	40	16	12.40
57	0	Sea water	12.60
60	20	Sea water	12.50
63	40	Sea water	12.25

TABLE 4.8 : Data on Carbonation Depth of the Exposure-Site Samples

Sample No.	Pozzolan (percent)	Chloride content (lb/yd³)	Average Depth of Carbonation, in millimeter
1	0	1	3.0
5	20	1	5.6
9	40	1	6.9
12	0	2	4.4
15	20	2	5.4
18	40	2	6.9
21	0	4	3.4
24	20	4	5.7
27	40	4	9.7
30	0	Saline tap water	2.9
33	20	Saline tap water	5.4
36	40	Saline tap water	8.0
39	0	8	3.5
42	20	8	5.2
45	40	8	9.8
48	0	16	5.1
51	20	16	6.0
55	40	16	9.8
57	0	Sea water	1.8
60	20	Sea water	4.3
63	40	Sea water	6.2

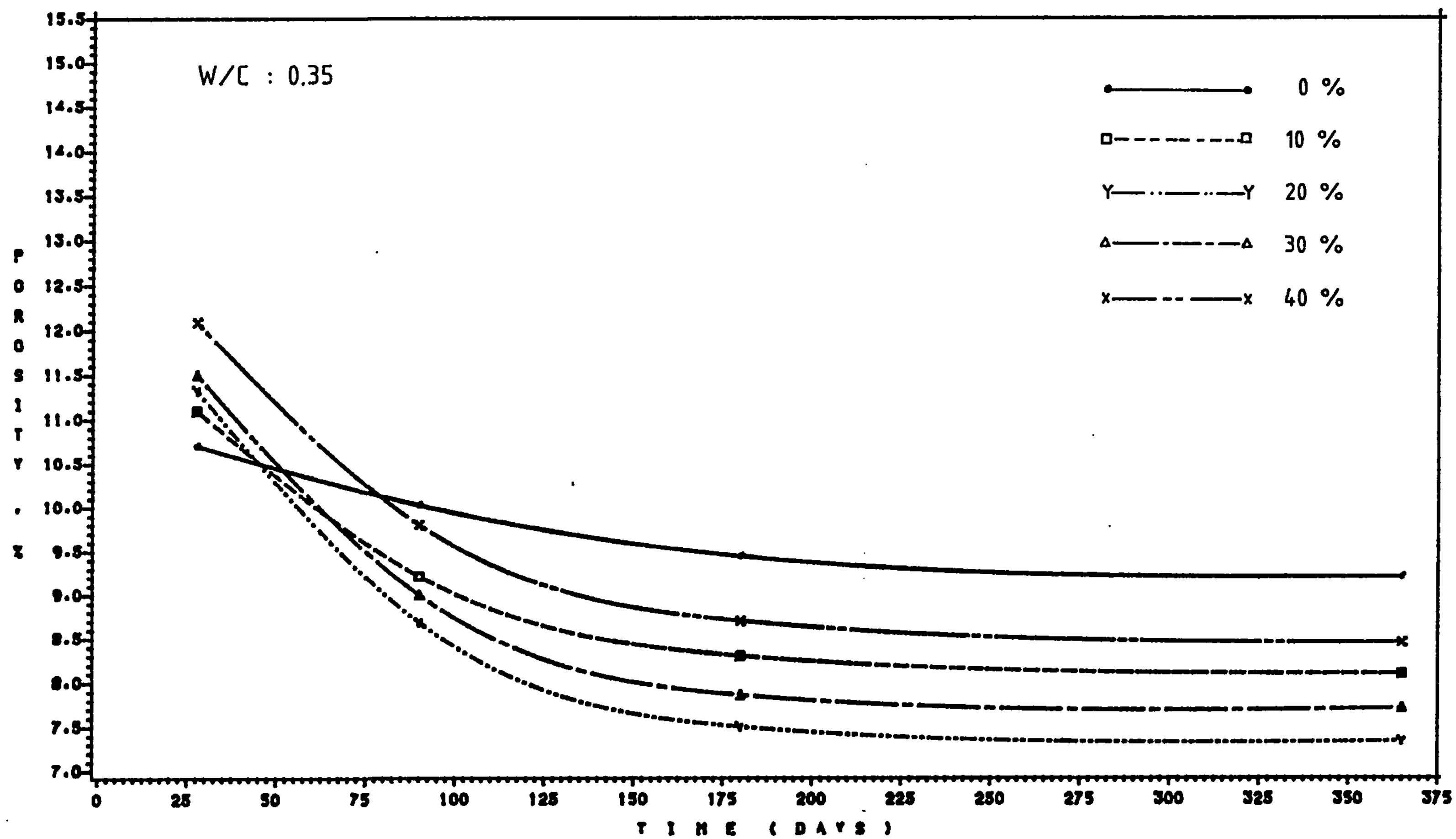

Figure 4.1 Relation between Porosity and Age for Plain and Pozzolan Concrete

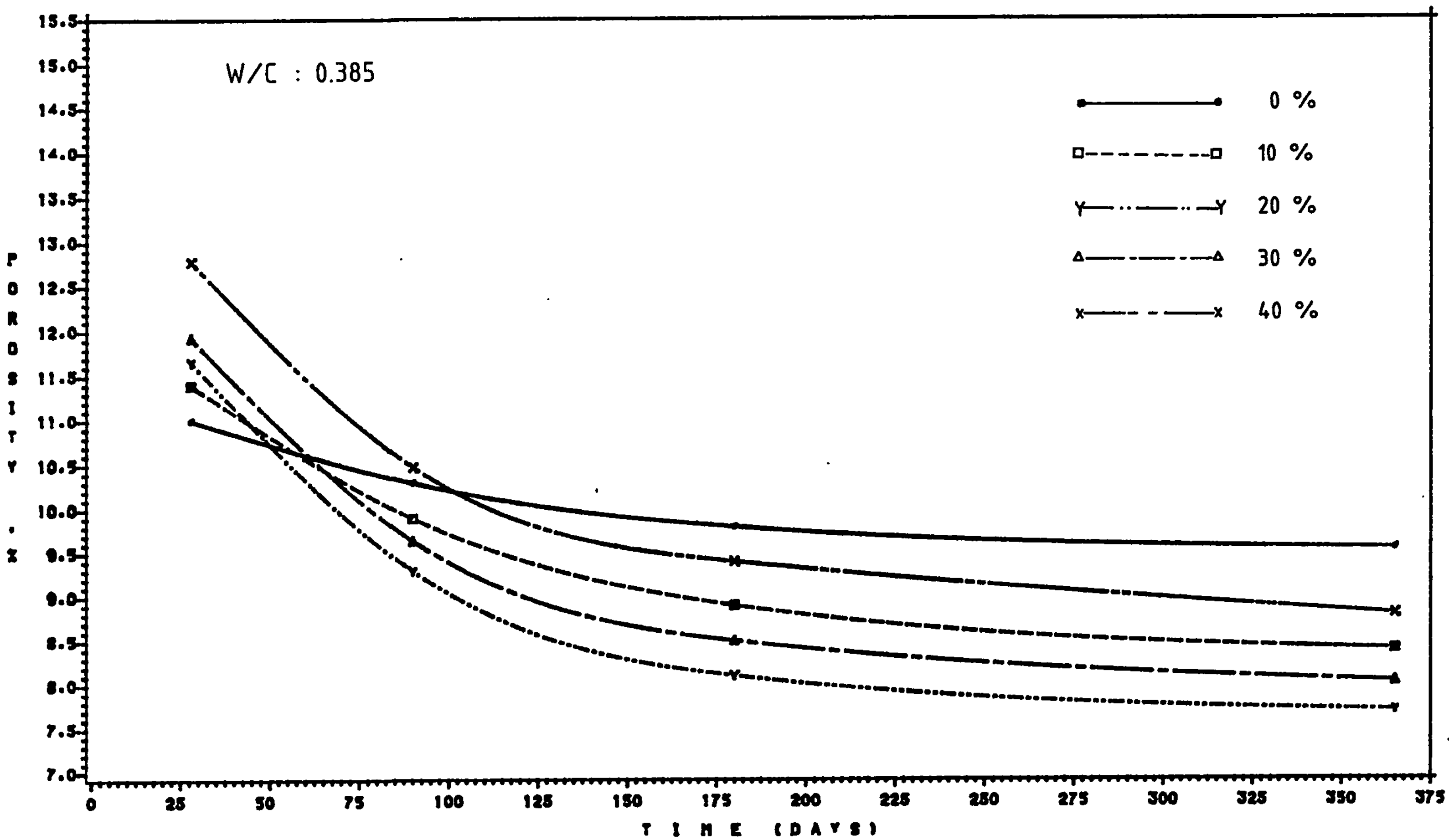

Figure 4.2 Relation between Porosity and Age for Plain and Pozzolan Concrete

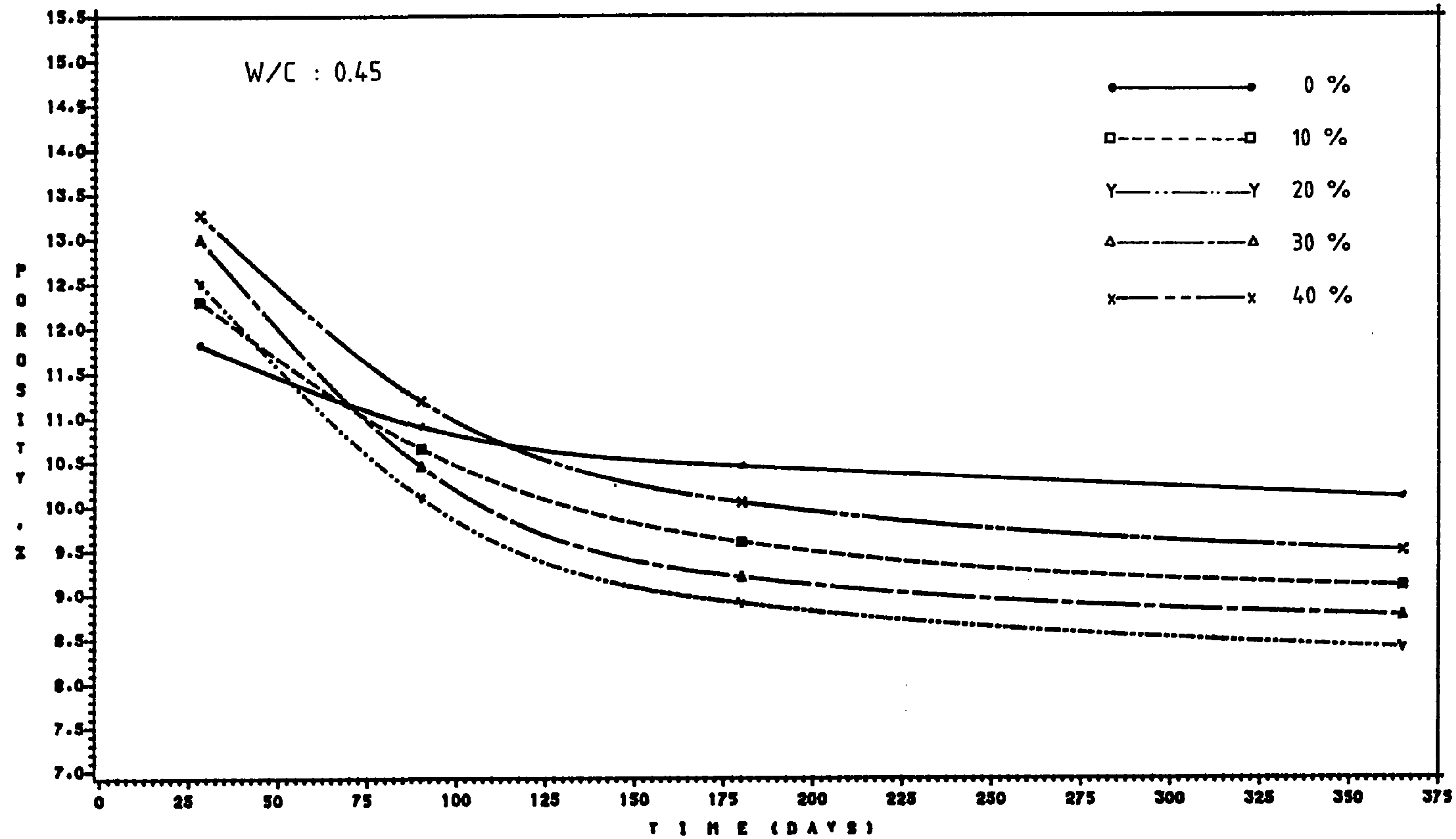

Figure 4.3 Relation between Porosity and Age for Plain and Pozzolan Concrete

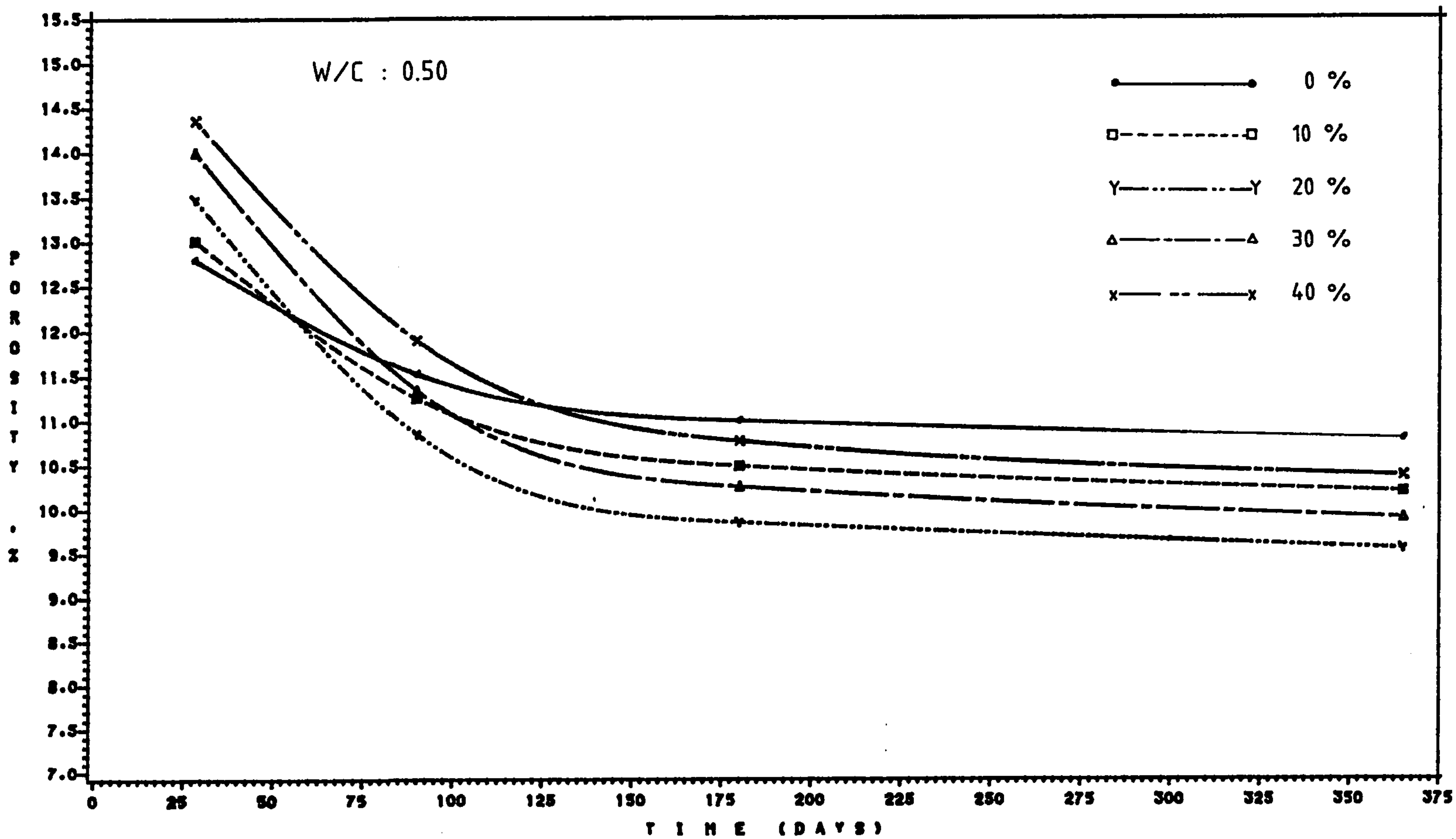

Figure 4.4 Relation between Porosity and Age for Plain and Pozzolan Concrete

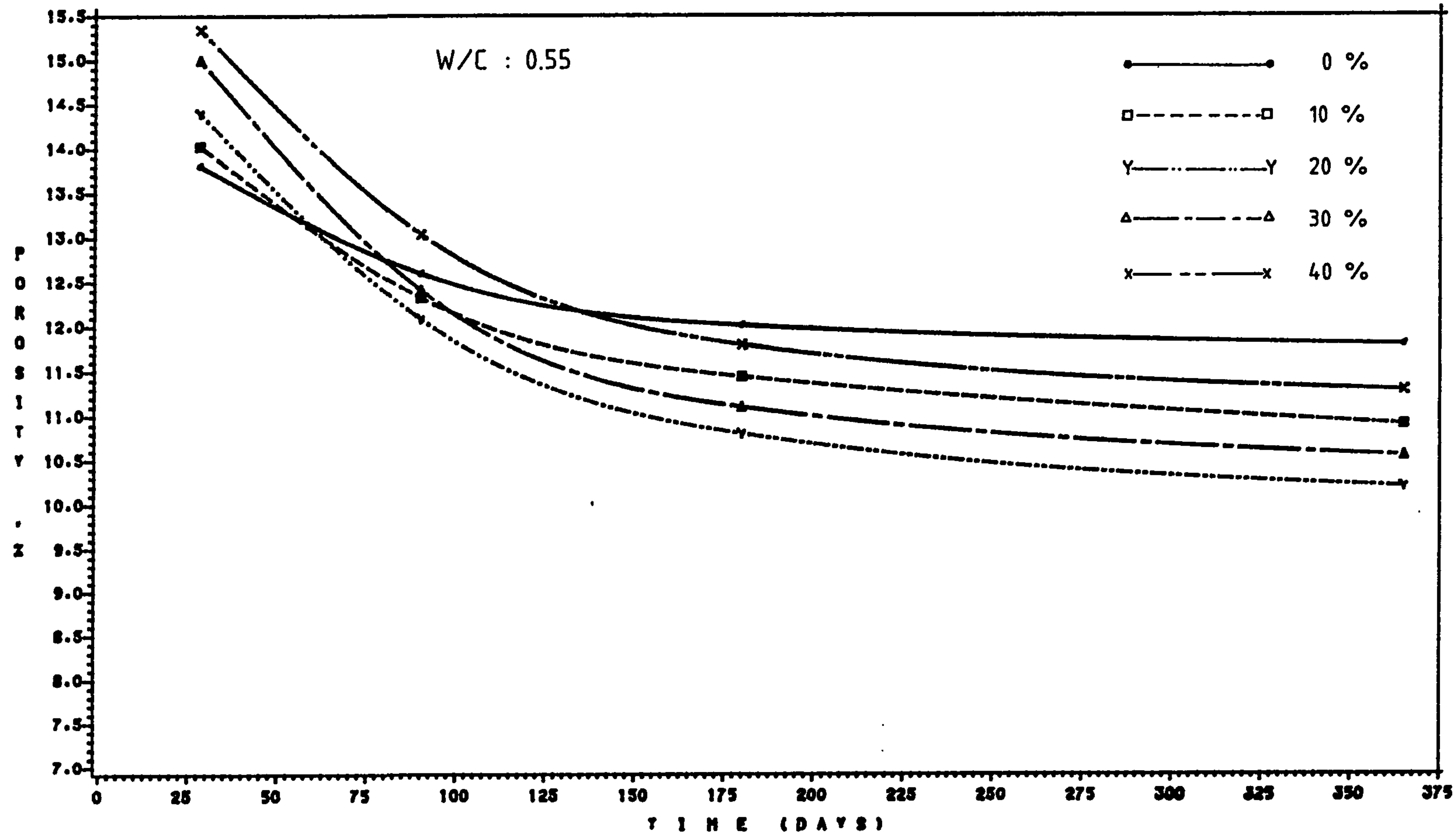

Figure 4.5 Relation between Porosity and Age for Plain and Pozzolan Concrete

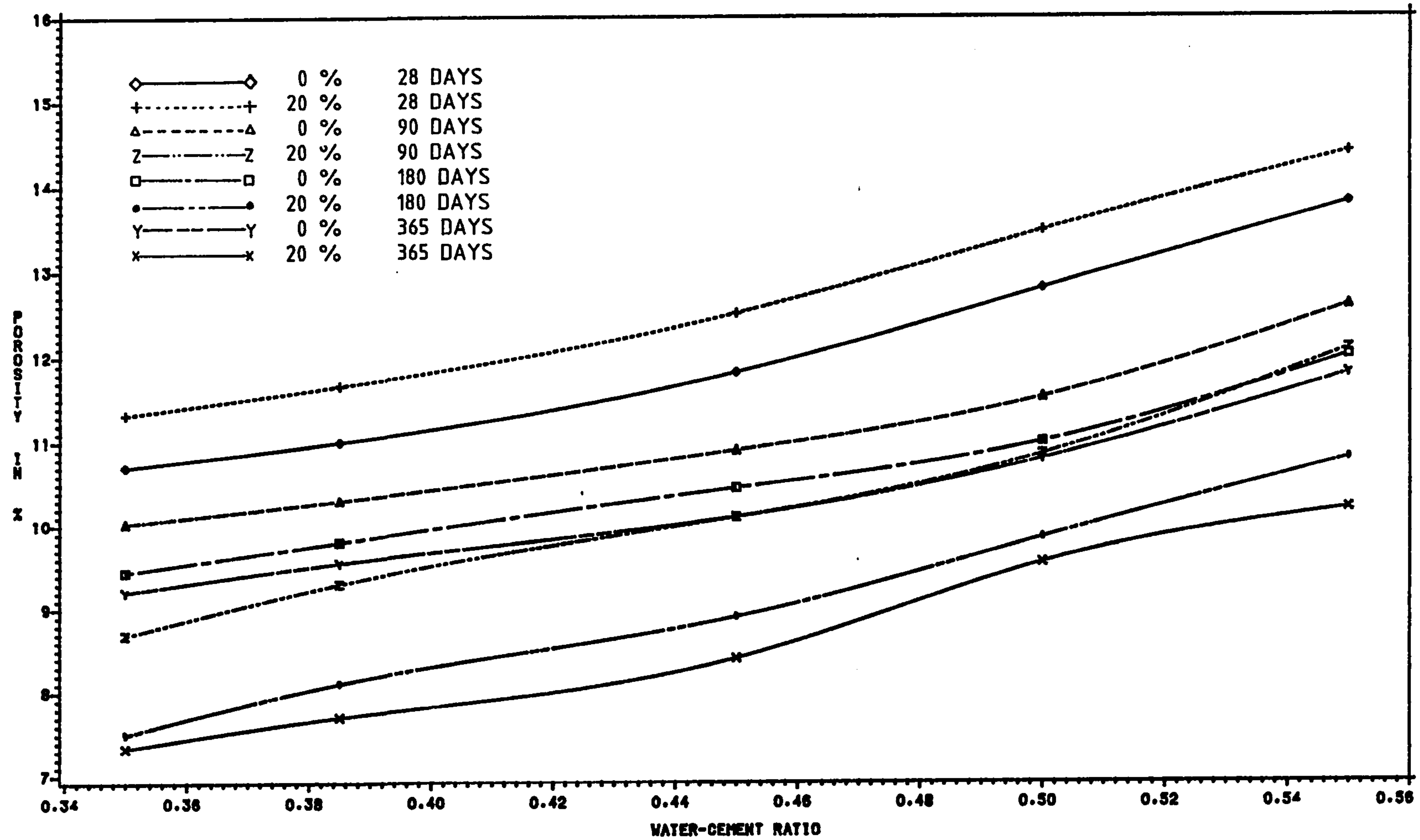

Figure 4.6 Effect of Water-Cement Ratio on the Porosity

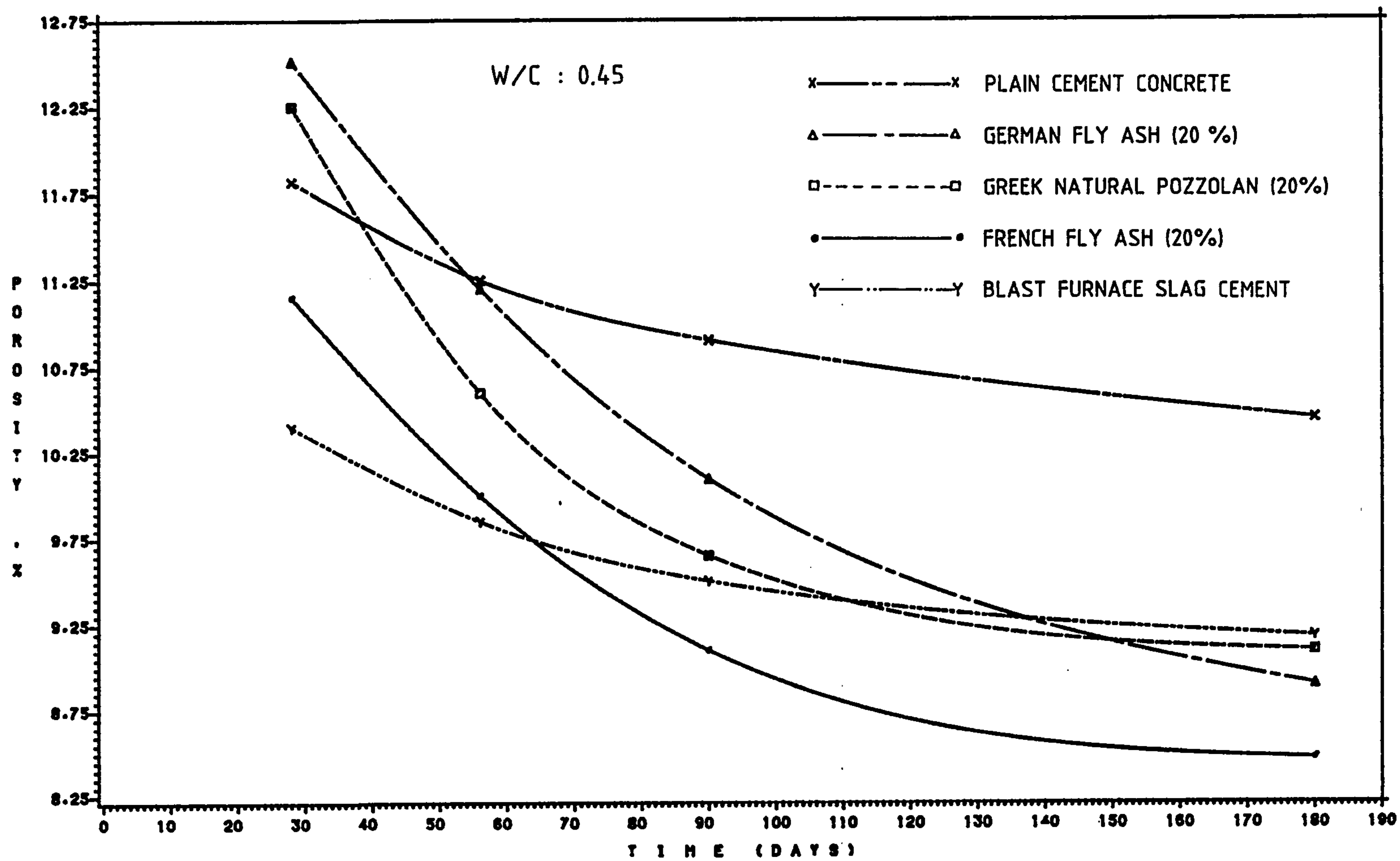

Figure 4.7 . Porosity of Concretes made with different Pozzolans

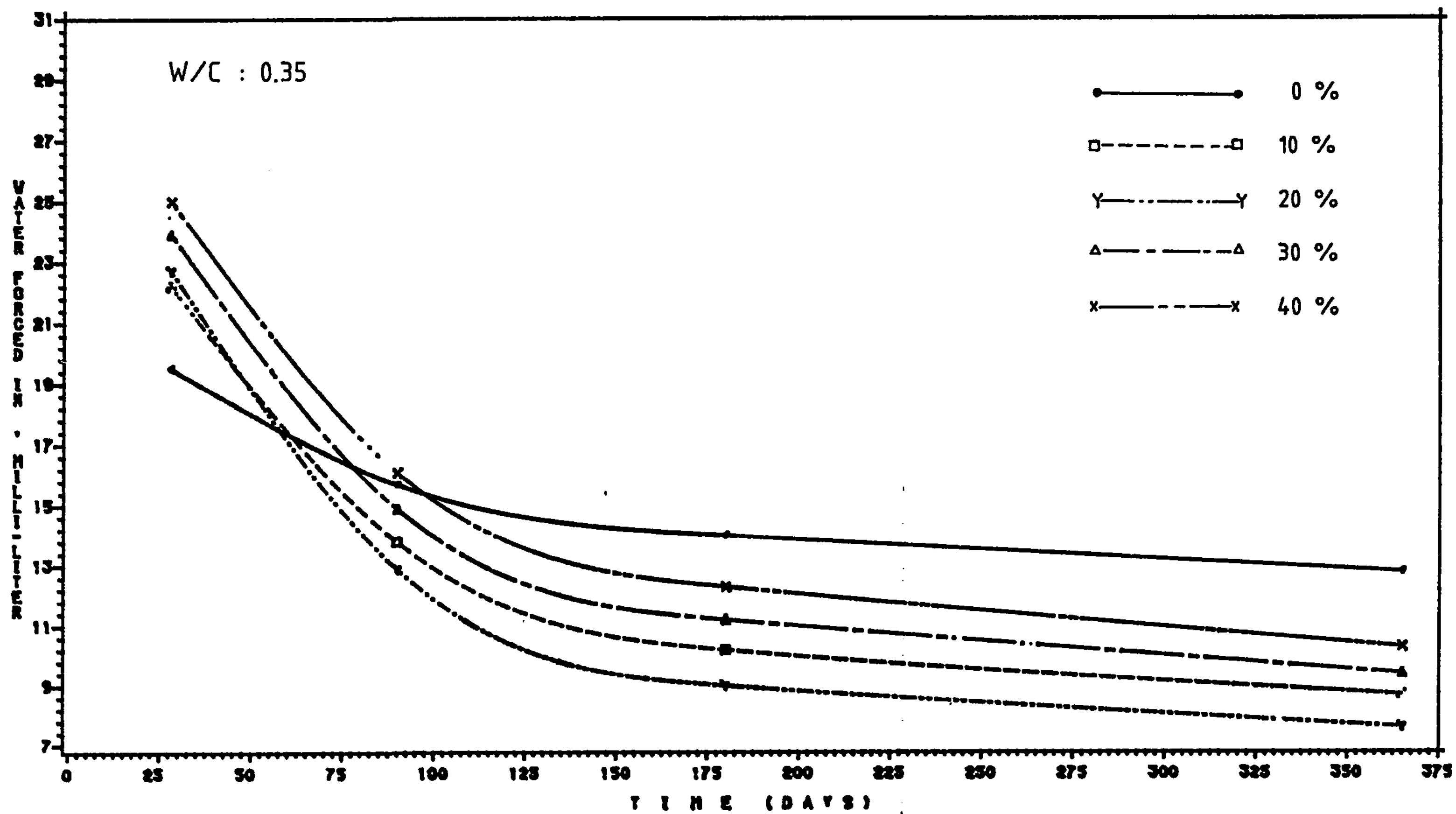

Figure 4.8 Relation between Permeability and Age for Plain and Pozzolan Concrete

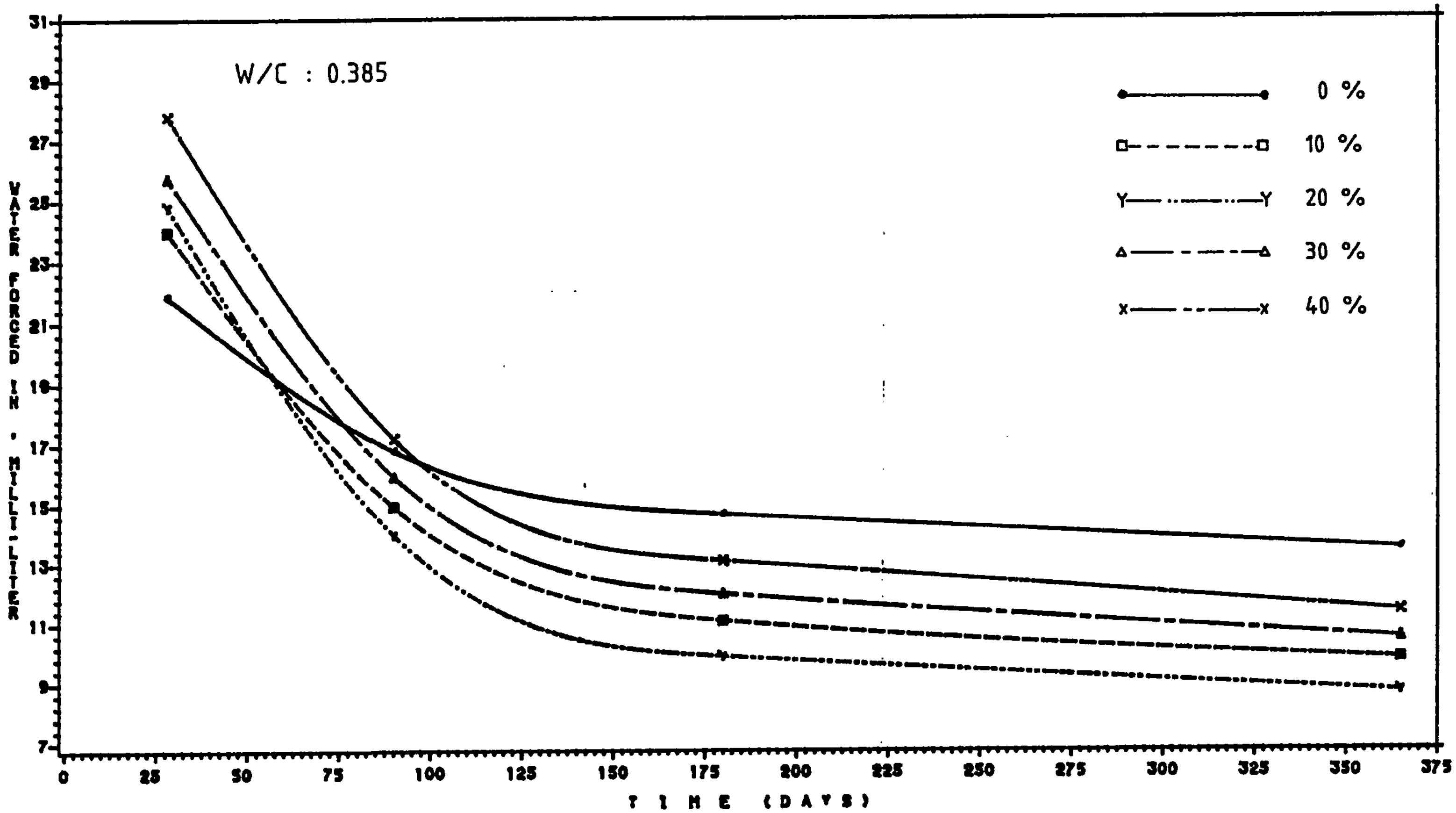

Figure 4.9 Relation between Permeability and Age for Plain and Pozzolan Concrete

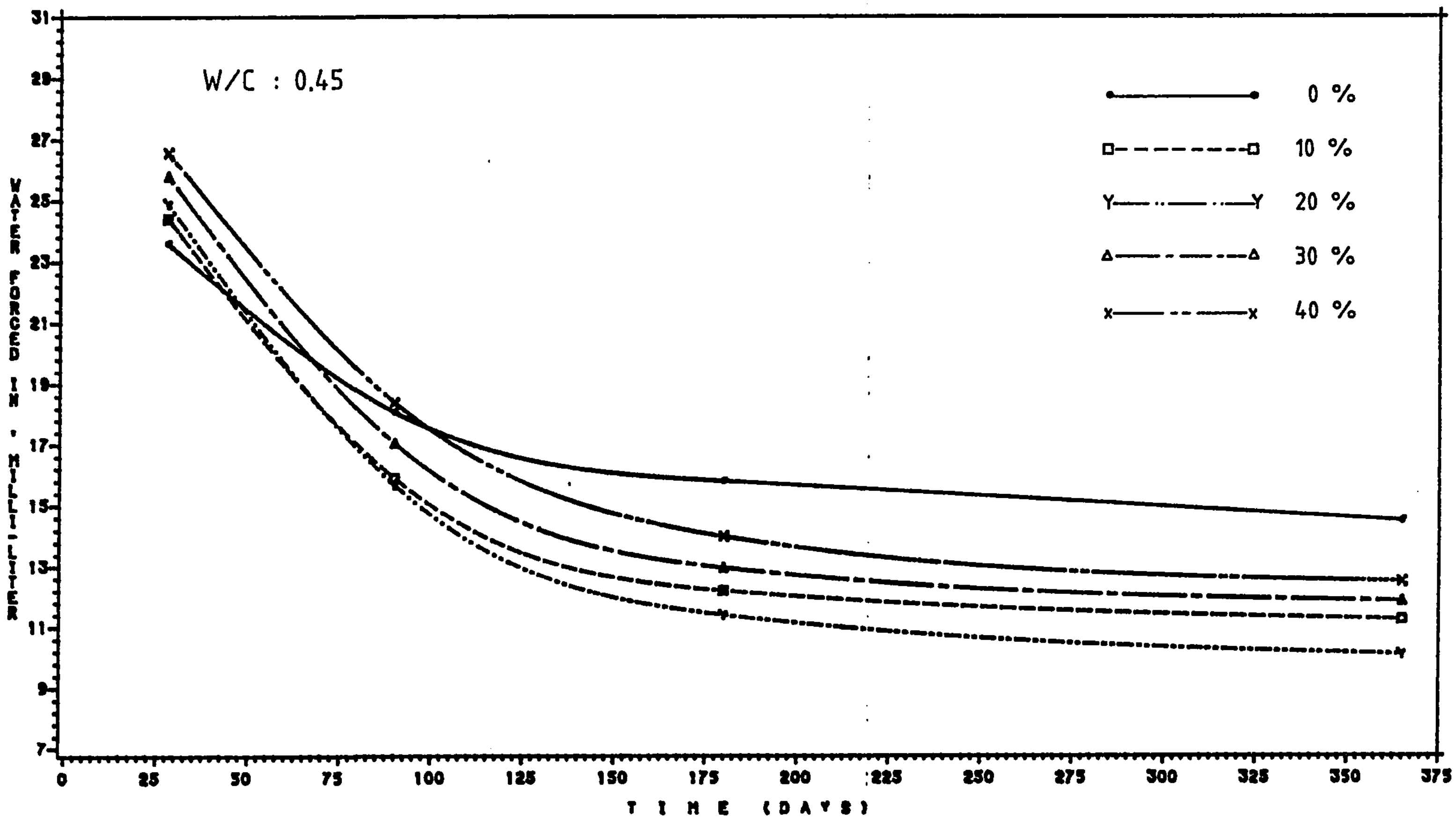

Figure 4.10 Relation between Permeability and Age for Plain and Pozzolan Concrete

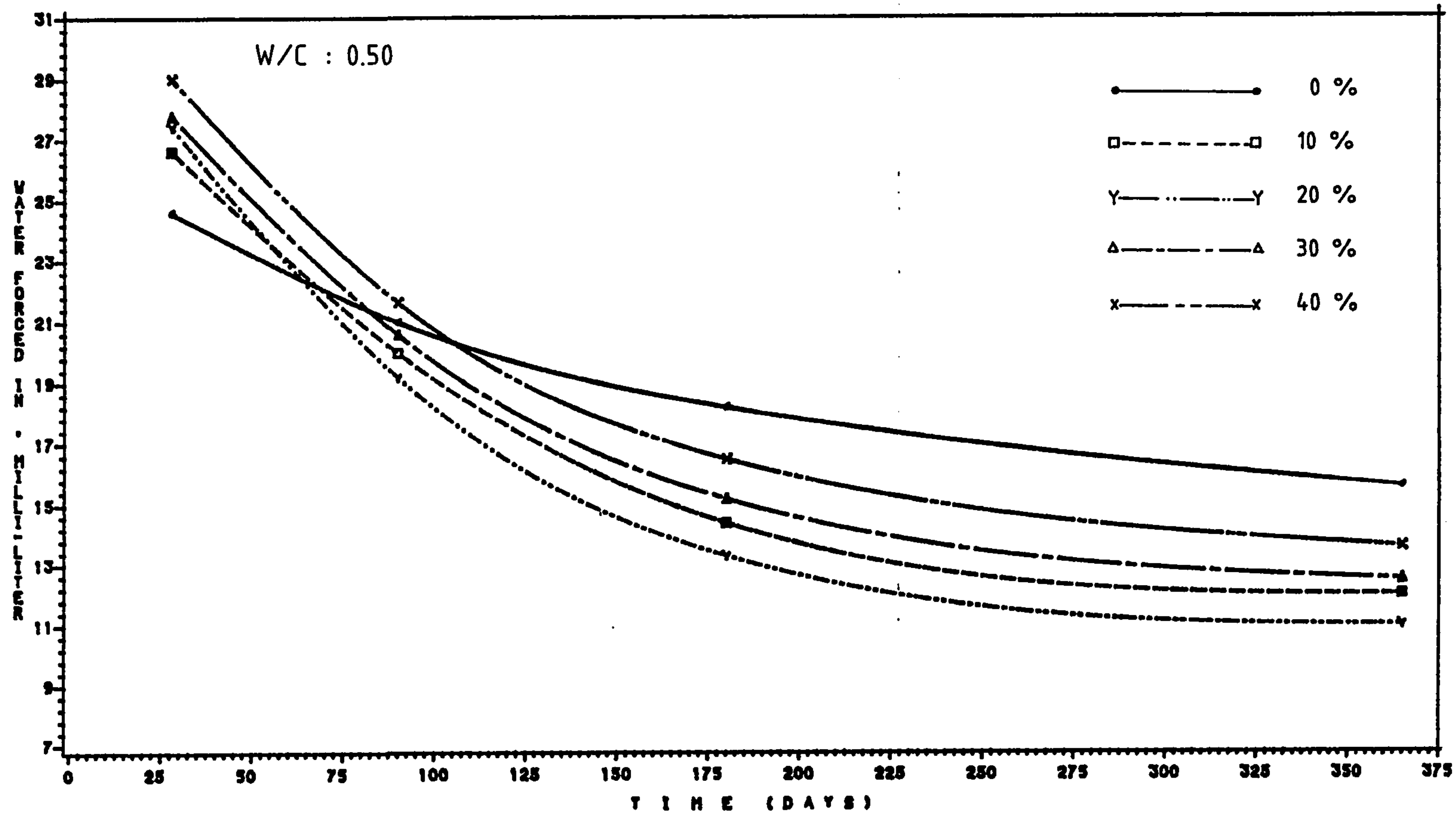

Figure 4.11 Relation between Permeability and Age for Plain and Pozzolan Concrete

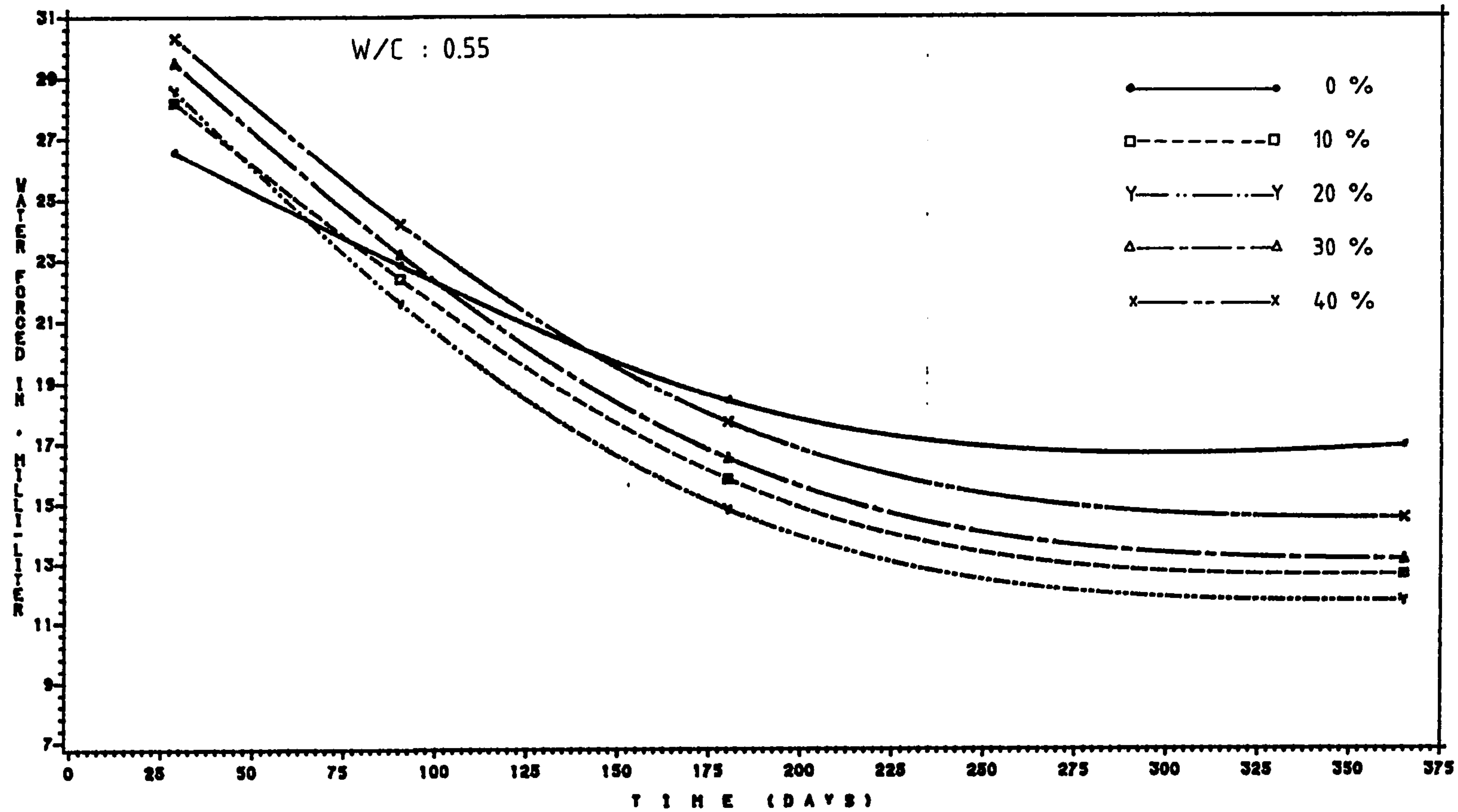

Figure 4.12': Relation between Permeability and Age for Plain and Pozzolan Concrete

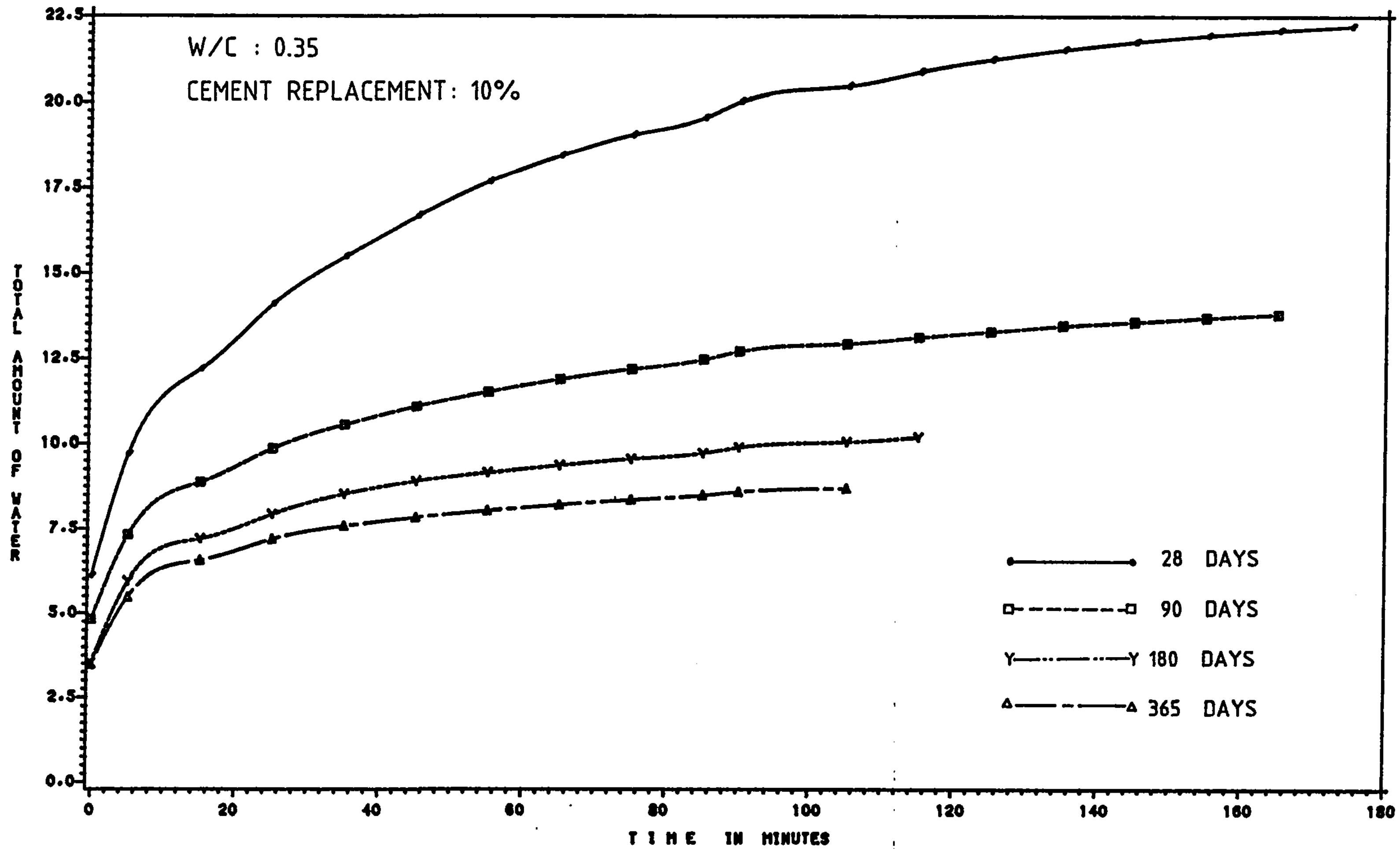

Figure 4.13 Relation between Water pumped in and Time

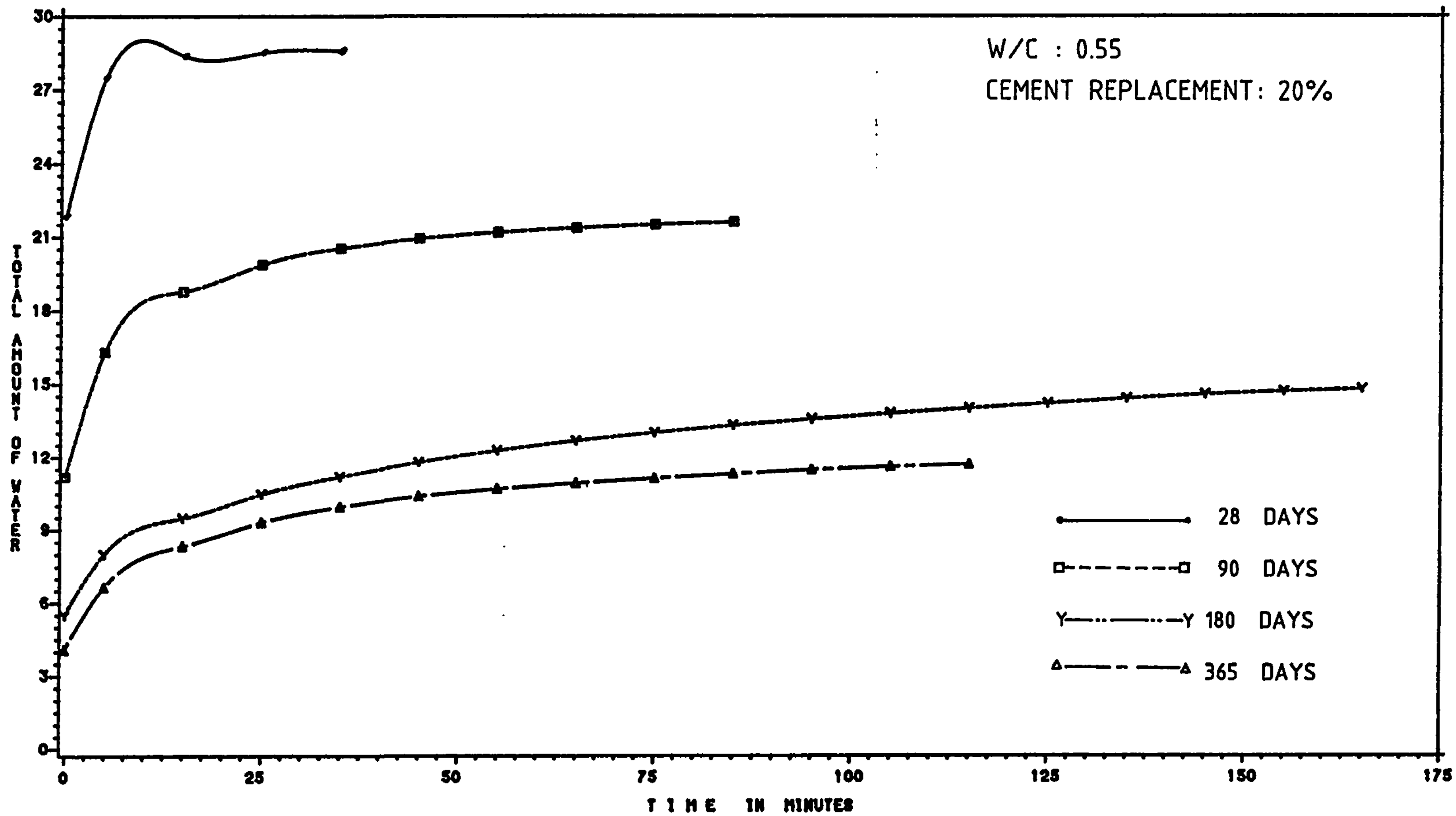

Figure 4.14 . Relation between Water Pumped in and Time

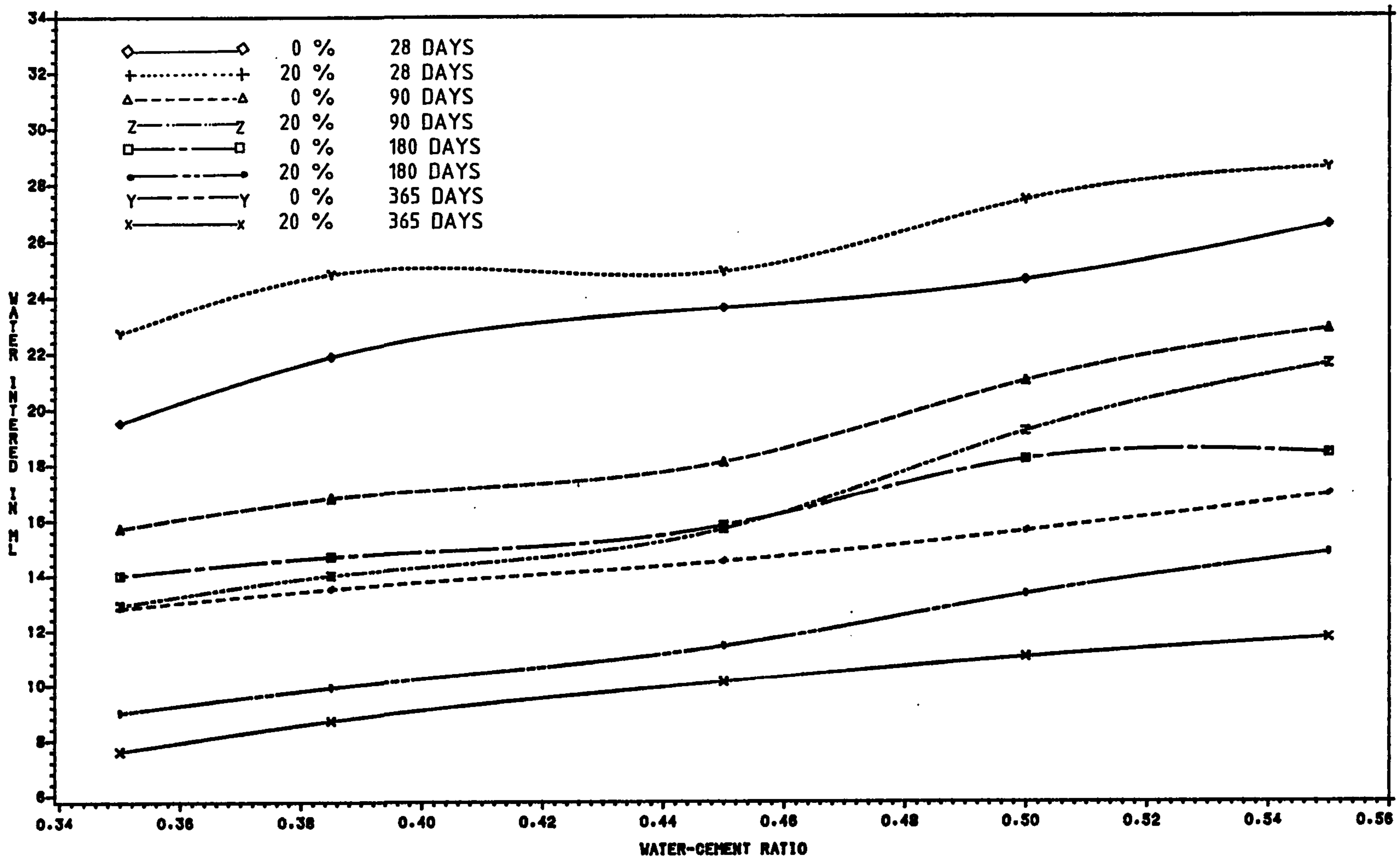

Figure 4.15 Effect of Water-Cement Ratio on Permeability

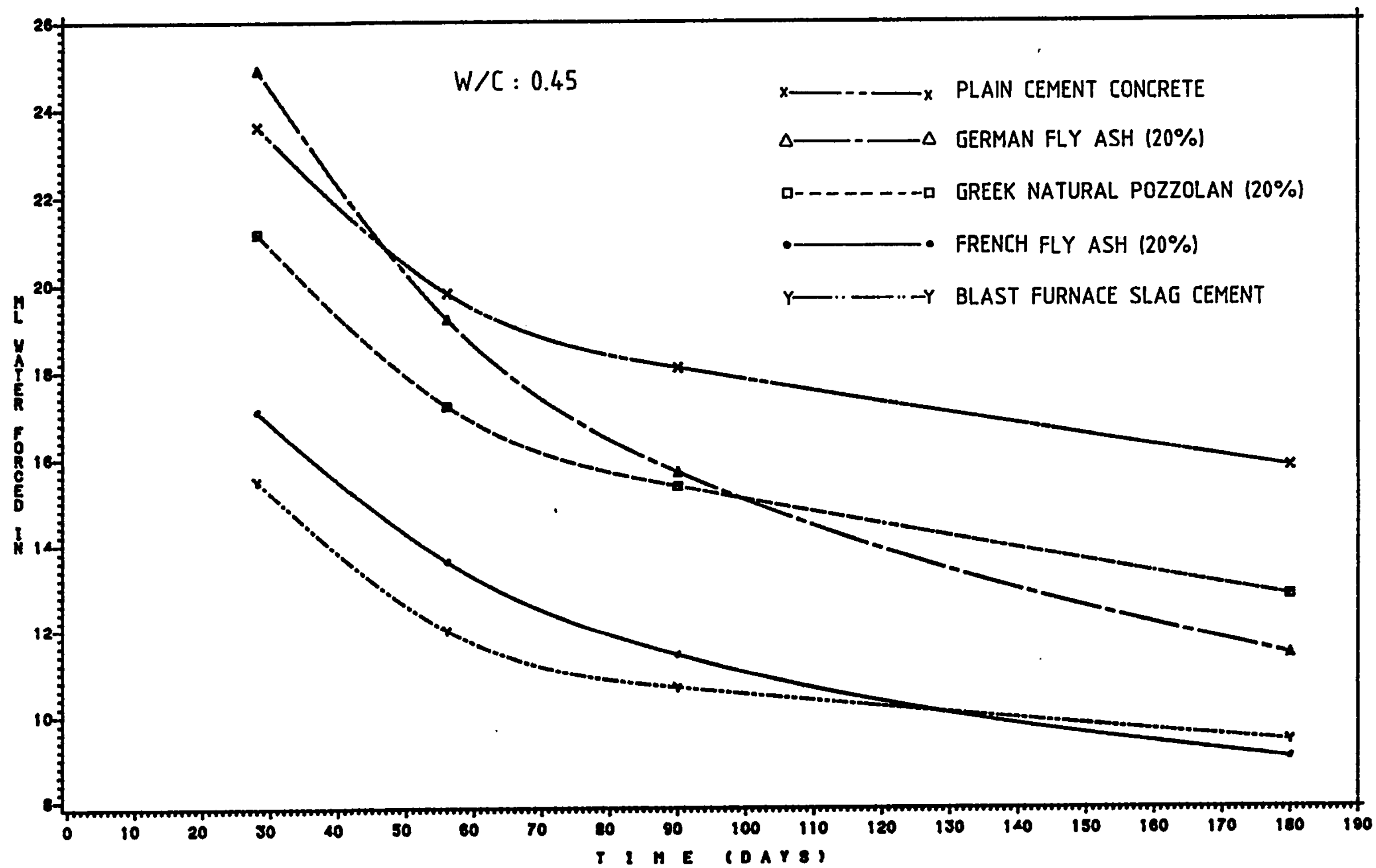

Figure 4.16 Permeability of Concretes made with different Pozzolans

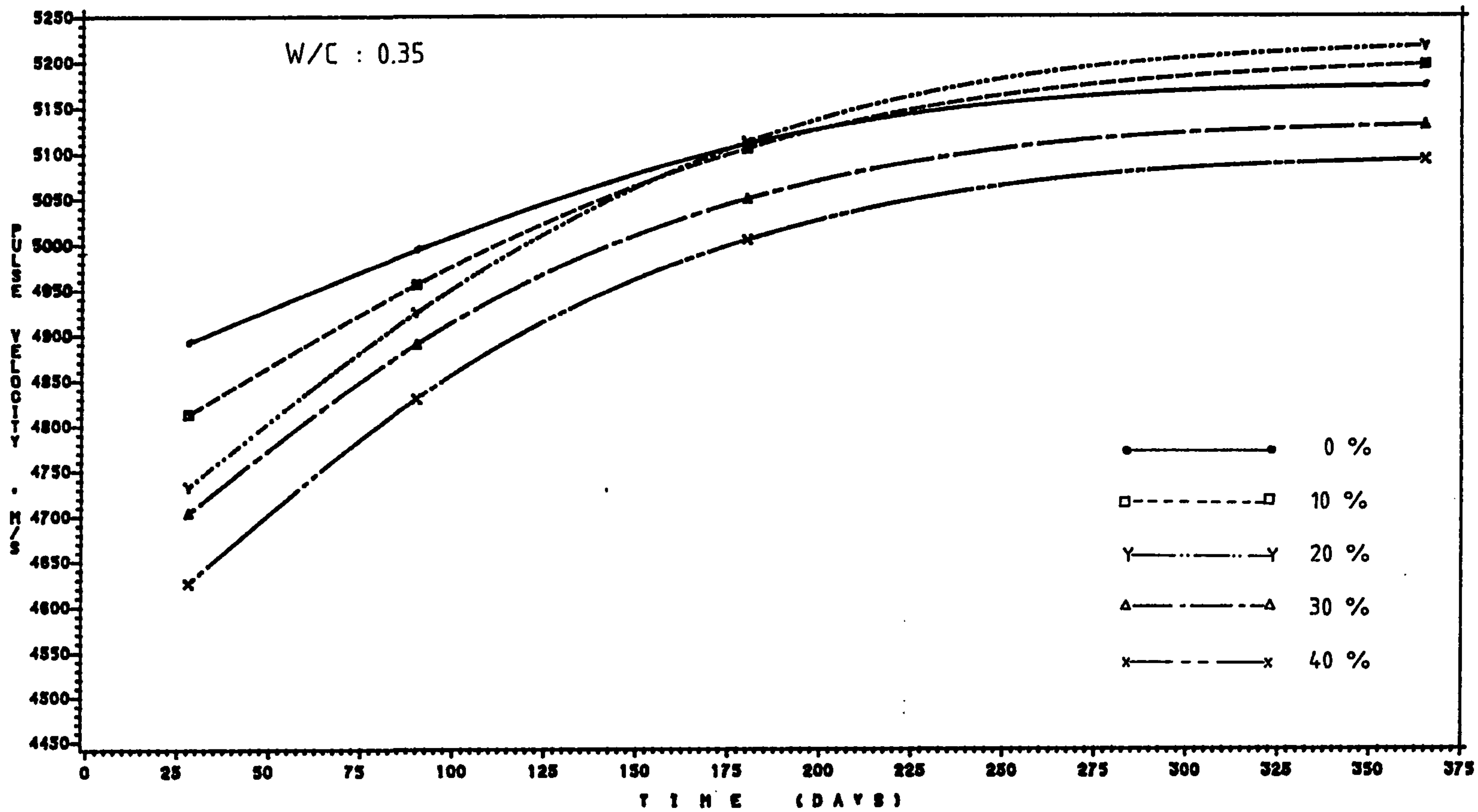

Figure 4.17 : Relation between Pulse-Velocity and Age for Plain and Pozzolan Concrete

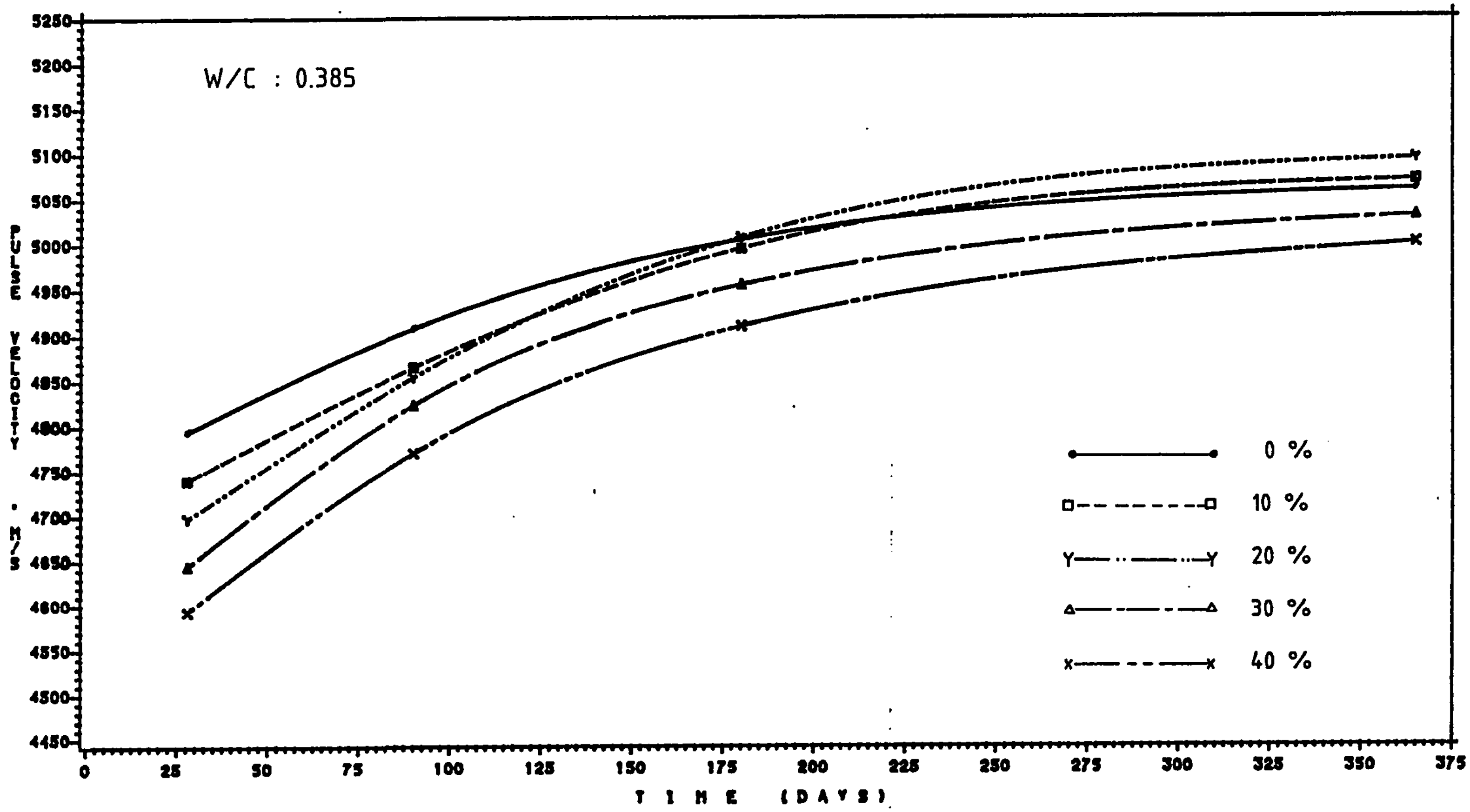

Figure 4.18 Relation between Pulse-Velocity and Age for Plain and Pozzolan Concrete

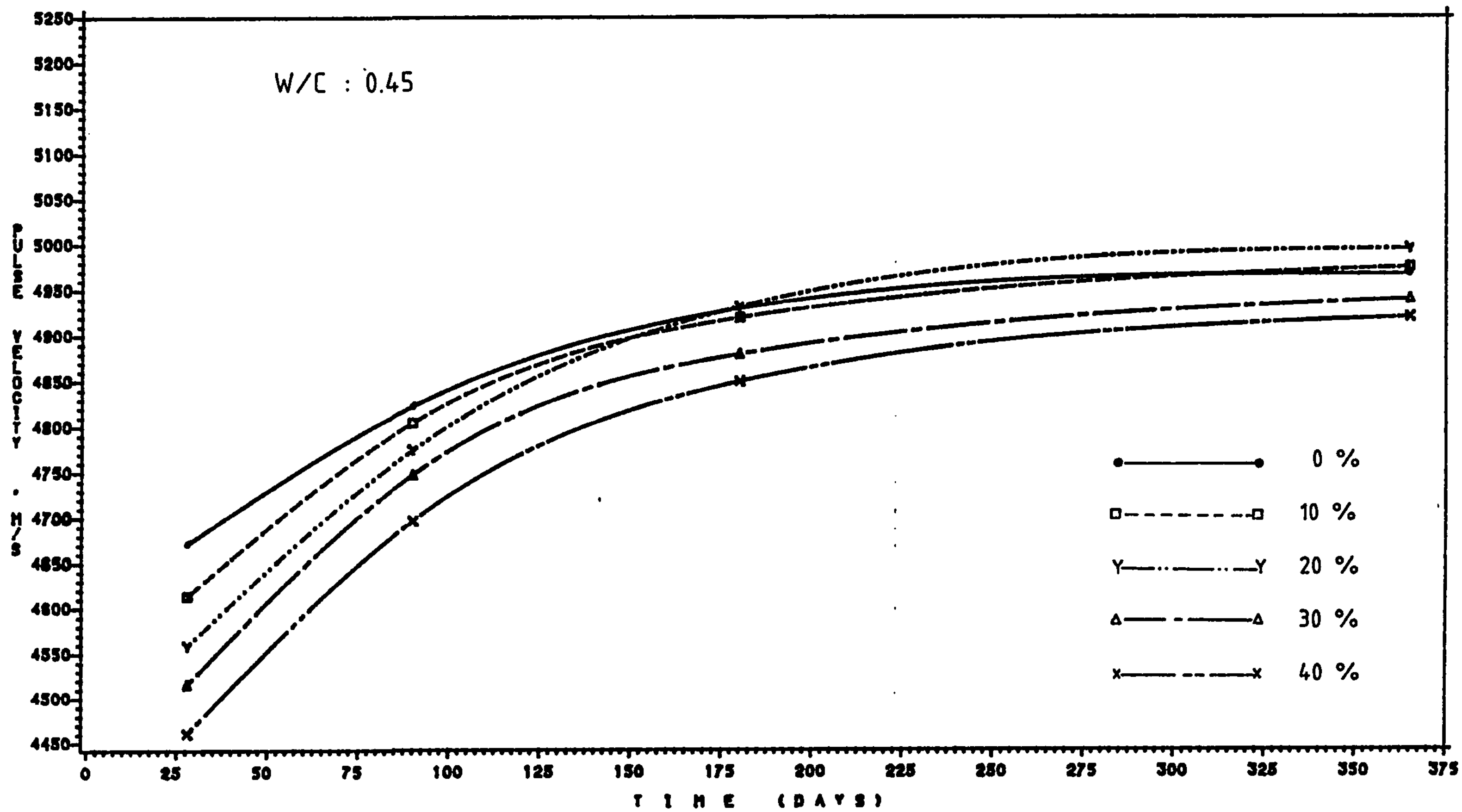

Figure 4.19 Relation between Pulse-Velocity and Age for Plain and Pozzolan Concrete

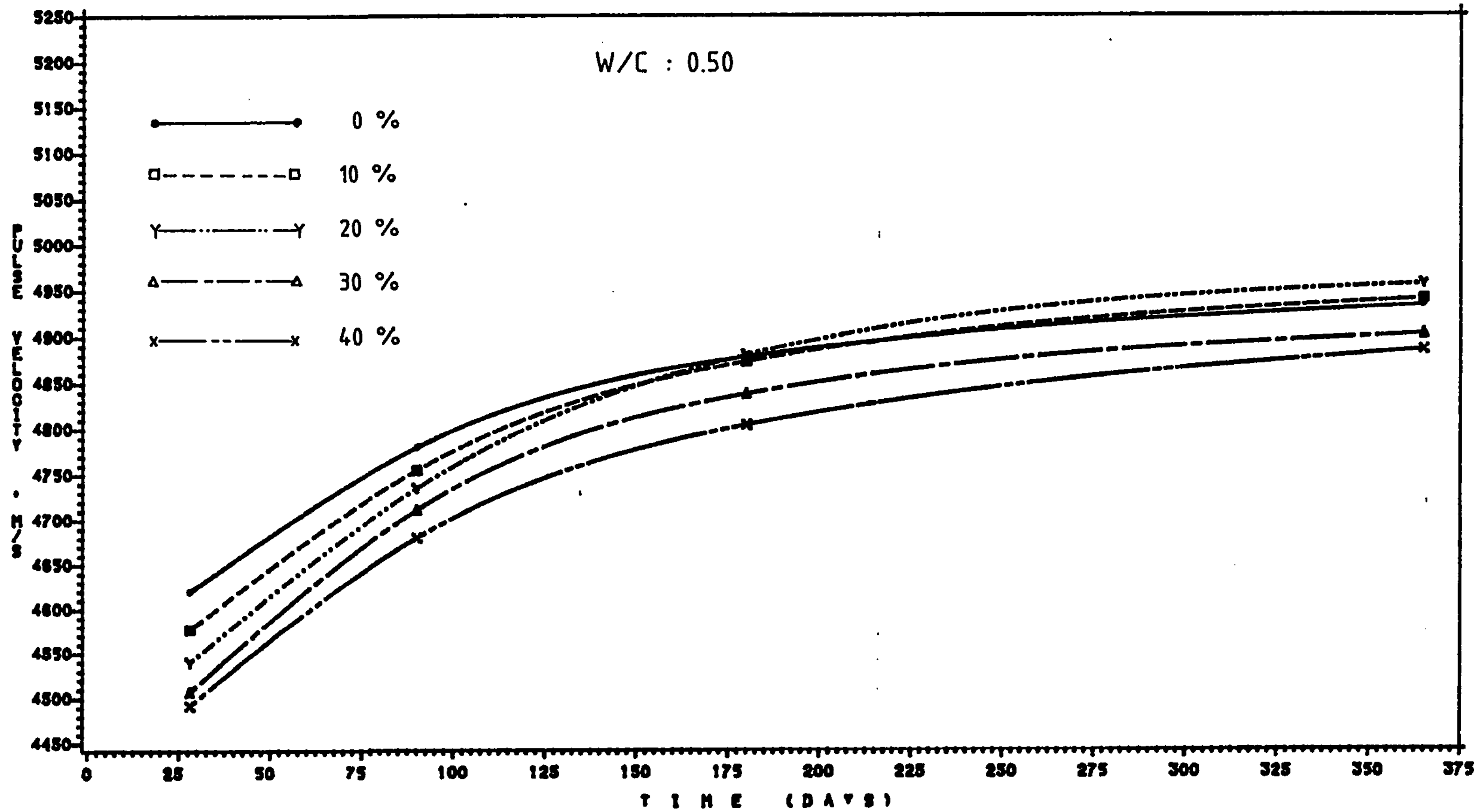

Figure 4.20 Relation between Pulse-Velocity and Age for Plain and Pozzolan Concrete

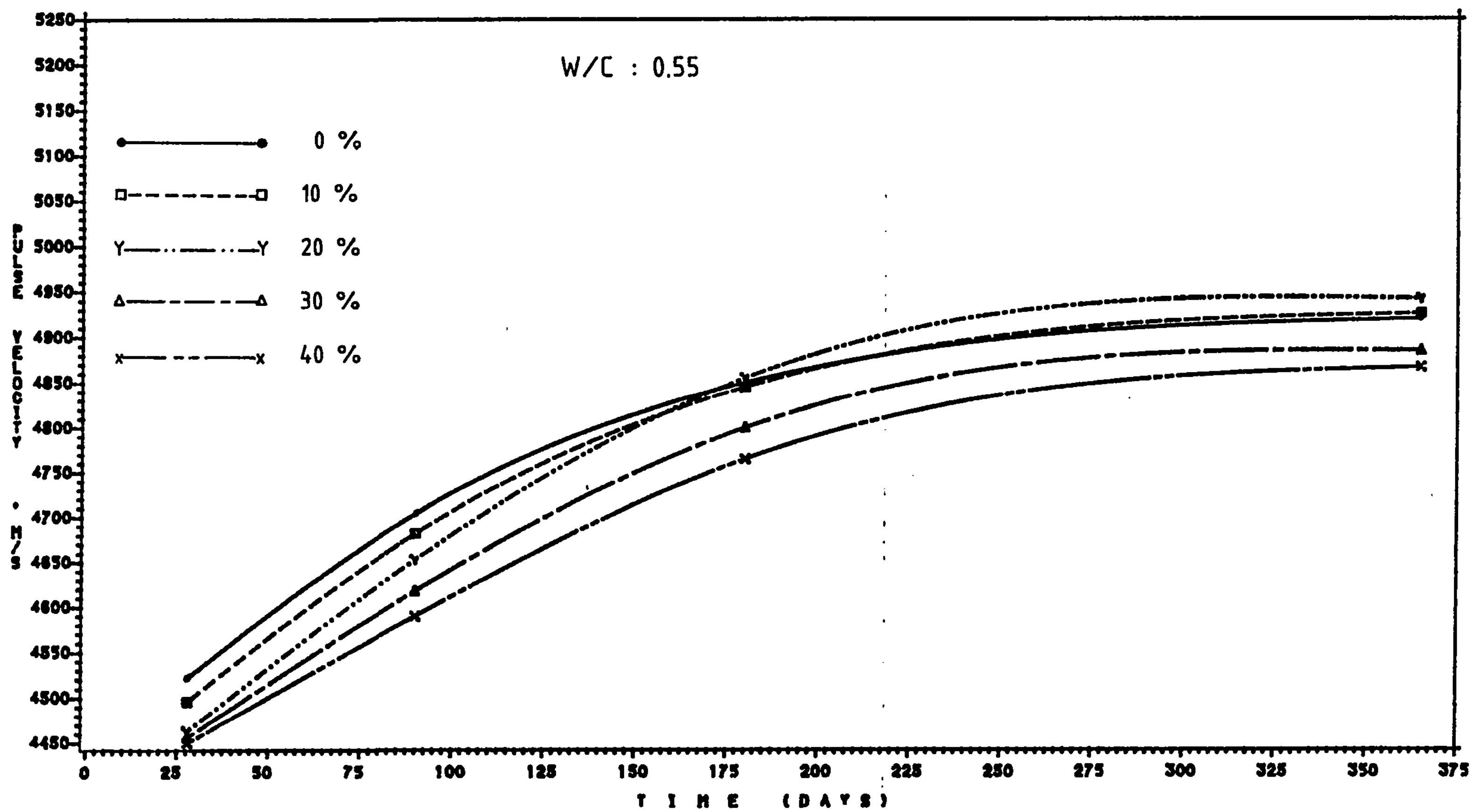

Figure 4.21 Relation between Pulse-Velocity and Age for Plain and Pozzolan Concrete

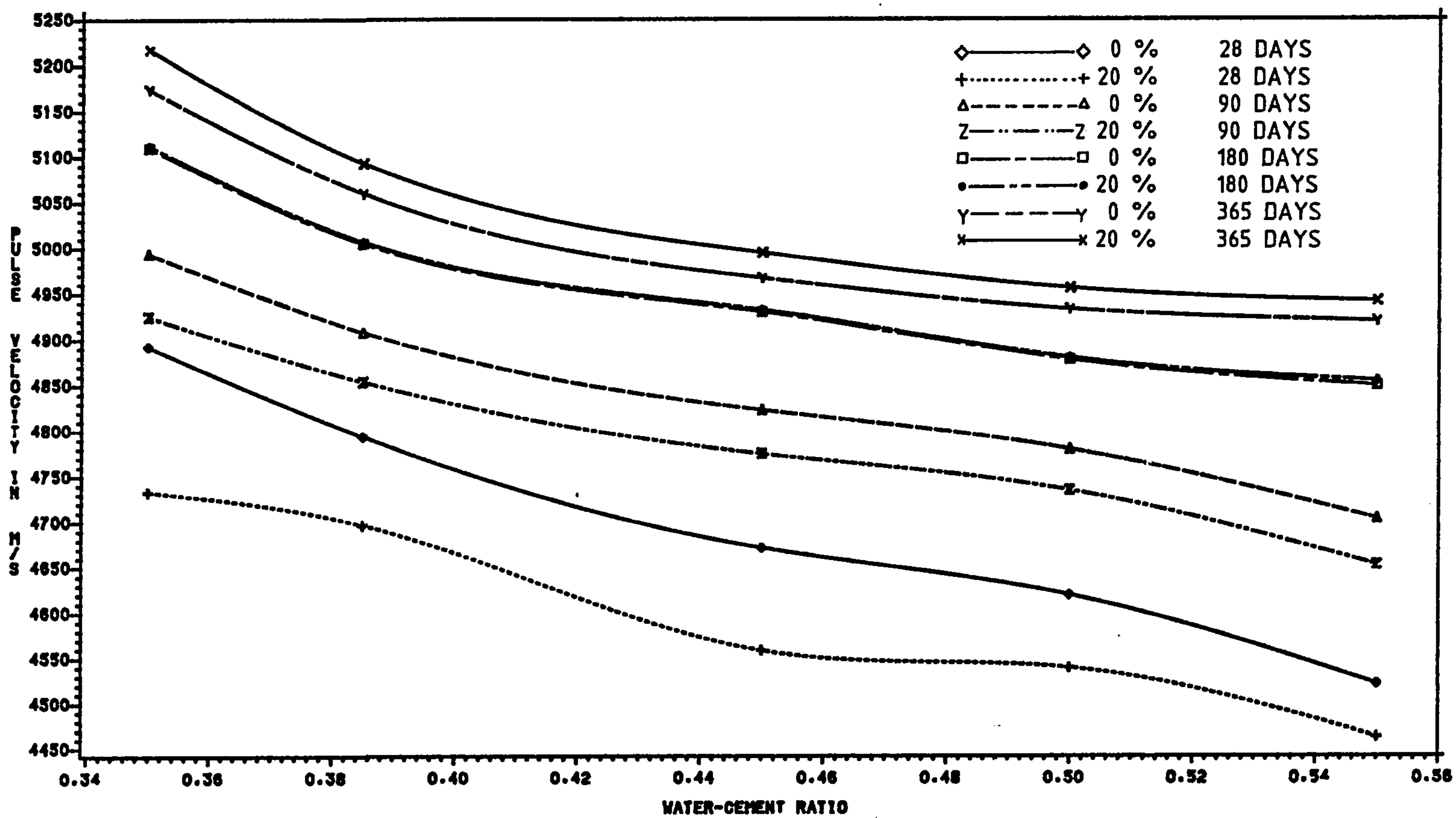

Figure 4.22 Effect of Water-Cement Ratio on the Pulse-Velocity

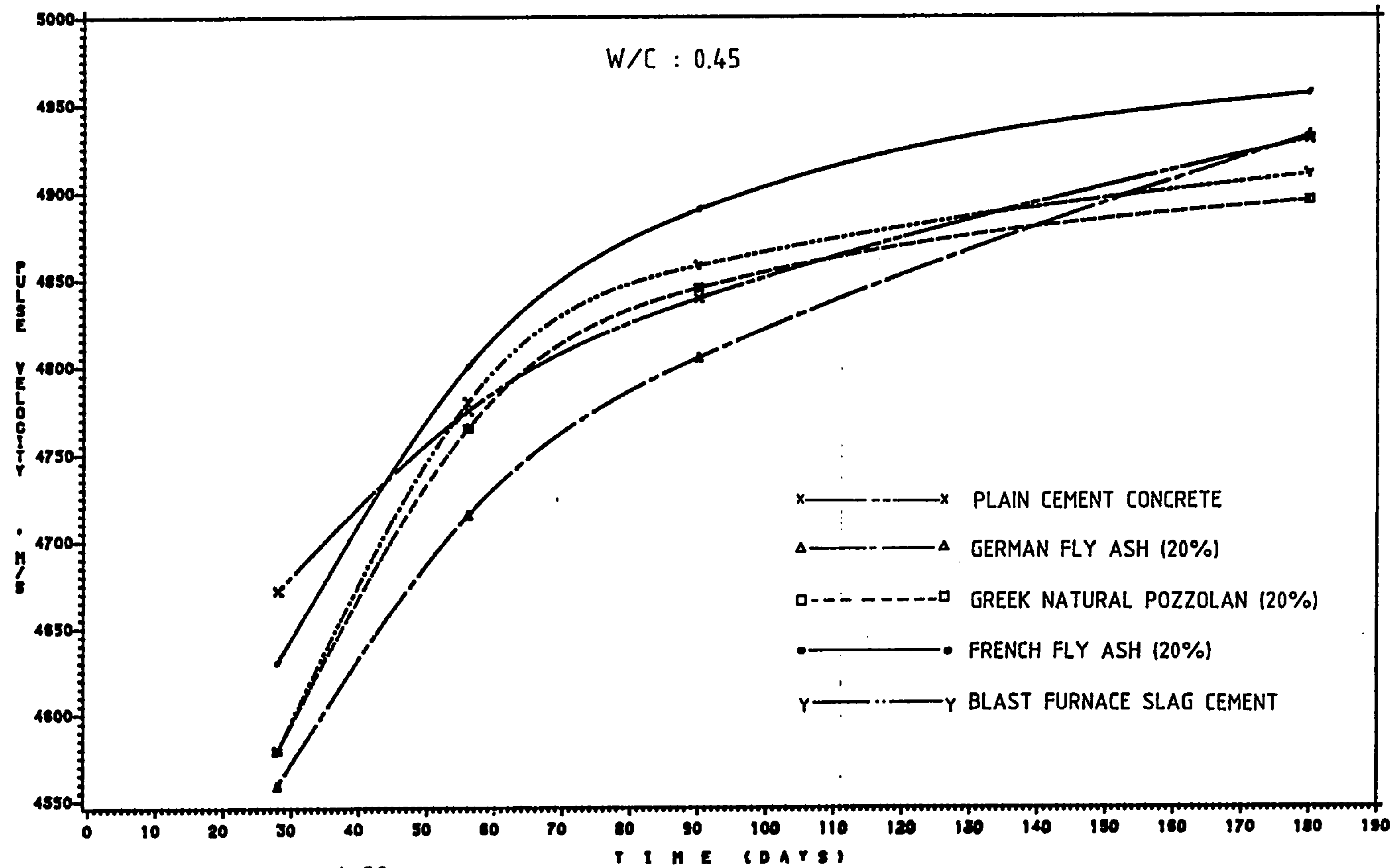

Figure 4.23 Pulse-Velocity of Concretes made with different Pozzolans

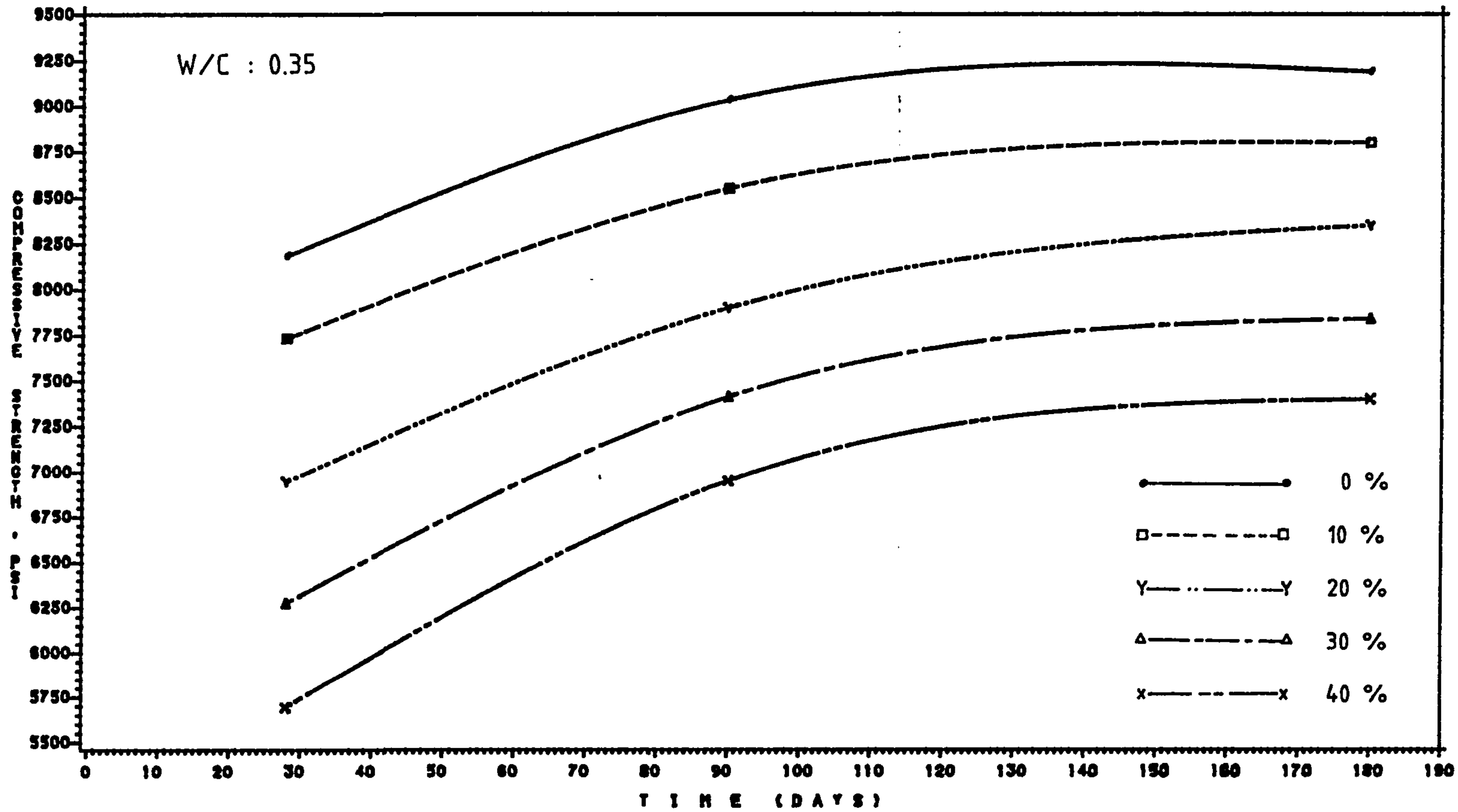

Figure 4.24. Relation between Compressive Strength and Age for Plain and Pozzolan Concrete

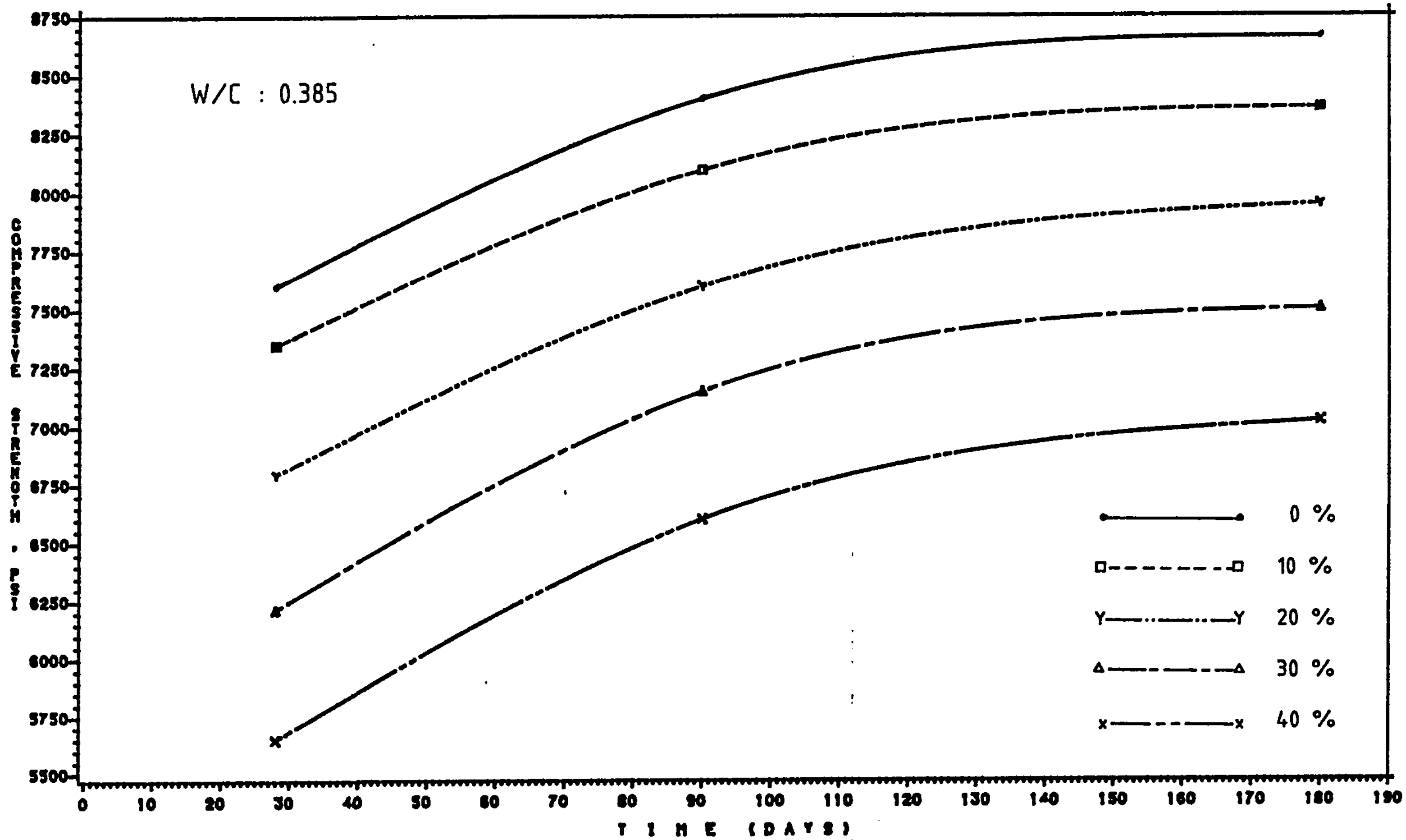

Figure 4.25 Relation between Compressive Strength and Age for Plain and Pozzolan Concrete

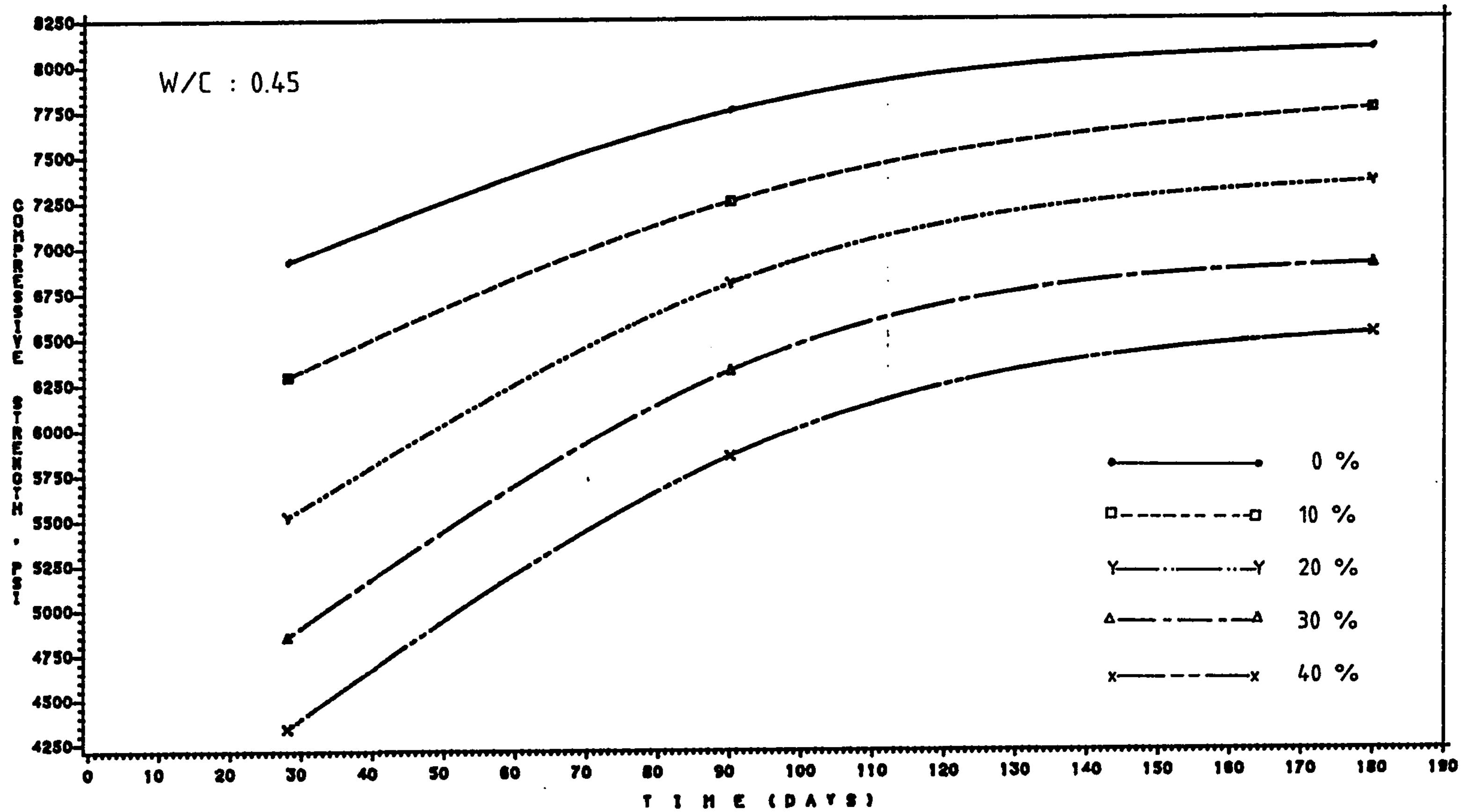

Figure 4.26 Relation between Compressive Strength and Age for Plain and Pozzolan Concrete

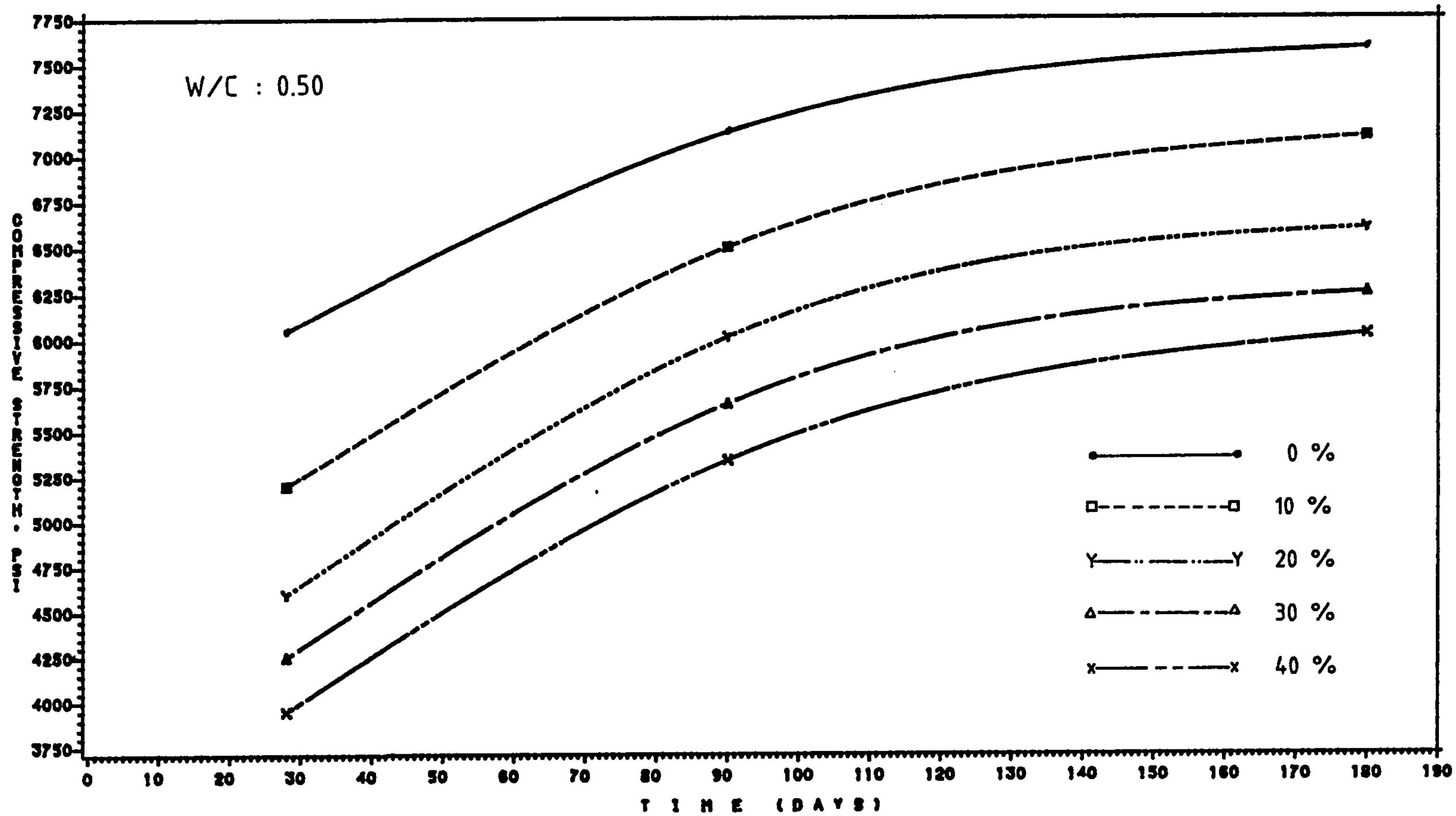

Figure 4.27. Relation between Compressive Strength and Age for Plain and Pozzolan Concrete

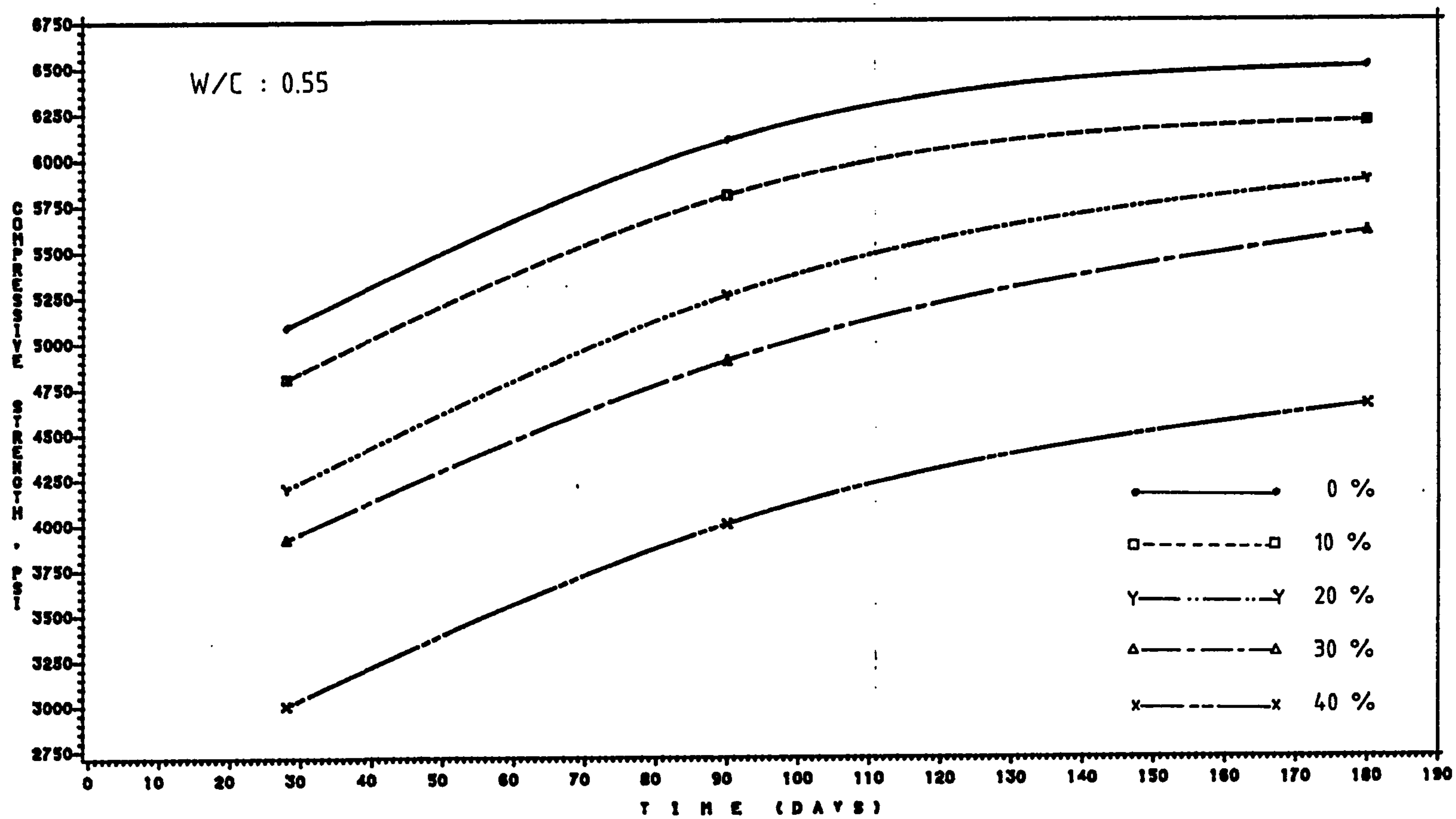

Figure 4.28 Relation between Compressive Strength and Age for Plain and Pozzolan Concrete

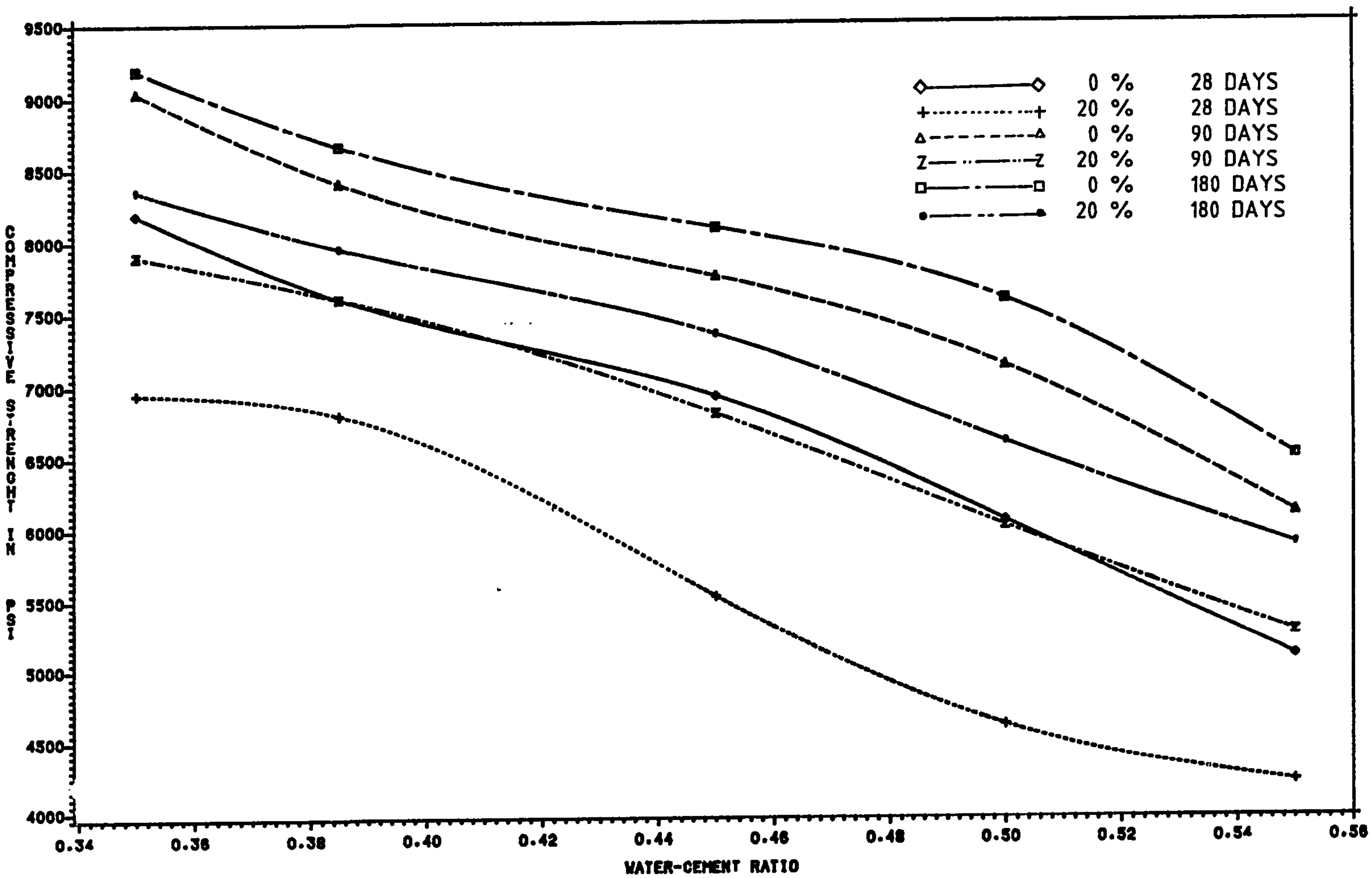

Figure 4.29 Effect of Water-Cement Ratio on the Compressive Strength of Plain and Pozzolan Concrete

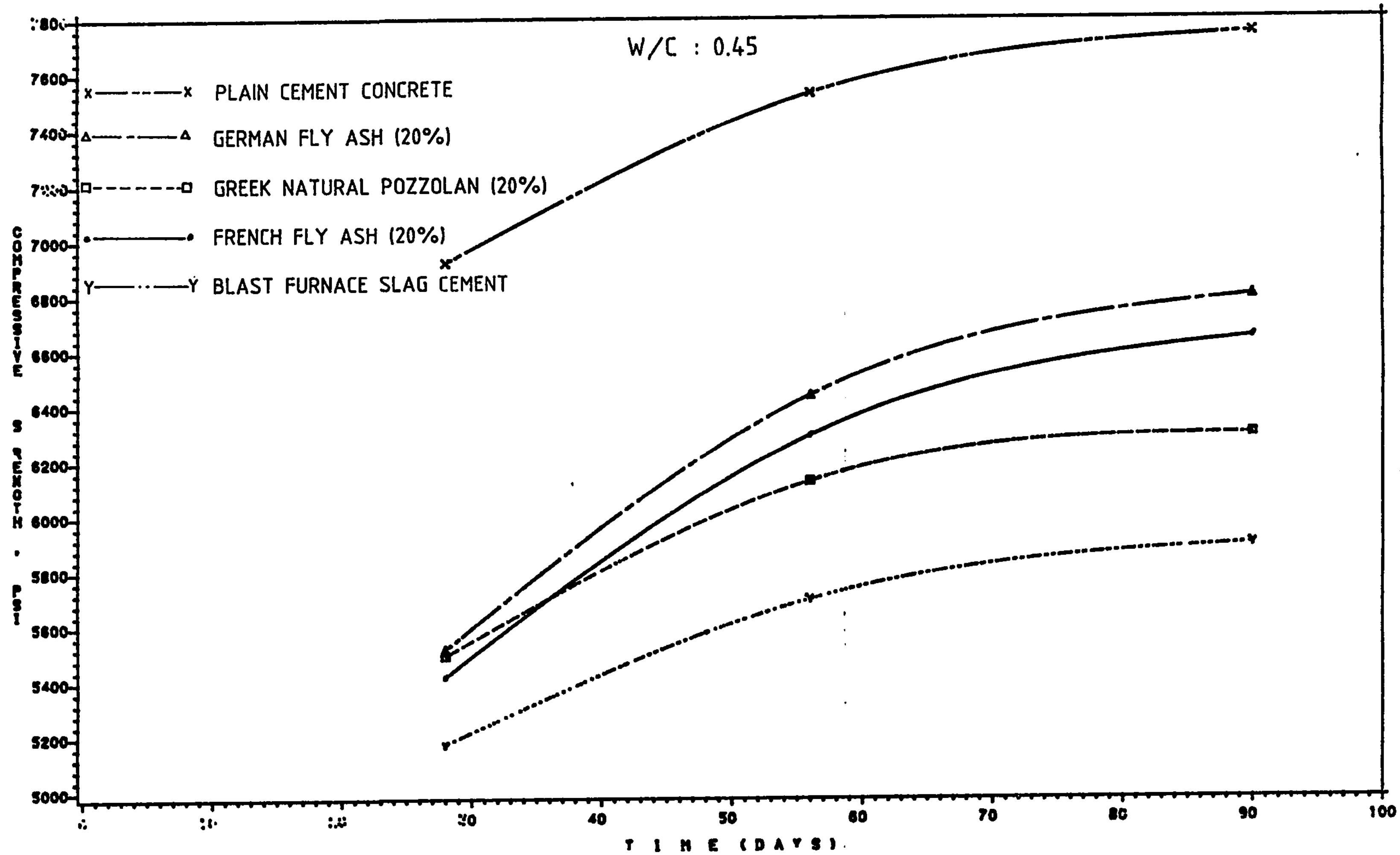

Figure 4.30 Compressive Strength of Concretes made with different Pozzolans

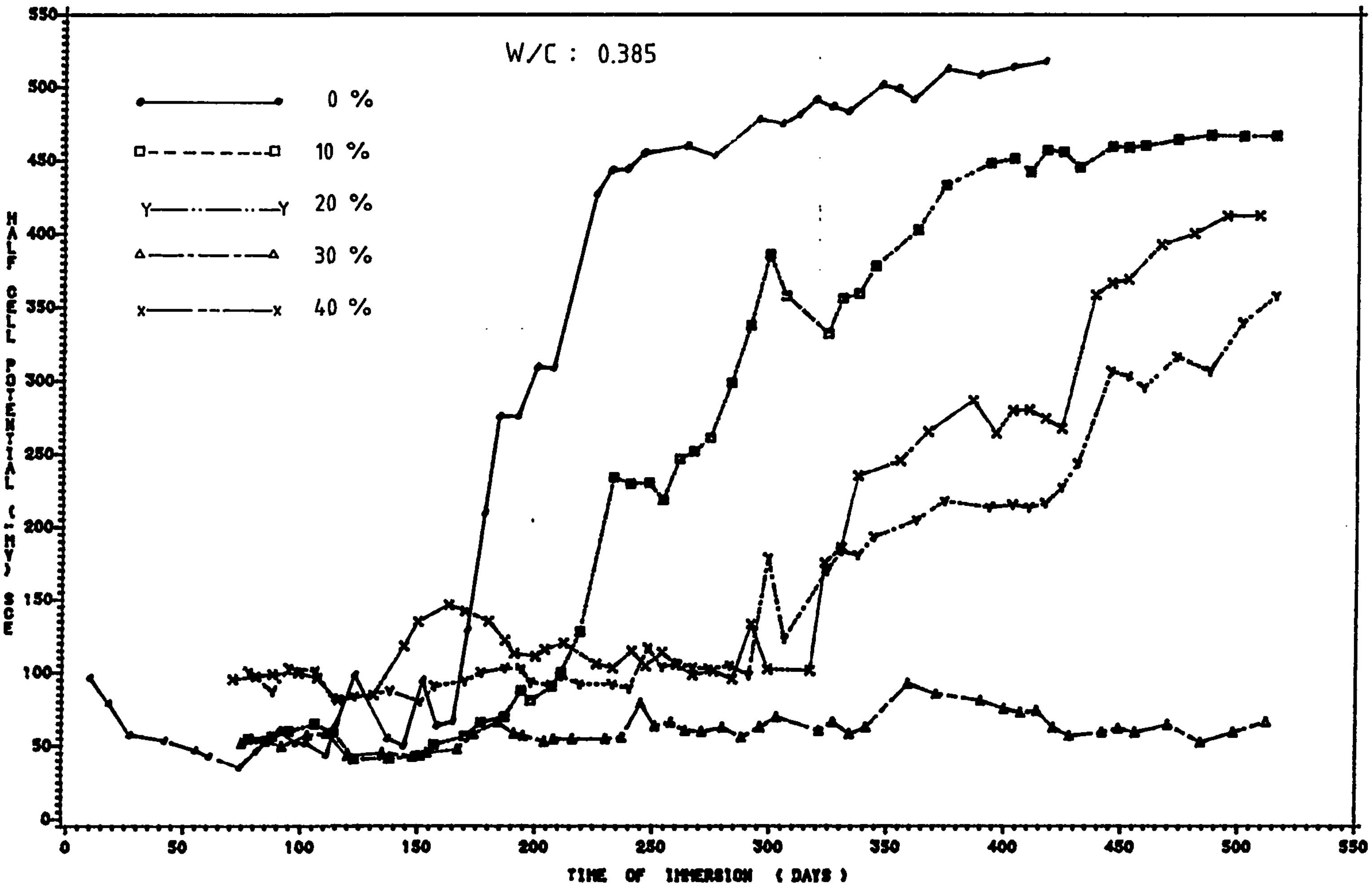

Figure 4.31. Half-cell Potential Data for Plain and Pozzolan Concrete

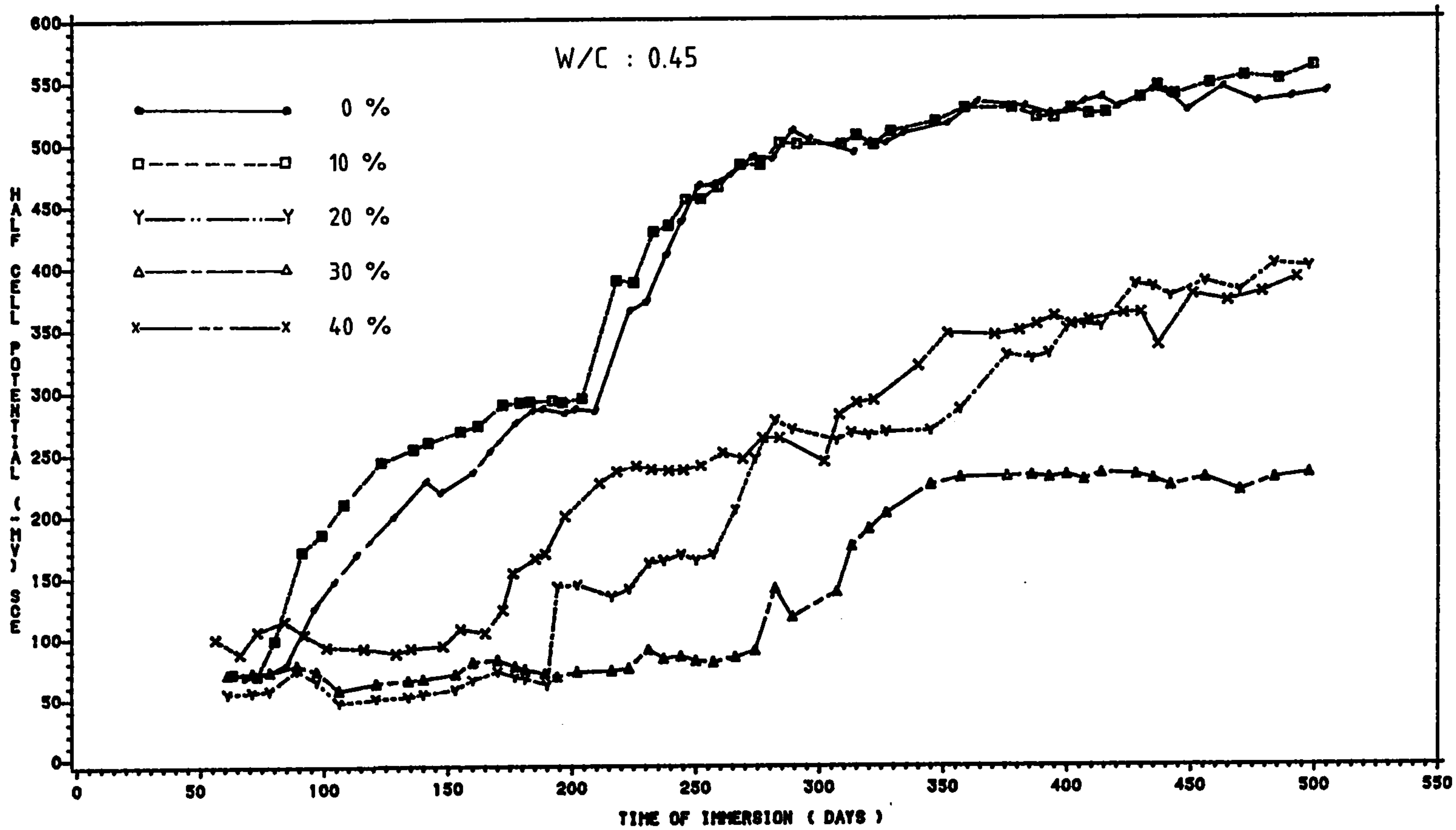

Figure 4.32 Half-cell Potential Data for Plain and Pozzolan Concrete

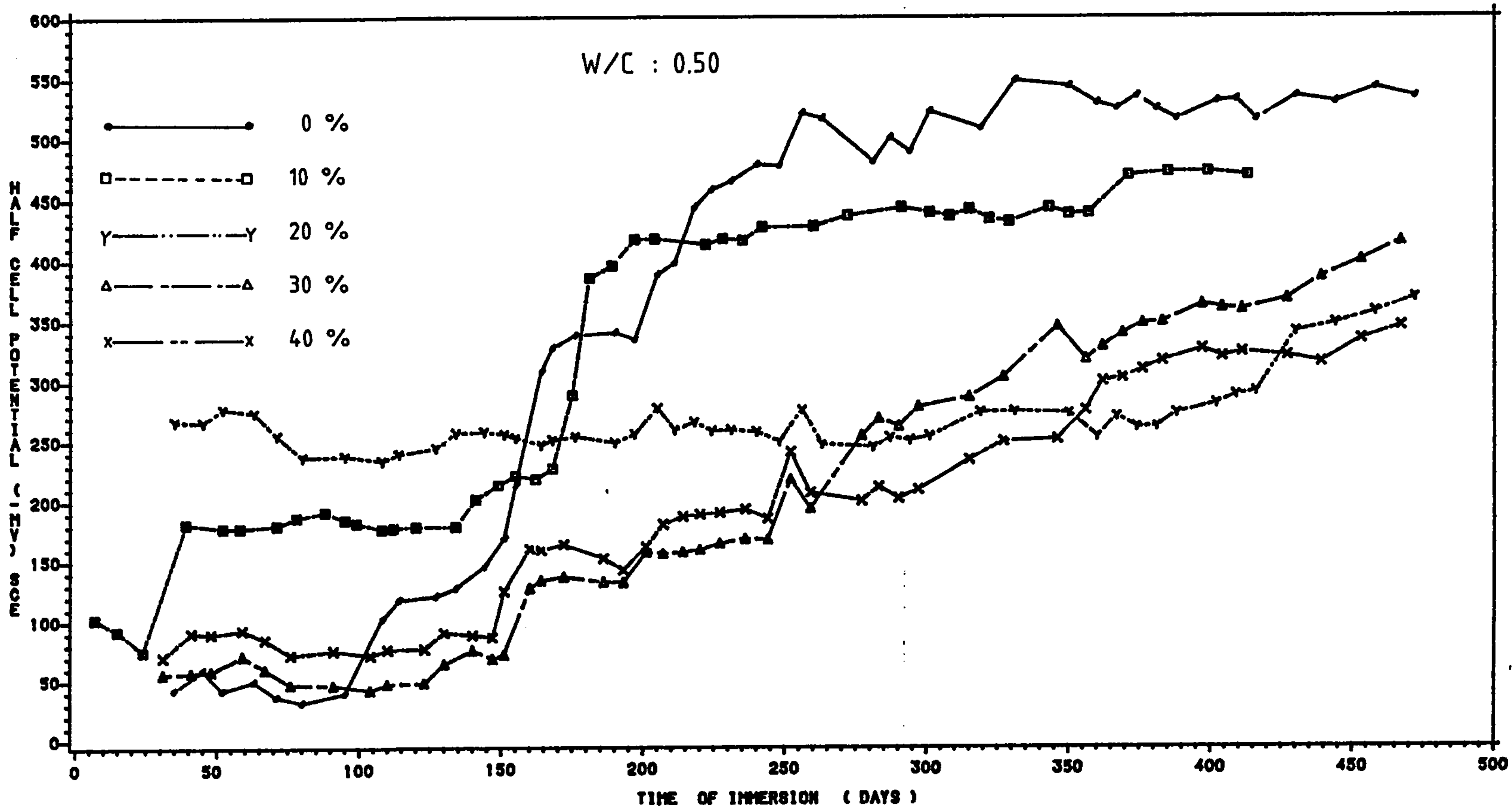

Figure 4.33 Half-cell Potential Data for Plain and Pozzolan Concrete

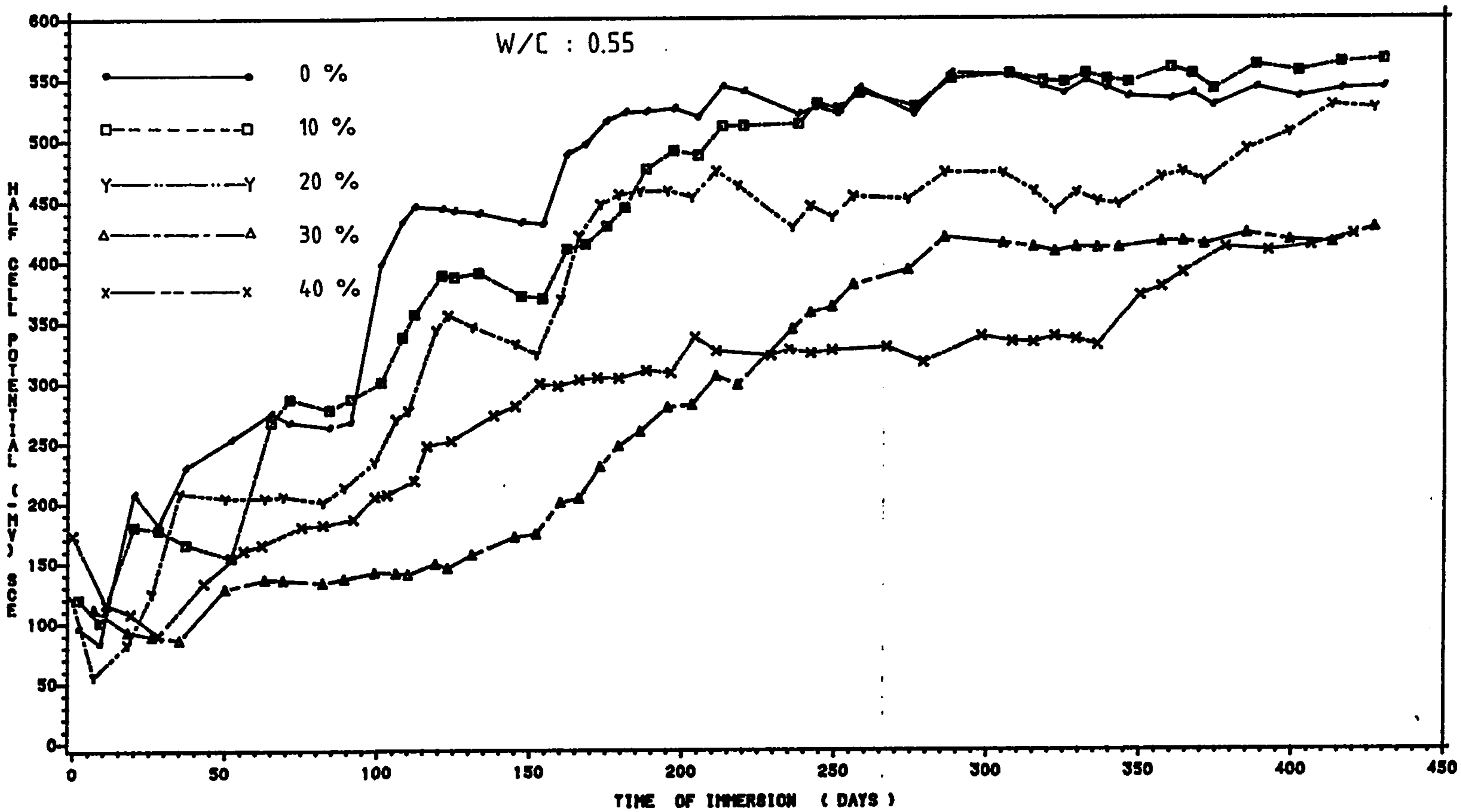

Figure 4.34 Half-cell Potential Data for Plain and Pozzolan Concrete

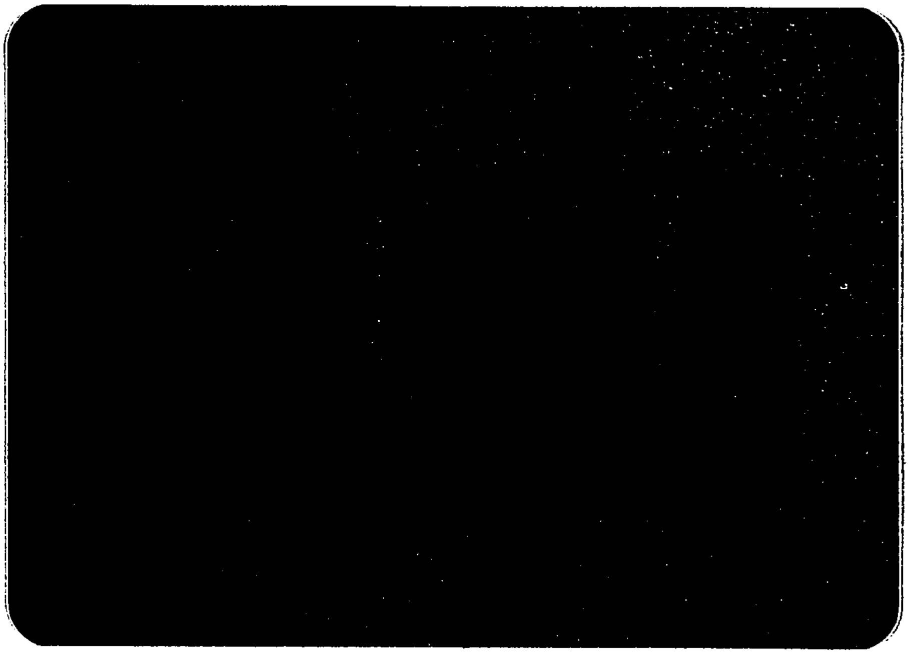

Figure 4.35 Typical Assortment of Specimens Showing Different Extent of Cracking

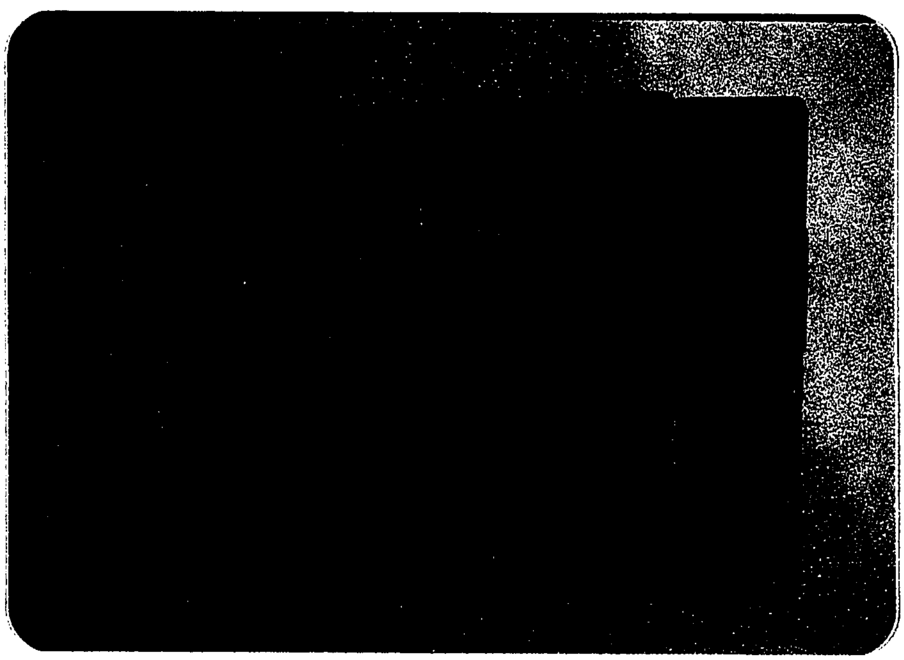

Figure 4.36 Typical Specimens used for Determination of Carbonation Depth

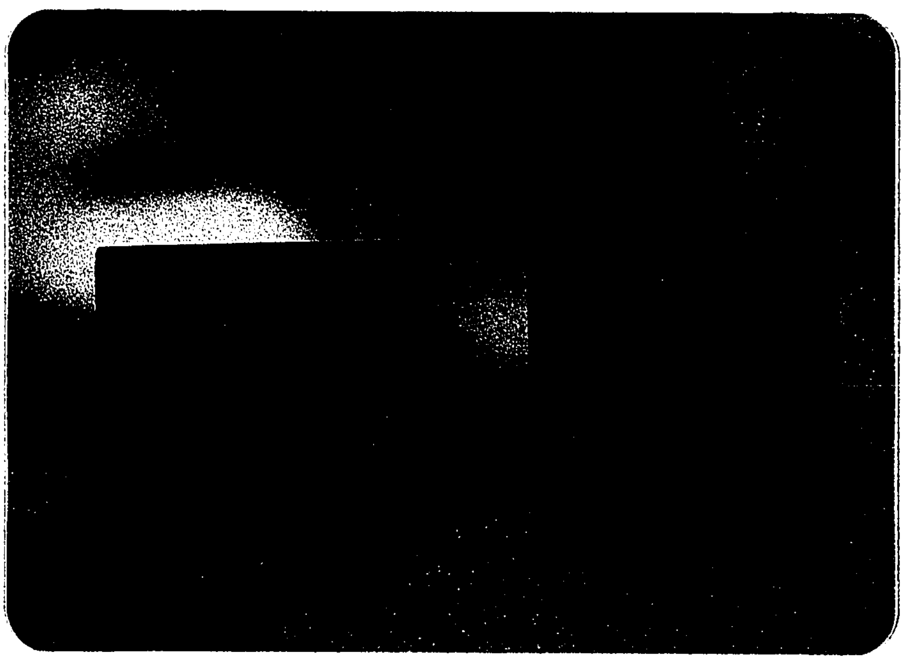

Figure 4.37 Typical Specimens used for the Determination of Carbonation Depth

Chapter 5

ANALYSIS AND DISCUSSION OF RESULTS

5.1 RESULTS RELATED TO POROSITY, PERMEABILITY AND GENERAL QUALITY OF PORTLAND-POZZOLAN CONCRETES

5.1.1 Effect of Cement Replacement by Pozzolans

The movement of aggressive solutions into a concrete mass or the removal of the dissolved products of hydration out of a concrete mass must play a primary role in determining the rate of progress of concrete deterioration due to sulfate and chloride salts which are the root cause of concrete durability problems in the Gulf region. Permeability of a concrete mass must therefore be fundamental to determining the rates of mass transport relevant to destructive chemical action. Given any combination of cement and aggregate, it is generally observed that the less permeable the concrete, the greater will be its resistance to aggressive salt action resulting in sulfate attack and rebar corrosion.

The results on porosity (Figures 4.1 through 4.5) and permeability to water forced under pressure (Figures 4.8 through 4.12) are by and large consistent. These data for different water-cement ratios show that the straight portland cement concrete is the most impermeable and the least porous in the initial period of 50 to 75 days. Thereafter a reversal takes place with pozzolan-portland cement concretes showing lesser porosity and permeability. This indicates that pozzolanic action takes place during the 28 to 60 days of hydration period. The situation in

terms of porosity and permeability is shown to improve for pozzolan-portland concretes upto a period of six months; no significant improvement is indicated after this period. These general trends of the results on porosity and permeability are shown to be independent of the water-cement ratios.

The best performance in terms of porosity and permeability at one-year period is indicated for the 20% cement replacement by fly ash. In terms of porosity data the best performance by 20% fly ash concrete is followed by 30%, 10% and 40% fly ash contents. The straight portland cement concrete is shown to be the most porous at the end of one-year period. In terms of permeability data the best performance by 20% fly ash concrete is followed by 10% or 30% and 40% fly ash concretes. Again the straight portland cement concrete is shown to be the most permeable to forced water at the one-year period.

Quantitatively speaking, for all the water-cement ratios studied in this investigation, the average maximum improvement in porosity for 20% fly ash concretes is 16.3% over plain concrete at a one-year period. The average improvement for water absorption is 33.4% (Table 5.1)

A brief summary of the porosity and permeability values of concretes with and without fly ash obtained in this investigation is given in Tables 4.1 and 4.2.

These results indicate modest improvements as compared to those reported by two other investigators. Davis [49] has investigated the

permeability of concrete pipes containing fly ash substituted for cement in amounts of 30% and 50%. Permeability tests were made on 150 by 150 mm cylinders at ages of 28 days and 6 months. The results are shown in Table 5.2. Although a precise comparison of no-fly ash and fly ash concretes investigated in the reference cited above is difficult as the water-cement ratios are somewhat different, but the 6 month values indicate a 3.5 to 5 fold improvement in concrete with fly ash addition. Elfert [50] has also reported data shown in Figure 5.1 comparing the permeability rates of fly ash and non-pozzolan concretes. These data also show a 7 to 10 fold improvement in fly ash concretes. The difference in these results could be attributed to the rather now familiar position that the reactive properties of pozzolans vary quite considerably depending on their origin. Unfortunately, no absolutely reliable chemical methods have yet been developed for determining the reactivity of pozzolanic materials.

The pulse-velocity data (Table 4.3 and Figures 4.17 through 4.21) indicate the general quality of concrete. These data also show the best performance is by 20% fly ash concretes for the various water-cement ratios studied. This is followed by 10% fly ash concretes. However, pulse-velocity data show the general quality of 30 and 40% fly ash concretes to be somewhat inferior to that of straight portland cement concretes. Further, the observed reversal in the initial higher performance position of no-fly ash concrete over the portland-pozzolan concrete is indicated at a period of about six months. It is seen from Table 5.1 that at one year period, the average performance of fly ash concretes is 0.59% superior over the straight portland cement concretes.

The porosity and permeability data shown in Figures 4.1 through 4.5 and Figures 4.8 through 4.12 can be explained on the basis of the fact that the permeability and porosity of concrete is directly related to the quantity of the hydrated cementitious material at any given time. The pozzolanic action leading to an eventual reduction in porosity and permeability can be attributed to the conjoint chemical and physical mechanisms. What is significant is the reaction kinetics involving siliceous compounds of pozzolanic material and calcium hydroxide on the one hand, and the normal hydration of clinker compounds on the other. The former reaction results in the partial conversion of non-cementitious and leachable calcium hydroxide into cementitious secondary calcium silicate hydrates. This reaction, however, is slower than the main hydration process. An increasing replacement of cement is akin to a reduction of cementitious material in the early phase of hydration and therefore results in a corresponding increase in the porosity and permeability of pozzolan-portland concretes in the early age period. However, at later ages, with suitable cement replacement by fly ash, the porosity and permeability position is reversed with respect to straight cement concrete mixes because in the former, part of the weak calcium hydroxide phase has been permanently replaced by hardly soluble and cementitious silicate hydrates. The eventual improvement in the porosity and permeability position of pozzolan concretes also involves the physical process of densification of the cement paste matrix as a result of the filling up of gel pores of original tobermorite skeleton by the secondary cementitious silicate hydrates generated by the aforesaid pozzolanic activity.

Another point which needs discussion is the indicated low porosity of concretes in the helium intrusion porosimetric measurement. This is of the order of 15 to 7% at young and mature stages of investigation, respectively. It is known that if we ignore the void volume in the aggregate, good quality concrete at a young age will have a total void volume of about 20-25% and at a mature age of about 10 to 15%. The void volume is made up of three types of pores: air voids (upto 2mm diameter), submicroscopic capillary spaces (0.000008 to 0.013 mm diameter) and gel pores (0.000001 to 0.000008 mm mean diameter). In the helium intrusion porosimetry, the volume that enters is the volume of the pore and the pressure required to cause entrance is related to the size of the pores. In this investigation the pressure of helium intrusion was kept low at 100 psi. The idea was to record the comparative position of the relatively bigger pore spaces which have a significantly higher probability of forming interconnected paths of water flow thereby giving rise to pore space characteristics of a permeable concrete. Data developed by Robson [51] pertaining to permeability tests of concrete clearly indicate the primary role of bigger pore spaces in creating permeable pore space characteristics. His test results indicate that water moves only along a small number of distinct paths. These paths arise from the relative impermeability of the spaces which comprise a large proportion of the total porosity. The greater the proportion of smaller spaces the greater the chance of paths being formed. Permeability is a function not of total porosity but of pore size distribution, and reflects the chance of occurance of the paths of linked pores.

Figures 4.7, 4.16 and 4.23 respectively show the porosity, permeability and pulse-velocity data for concretes made with German fly ash, French fly ash, Greek natural pozzolan and blast furnace slag cement. It is seen from these data that pozzolans drawn from different sources may exhibit significantly different levels of performance. This necessitates pre-testing, evaluation and characterization of the pozzolans to be used to get a precise idea of their level of contribution toward the improvement of engineering properties of concrete. In this investigation French fly ash performs best and its porosity and permeability performance at six months is 7% and 30% superior to that of Greek natural pozzolan.

5.1.2 Effect of Water-cement Ratio

The effect of water-cement ratio on the porosity, permeability and pulse-velocity is shown in Figures 4.6, 4.15 and 4.22 for straight portland cement concrete and the 20% fly ash concrete for a one-year age. It is seen that there are 28%, 35%, and 5.56% improvements in porosity, permeability and pulse-velocity at one year period when the water-cement ratio is reduced from 0.55 to 0.35.

5.2 RESULTS RELATED TO STRENGTH OF CONCRETE

The strength data for different cement replacements by fly ash and for different water-cement ratios are summarised in Table 4.4 and are shown in Figures 4.26 through 4.30. In all the cases the highest strength is indicated for no-fly ash concretes upto a period of 180 days. This is

followed generally by 10, 20, 30 and 40% replacements. These results are not consistent with the porosity, permeability and pulse-velocity data and there appears to be no satisfactory explanation for this behaviour.

5.3 DURABILITY PERFORMANCE OF PORTLAND-POZZOLAN CONCRETE AGAINST REBAR CORROSION

From Figures 4.31 through 4.34, which show the half cell potentials of rebars embedded centrally in plain and portland-pozzolan concrete specimens, it is clear that portland-pozzolan concretes have a higher protective performance against the corrosion of the embedded steel than plain portland concrete. Generally speaking, a 10% cement replacement by fly ash shows the least improvement specially for water cement ratios higher than 0.385 which have been included in this program. Best performances are shown by 20% (water-cement ratio of 0.50), 30% (water-cement ratios of 0.385 and 0.45) and 40% (water-cement ratio of 0.55) cement replacements by fly ash for different water-cement ratios, although the overall best performance is indicated for the 30% replacement. The long term differential in the performance between plain portland concrete and the portland-pozzolan concrete is best indicated for the lowest and the highest water-cement ratios of 0.385 and 0.55. This may be explained by the dominant effect of water-cement ratio which in the long run may be a more significant parameter than the addition of admixtures like pozzolans in providing corrosion protective concrete.

The corrosion monitoring of the field specimens is shown in Tables 4.5 to 4.8. Table 4.5 shows the observed date of first cracking and average crack widths. It is clear from these data that chloride content is the controlling factor in the durability performance. Only specimens with 16 lb/yd^3 chloride content and the specimen with sea water have cracked. All others are uncracked. There are hardly any significant differences in the dates of first crack appearance in the 16 lb/yd^3 series to suggest any definite role of the fly ash content in conjunction with chloride salts on rebar corrosion. The only indication of higher fly ash content in conjunction with chloride salt being conducive to higher corrosion is the cracking of the one 40% fly ash specimen in the sea water series. However, the other specimen with the same parameters has not cracked as yet.

The weight loss measurements listed in Table 4.6 also confirm the controlling effect of chloride content and not of pozzolan content. The average weight loss increases consistently with chloride content ranging from 9.66% for 1 lb/yd^3 chloride to 14.08% for 16 lb/yd^3 chloride content. Increase in fly ash content from 20 to 40% does not show any consistent format in terms of increase or decrease in weight loss of rebar metal. A discussion related to an evaluation of the corrosion-inhibiting role of pozzolan in reinforced concrete needs a brief review of the corrosion mechanism and the influencing parameters.

Steel is passivated against corrosion if embedded in an alkaline environment corresponding to a pH range of 10 to 13. The hydrated cement medium around rebars in concrete provides exactly such an

environment (pH = 12.5). At this pH, a protective film of gamma ferric oxide forms on the steel surface, effectively inhibiting the corrosion process. Such a protective environment, however, may be disrupted by two specific circumstances. First, when atmospheric carbon dioxide makes a possible ingress into the concrete matrix and its penetrating front advances so deeply as to intercept the steel reinforcement. Carbon dioxide reacts with the alkaline medium (constituted by alkalies existing as products of hydration) and neutralizes it by forming carbonates, therby damaging the quality of the protective environment. Second, the chloride ion, being a specific destroyer of the protective film, is especially effective in eliminating passivity against corrosion. Once the passivating film is broken corrosion in reinfoced concrete is an electrochemical process necessitating the presence on rebar surface of anodes and cathodes associated with the flow of direct current in the corrosion cell. Conducive to the electrochemical process of corrosion in reinforced concrete are:

Firstly, diffusion of oxygen and chloride and sulfate salts to the steel-concrete interface. Presence of oxygen at the cathode causes cathodic depolarization and significantly accelerates and controls the corrosion process. The second factor of chloride presence is significant because the chloride ion is a specific destroyer of the passivating hydrated ferrous oxide film on rebar surface which acts as a thin impermeable layer restricting the passage of water and oxygen to the steel surface.

Secondly, pore water, specially containing dissolved salts, acts

as an effective electrolyte with low electrical resistivity that favors the flow and passage of the corrosion current.

This mechanism entails that the more permeable the concrete is the more profuse would be the diffusion of oxygen and chloride bearing moisture into the concrete pores with their ready movement to the steel-concrete interface. Also, the pore water acting as an electrolyte would be more readily available in a porous concrete than in an impermeable, water-tight and dense concrete. There is a measure of agreement on the evaluation that the single most significant protective property of the concrete against corrosion of the embedded steel is its permeability and porosity. As has been clearly indicated by the test results in Figures 4.8 through 4.12, one of the significant contribution made by the pozzolan addition to concrete is a noticeable reduction in its permeability over that of concrete made without pozzolan. This position indicates that in concretes made with pozzolan-portland cement the diffusion of oxygen and chlorides and the presence of pore-water will be reduced significantly thereby lowering the probability of corrosion of the embedded steel. Similar contentions have been made by Davis [49], Ryan [52] and Larsen et al. [11].

A second factor in the activation and progress of the electrochemical rebar corrosion process is the electrical resistivity characteristics of the concrete. This property has been specifically investigated in one of the investigation carried out at UPM [53]. Figure 5.2 typically shows the effect of 10 and 25 per cent cement replacement by pozzolan (fly ash) on the electrical resistivity characteristics of portland-pozzolan

concretes made with a water-cement ratios of 0.35. Similar results were obtained for concretes with water-cement ratios of 0.45, 0.55 and 0.65. In each of the four water-cement ratios it is seen that the addition of pozzolan increases the electrical resistivity of concrete thereby reducing the probability of rebar corrosion. It was observed that the electrical resistivity increases with an increasing addition of pozzolan.

These data on electrical resistivity characteristics of concrete also dispose off the concern often expressed to the effect that the presence of pozzolan in the form of fly ash would induct carbon, which is one of fly ash constituents, thereby increasing the electrical conductivity of concrete resulting in an acceleration of the electrochemical action and rebar corrosion. The carbon content of the fly ash used in the aforesaid research program was 6.24% by weight which is significantly in excess of the usual limits of 3% now commonly imposed on fly ash composition by concrete users. Even this percentage of carbon had no decisive effect in lowering the electrical resistivity of concrete. The reason appears to be based on the fact that in the commonly adopted cement replacement of 25% by fly ash, the fly ash would constitute about 2.3 to 2.5 percent by weight of the concrete. With carbon normally constituting only 3 to 5% of the fly ash by weight, it would be such a small amount in the concrete, and so well dispersed through the mass that the electrical resistivity of the concrete and the corrosion rate of the embedded steel would be hardly affected at all.

Another concern sometimes expressed [54] in relation to the fly ash

addition to concrete as a possible source of increased corrosive action is in terms of the presence of sulfur compounds in fly ash. The sulfur content of twenty samples of fly ashes collected from different parts of the United States has been reported by Davis [49]. The total sulfur and sulfur compounds, computed as SO_3, ranged from 0.01 to 3.26 percent with an average of 1.20 percent. In another reference [55], Davis reports sulfur content (computed as SO_3) of a large number of samples ranging from 0.42 to 2.34 percent. An analysis of 29 samples of Type-II portland cement indicated an average SO_3 content of 1.77 percent. It would seem, therefore, that the fly ash would cause little if any, more corrosion than would an equal volume of portland cement and would not be an additional factor in influencing the corrosion rate.

Another factor which corroborates this conclusion is the fact that an analysis of fly ashes by the Bureau of Reclamation has shown that the sulfur present in fly ashes is in the sulfate form. This highlights the possibility of sulfur existing in fly ashes as calcium sulfate and alkali sulfate and would have an effect similar to gypsum in cement. Also, Figure 5.3, which is a plot of the chlorides, and sulfates contents against rebar corrosion (measured as loss of metal) based on field samples obtained during field studies at UPM [3] show clearly that even high sulfate contents do not promote significant corrosion. Evans [56] experiments on corrosion rates where solutions of calcium and magnesium sulfates were used showed that the corrosion rates in these solutions were far less than in the presence of distilled water.

This leaves only one aspect which may be of considerable importance in

terms of establishing a relationship between fly ash and corrosion; this pertains to the effect of fly ash on the pH value prevailling in concrete. Steel is passivated against corrosion in an alkaline environment corresponding to a pH in the range of 10 to 13. The hydrated cement medium around rebar in concrete is characterized by the liberation of calcium hydroxide [$Ca(OH)_2$] during the setting process of portland cement and provides exactly such an alkaline passivating environment (pH = 12.5). At this pH, a protective film of gamma ferric oxide forms on the steel surface, effectively inhibiting the corrosion process. Any circumstance which reduces the alkalinity of the concrete environment to below a pH value of 10 would be of a potential danger as it lowers the level of protection against corrosion and would eventually promote corrosion. Well hydrated straight portland cements have a [$Ca(OH)_2$] content varying from 15 to 30 per cent by weight of unhydrated cement [7]. This represents not only a high degree of basisity but also a high order of reserve basisity. However, the pozzolanic action in cements and concretes is primarily characterized by a reaction involving the siliceous compounds of pozzolanic material and calcium hydroxide. This reaction results in the partial conversion of non-cementitious and leachable calcium hydroxide into cementitious secondary calcium silicate hydrates. Although this conversion is good in terms of the general quality of concrete as it results in a reduction of permeability and in a densification of concrete matrix, it may be bad in terms of corrosion kinetics as it may also result concurrently in a reduction of the pH which may lower the level of protection offered to the embedded steel against corrosion.

An attempt has been made to develop data on this aspect by exposing

samples made of straight portland cement and pozzolan-portland cement. The specimens were sliced after about 300 days of exposure at the exposure-site and pH values of the hardened cementitious material determined in several slices removed from each specimen. The results are shown in Table 4.7. It is seen that the pH remains in the range of 12.20 to 12.75 even after 300 days of reaction between fly ash upto 40% by weight of the cementitious material and the calcium hydroxide of the cement paste. These high values of alkalinity are adequately protective against corrosion. There does not appear to be any reduction in pH either due to fly ash addition or due to the chloride salt addition in conjunction with fly ash as the values for the no-fly ash concrtes are also in the range of 12.25 to 12.70. Further, it is observed from these data that 40% fly ash addition and 16 lb/yd^3 by chloride salt are in no way more detrimental than the 20% fly ash or 1 lb/yd^3 of chloride salt addition.

As pointed out earlier, carbonation of concrete is a potential source of corrosion initiation due to the lowering of the pH value below 10. Data were developed to investigate the effect of fly ash addition on carbonation. These data are presented in Table 4.8 of the previous chapter. Figures 4.36 and 4.37 show the typical specimens investigated for depth of carbonation. It may be noted that within a relatively short period of about 11 months, a maximum carbonation depth upto 1.00 cm. (about 0.5 inch) has been observed. This is sufficient penetration of atmospheric carbon dioxide in a good quality concrete to initiate severe corrosion in cases of concrete components, specially slabs, the cover to reinforcement is 0.5 inch or less. It is by now well known

that not maintaining an appropriate cover is one of the important causes of widely prevalent rebar corrosion in this region. Another observation which needs attention is that the carbonation depth is observed to generally increase in the fly ash addition.

Until recently there has been a widespread tendency to discount atmospheric carbonation as a serious cause of steel corrosion in ordinary structural concrete. However, in the climatic conditions of the Gulf region where evaporative drying of concrete almost completely supersedes the hydration drying, carbonation could be a potentially dangerous possibility and should be thoroughly researched. The effect of carbonation is all the more important in the Gulf environment as it appreciably helps in the ingress of chlorides by causing a breakdown of hydrated cement phases which had initially rendered the chloride insoluble through chemical reactions such as the formation of chloroaluminate hydrate.

TABLE 5-1 Improvements in Porosity, and Permeability and Pulse velocity at One-year Period for 20% Cement Replacement Pozzolan Concrete.

W/C Ratio	Porosity			Permeability			Pulse Velocity		
	Straight Cement	20 % Fly ash Cement	% Improvement	Straight Cement	20 % Fly ash Cement	% Improvement	Straight Cement	20 % Fly ash Cement	% Improvement
0.35	9.207	7.335	20.3	12.80	7.60	40.6	5174	5217	0.831
0.385	9.55	7.70	19.4	13.50	8.70	35.6	5060	5093	0.652
0.45	10.10	8.40	16.83	14.50	10.10	30.3	4967	4995	0.564
0.50	10.795	9.55	11.5	15.60	11.00	29.5	4933	4956	0.466
0.55	11.80	10.20	13.6	16.90	11.70	30.8	4920	4942	0.447

TABLE 5.2: Relative Permeability of Concretes with and without Fly Ash (Ref. 49)

Fly Ash		W/(C + F) by weight	Relative Permeability	
Type	Percent by Weight		28 days	6 months
None	----	0.75	100	26
Chicago fly ash	30	0.70	220	5
Chicago fly ash	50	0.65	1410	2
Cleveland fly ash	30	0.70	320	5
Cleveland fly ash	50	0.69	1880	7

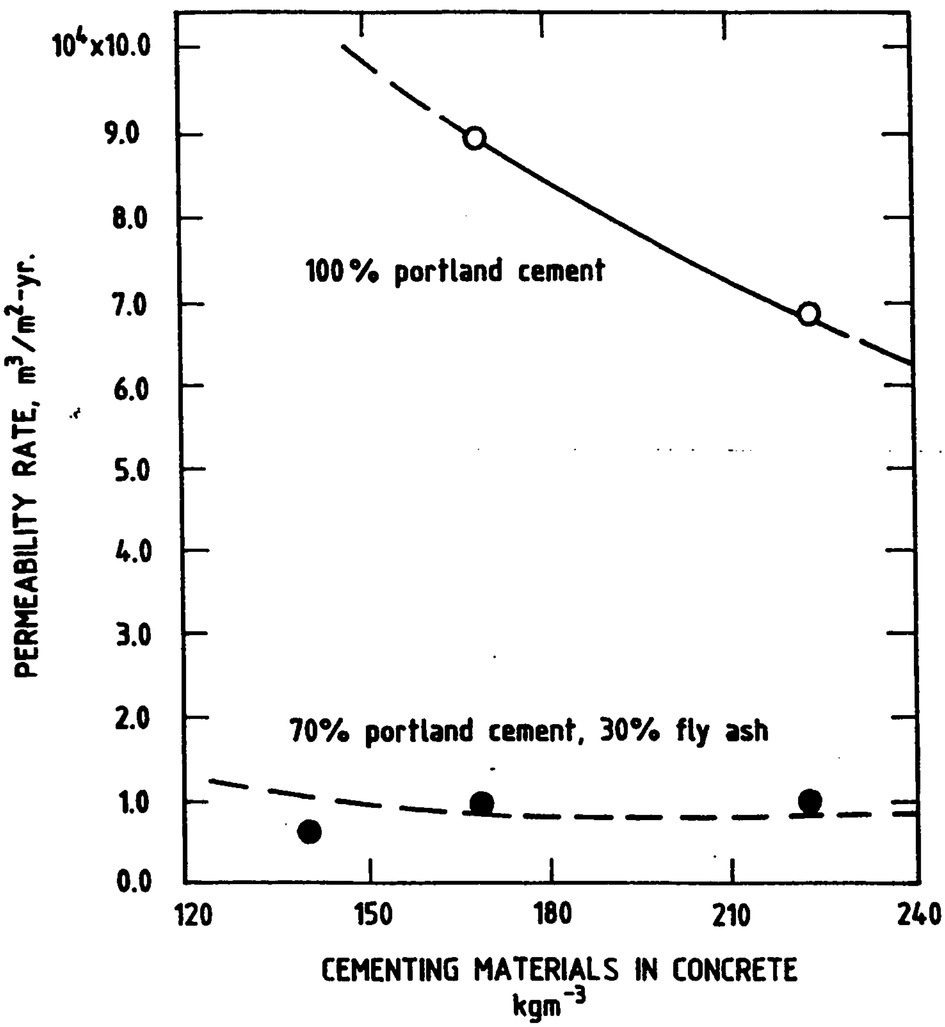

Figure 5.1 Permeability of Plain and Pozzolan Concrete

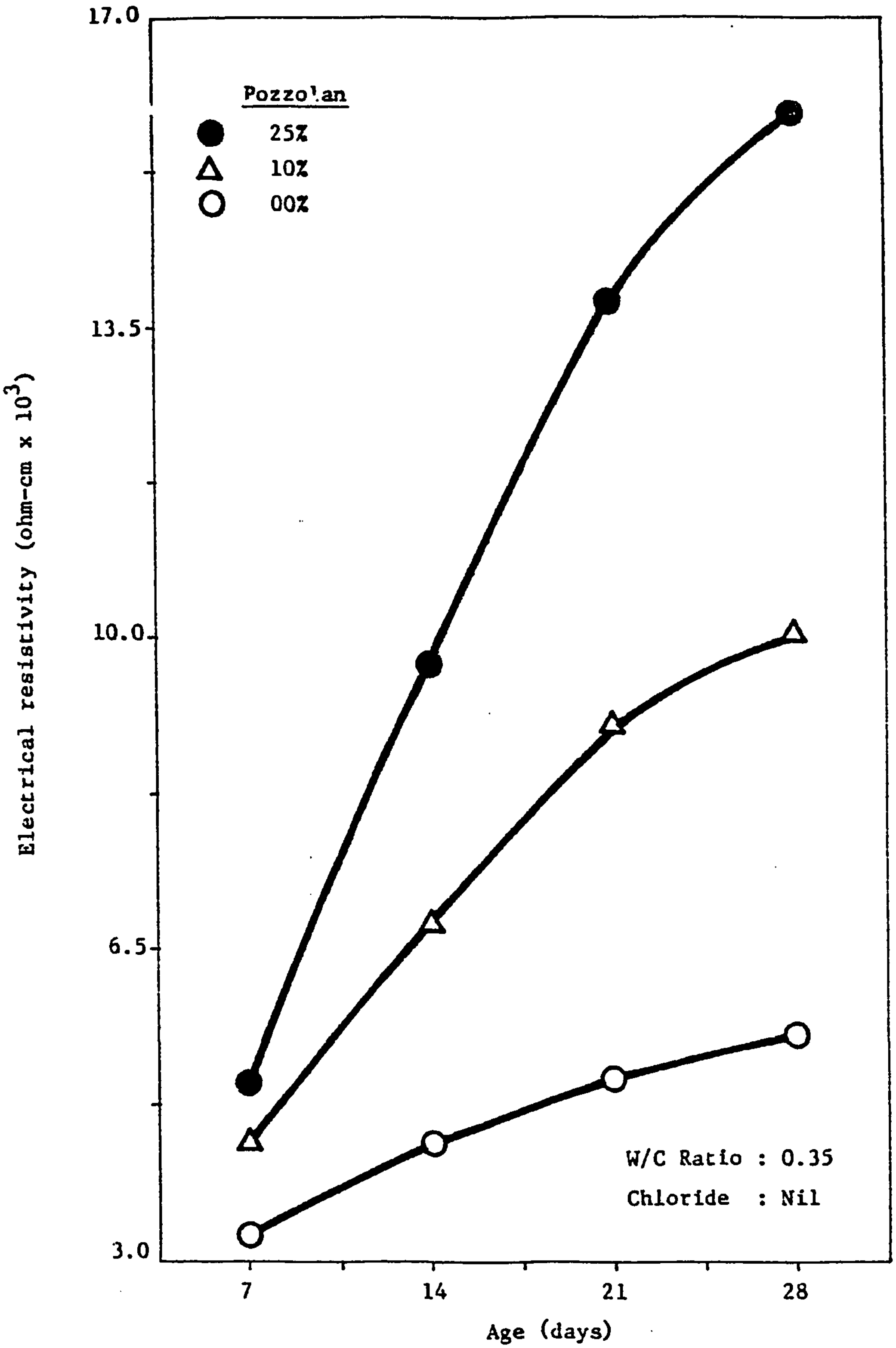

Figure 5.2 Electrical Resistivity Characteristics of Plain and Pozzolan Concrete

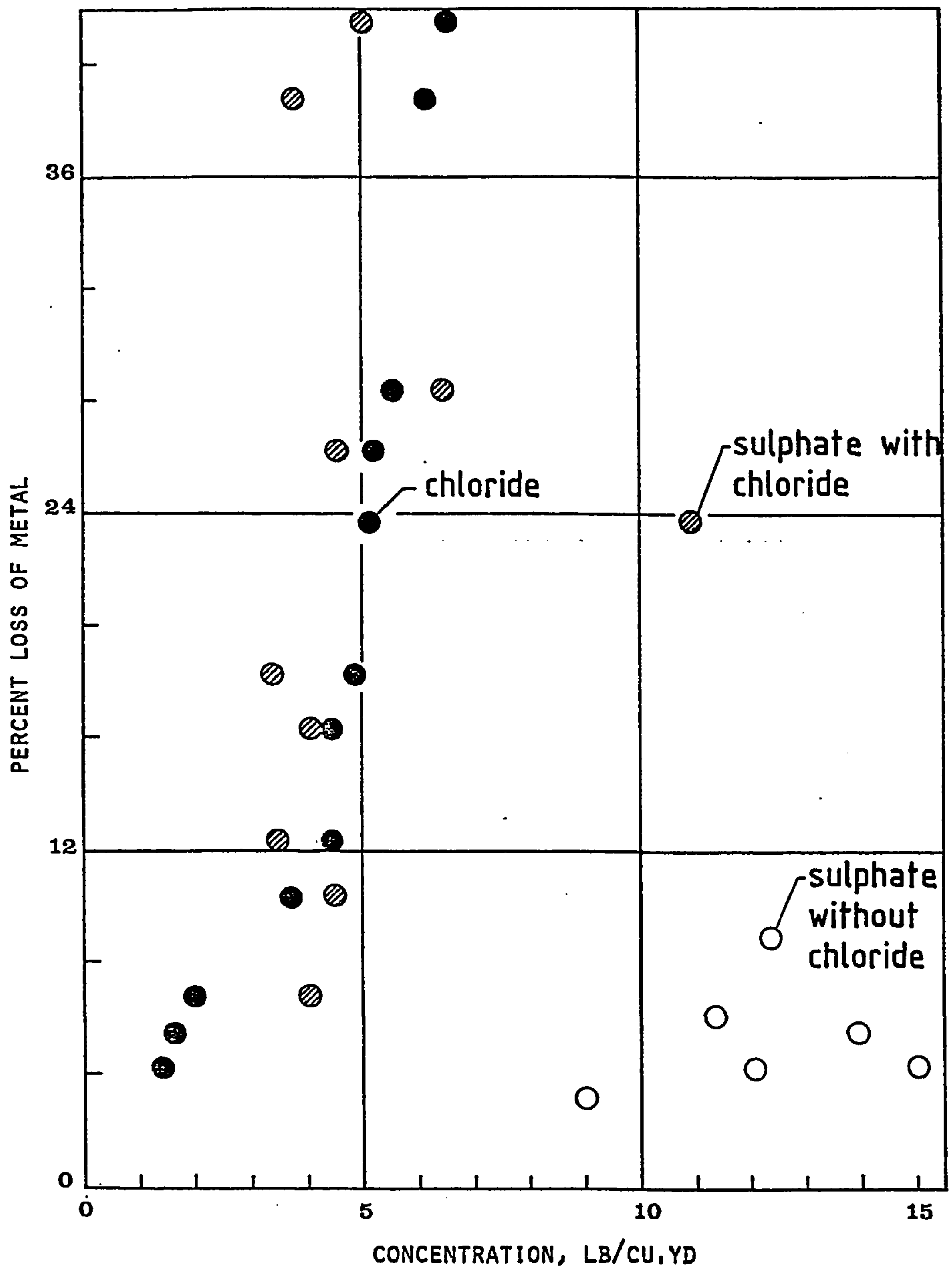

Figure 5.3 Relation between Chloride and Sulfate content in Concrete and Rebar Corrosion (Ref. 3)

Chapter 6

CONCLUSIONS

1. Blending of pozzolan with portland cements in appropriate proportions improves the porosity, permeability, and general quality characteristics of the resulting Portland-pozzolan concretes.

2. There is a 21.0% maximum improvement in the porosity characteristics measured by helium porosimetry technique in a one-year period. The best performance is shown by Portland-pozzolan concretes with 20% cement replacement by fly ash.

3. The maximum improvement in permeability at the end of one-year period is of the order of 41.0%. This maximum improvement is also shown by Portland pozzolan concretes made with 20% replacement by fly ash.

4. The pulse-velocity measurements also show improvement in the general quality of Portland-pozzolan concrete. However, in terms of percentage improvement in the results are significantly below those observed by porosity and permeability measurement techniques.

5. During the first 50 to 75 days, the best performance in terms of porosity, permeability characteristics is shown by straight Portland-cement mixes. However, at the end of one-year period worst performance is shown by the straight Portland cement concrete compared with pozzolan concretes.

6. In terms of compressive strength, the Portland-pozzolan concretes show a consistently inferior performance in comparison with the straight Portland-cement concrete.

7. The results also show a significant effect of W/C ratio on the porosity, permeability, and pulse-velocity data. There are 28,

35, and 5.56% improvements in the porosity, permeability, and pulse-velocity at a one-year period when the W/C ratio is reduced from 0.55 to 0.35.

8. Pozzolans drawn from different sources may exhibit significantly different levels of performance necessitating careful evaluation and characterization before actual use.

9. Of the four pozzolans evaluated, the best performance is shown by French fly ash. Its porosity and permeability characteristics are 7% and 30% better than those of Greek natural pozzolan.

10. Portland-pozzolan concretes show significantly better performance than straight Portland cement concrete in terms of resistance against rebar corrosion. This may be ascribed to the interactive effect of decreased impermeability and increased electrical resistivity characteristics shown by Portland-pozolan concretes.

11. The best overall performance in terms of resistance against corrosion is shown by concretes with 30% cement replacement by fly ash.

12. Portland-pozzolan concretes contaminated with salts do not show any noticeable aggravation in the rebar corrosion process due to the presence of fly ash. The extent of chloride content in concrete controls the corrosion process.

13. Reaction between fly ash and calcium hydroxide of the hydrated cement paste does not reduce the pH value below those observed for no-fly ash concretes. The observed pH values for fly ash concrete were in the range of 12.20 to 12.75 whereas those for no-fly ash concrete varied between 12.25 to 12.70.

14. Carbonation depths upto about 1.0 cm were observed in a relatively short period of 11 months of concrete exposure. Increase in cement replacement by fly ash increased the average depth of carbonation.

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