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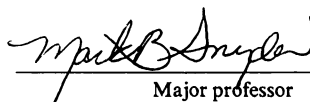
Frost Resistance of Portland Cement Concrete Prepared
With Chemical and Mineral Admixtures at
Marginal Air Content

presented by

Shamshad Ahmad Khan

has been accepted towards fulfillment
of the requirements for

Doctor of Philosophy degree in Civil Engineering


Major professor

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**FROST RESISTANCE OF PORTLAND CEMENT CONCRETE PREPARED
WITH CHEMICAL AND MINERAL ADMIXTURES AT
MARGINAL AIR CONTENT**

By

Shamshad Ahmad Khan

Volume I

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

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Department of Civil and Environmental Engineering

1992

ABSTRACT

FROST RESISTANCE OF PORTLAND CEMENT CONCRETE PREPARED WITH CHEMICAL AND MINERAL ADMIXTURES AT MARGINAL AIR CONTENT

By

Shamshad Ahmad Khan

Freeze-thaw durability is considered to be one of the most important factors affecting the performance of portland cement concrete in temperate regions. Frost resistance, which is believed to be a function of the air void and water pore systems, is affected by the use of different types of chemical and mineral admixtures. Air entrainment has traditionally been considered the single most important factor for making frost-resistant concrete, but the use of silica fume has recently shown some promise in the preparation of nonair-entrained frost-resistant concrete at very low water-cement ratios. This research was conducted to determine qualitatively and quantitatively the effects of various chemical and mineral admixtures on the frost resistance of portland cement concrete at marginal air contents and typical water-cementitious ratios.

A laboratory experiment was designed and conducted on concrete mixes that represented a broad range of admixture applications. Most of the test mixes were designed to contain only small amounts of entrained air so that the effects of the admixtures on concrete durability would be more apparent. Durability testing was

performed, along with strength testing and microscopic analyses of the air void and water pore structure. Permeability and the freezable moisture testing was conducted on the companion specimens at the University of Washington under the same project. Several measures of the concrete air void systems were computed and compared to determine which parameters are the best predictors of concrete frost resistance. Results indicated that spacing factor based on entrained air content was the best predictor of concrete frost resistance for the mixes tested in this work. It was also concluded that the maximum allowable spacing factor can be increased from 0.2 to 0.3 millimeter without loss of durability for many mixes prepared with chemical and mineral admixtures.

The results indicated the possibility of producing frost-resistant concrete at marginal air contents with 15% class F fly ash, and 8% and 15% silica fume (replacement by weight of cement). The good performance of class F fly ash was attributed to the effects of type, amount pozzolan, and particle size distribution. In the case of silica fume, the fineness and the pozzolanic properties of the material were considered the most likely sources of improved performance, producing significant reductions in the permeability and the freezable moisture.

Finally, a model was developed to predict concrete durability as a function of spacing factor, freezable moisture, and compressive strength. Freezable moisture was found to be an especially important indicator of frost-resistant concrete. It is recommended that additional work be performed to validate this finding on a wider range of mix designs and to develop design criteria that utilize freezable moisture measurements.

To My **ALLAH**
The Most Merciful
and
The Most Beneficent

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LIST OF ABBREVIATIONS

Abbreviation	Meaning
#/cyd	pounds per cubic yard
AC	air content
ACI (mm)	average chord intercept in millimeters
ACI	American Concrete Institute
ACLEA	air void chord length based on entrained air content
ACLTA	air void chord length based on total air content
AEA	air entraining agent
AEA1	air entraining agent type 1, Daravair
AEA2	air entraining agent type 1, Microair
AMS	Attiogbe mean spacing
ARSq	adjusted R square
ASTM	American Standards for Testing Materials
AVEA	air voids based on entrained air content
AVS	air void system
AVTA	air voids based on total air content
BSG	bulk specific gravity
C-S-H	calcium silicate hydrates
C ₂ S	dicalcium silicate
C ₃ A	tricalcium aluminate
C ₃ S	tricalcium silicate
C ₄ AF	tetracalcium aluminoferrite
CA-SSD	coarse aggregate in SSD condition
Ca(OH) ₂	calcium hydroxide
CDS	critical degree of saturation
Cl	class
CSA	Canadian Standards Association
CSF	condensed silica fume
C-str	compressive strength
CT	curing time
Cyc	cycles
DF	durability Factor
Eqs	equations
FA	fly ash
FA-SSD	fine aggregate in SSD condition

Abbreviation	Meaning
FAC	fresh air content
FM	freezable moisture
FTC	freeze-thaw cycles
FTD	freeze-thaw durability
GGBF slag	granulated ground blast furnace slag
H-water	hydration water
HEA	hardened entrained air content
HRWR	high-range water-reducer
HTA	hardened total air content
JSCE Standard	Japanese Society of Civil Engineers Standard
k	coefficient of permeability
L-chg	change in length
max	maximum
min	minimum
ml/cyd	milliliter per cubic yard
mm	millimeter
n	void frequency
nm	nanometer
P	paste content
P/A	paste to air ratio
P/A-T	paste to air ratio based on total air content
P/A-E	paste to air ratio based on entrained air content
PCC	portland cement concrete
Perm	permeability
PF	Philleo factor
Pozz	pozzolan
Recomm	recommended
RDM	relative dynamic modulus
RH	relative humidity
RSq	R square
s	standard deviation
SAI	slag-activity index
SE	standard error
SF	spacing factor
SFEA	spacing factor based on entrained air content
SFTA	spacing factor based on total air content
Slp	slump
SS	specific surface
SSD	surface saturated dry
SSE	specific surface based on entrained air content
SST	specific surface based on total air content
TGA	thermal gravimetric analysis
VPMEA	voids per millimeter based on entrained air content

Abbreviation	Meaning
VPMM	voids per millimeter
VPMTA	voids per millimeter based on total air content
W/C+P	water-cementitious ratio
W/C	water-cement ratio
WPS	water pore system
WR	water-reducer
Wt-chg	change in weight
Å	angstrom
α	specific surface
μm	micron

CHAPTER I

INTRODUCTION

1.1 Problem Statement

Concrete has been widely used as a construction material since the Roman era about 2000 years ago [1]. While many concrete structures have withstood the disruptive forces of nature (in some cases for centuries), others have shown signs of deterioration after only a few months. One major source of poor durability in concrete was identified in the early 1930s: the deterioration of concrete due to repeated cycles of freezing and thawing. Many studies since then have verified that concrete is susceptible to the phenomenon of frost action in the presence of moisture [2].

There have been dramatic improvements in the properties and performance of portland cement concrete (PCC) over past decades, particularly with respect to durability. The discovery of the beneficial effects of air entrainment followed by the cooperative research efforts of many organizations finally resulted in the establishment of current

specifications for providing frost-resistant concrete. These specifications are based primarily upon air content, strength, and air void characteristic requirements. The criteria recommended by American Concrete Institute (ACI) committees 201, 211, 212, and 318 [3,4,5,6] are being used internationally.

However, it has been established that the use of different kinds of air-entraining agents (AEA) affect the frost resistance of concrete in different ways, resulting in the production of concretes ranging from highly frost-resistant to totally non-frost-resistant, depending on the bubble size and spatial distributions as well as the total volume of air produced [7]. It has also been documented that, for normal strength concrete, each percentile of air entrainment reduces the compressive strength of the concrete by about 2 to 10 percent [8,9,10,11].

The development and use of other types of admixtures during the past few decades have also revolutionized the use of concrete in many ways. For example, the use of water reducers (WR) or high-range water reducers (HRWR), also known as superplasticizers, has now made it possible to produce workable concrete with extremely low water-to-cement ratios (W/C), which was almost impossible in the past [3,4,12]. These admixtures have often produced frost-resistant concretes with higher spacing factors than allowed by standard specifications [13]. The stability of the air void system of the concrete in the presence of superplasticizers has also been questioned and spacing factors two to three times higher than those produced by AEA have been observed in the hardened concrete [14].

The partial replacement of the portland cement with different types of mineral admixtures, such as fly ashes (FA), ground granulated blast furnace slag (GGBF slag),

and condensed silica fume (CSF), is also becoming more common. These materials improve some properties of the concrete and have economic and environmental advantages. These mineral admixtures, have different origins and different chemical and physical characteristics, have great potential for altering the PCC air void characteristics of permeability and pore structure, which may greatly affect the frost resistance of the portland cement concrete [18,19,20,21,22,23].

Tynes [21], Malhotra [22], Whiting [23] and others generally agree on the effects of admixtures on many PCC properties. However, there is considerable disagreement concerning their effects on the frost resistance of concrete. Furthermore, there are no separate specifications for the production of frost-resistant concrete made with chemical and/or mineral admixtures; the specifications that have been prepared for normal concrete with AEA are expected to apply to all concretes without distinction, which may or may not be true.

The frost resistance properties of PCC produced using various kinds of admixtures must be used to evaluate existing criteria for the production of frost-resistant concrete because these criteria may or may not be generally applicable to today's materials. The chemical and physical properties of the admixtures, together with the fine particle size and pozzolanic and cementitious properties of the pozzolans, greatly affect the pore structure and the air void system of the concrete, and thus, the concrete frost resistance. These factors have not yet been thoroughly evaluated in the context of concrete frost resistance and its relationship to the air void and water pore system parameters.

Given the above, there is a need to evaluate and study the effects of chemical and mineral admixtures on the air void system, water pore system, and frost resistance of

portland cement concretes. Criteria for the production of frost-resistant PCC must also be improved.

1.2 Objective

The overall objective of the study here is to advance the state of the knowledge on the frost resistance of concrete, and study the effects of various types of chemical and pozzolanic admixtures on the durability of portland cement concrete exposed to repeated cycles of freezing and thawing.

The specific objective of the experiment in this study is to determine qualitatively and quantitatively the effects of various kinds of admixtures on the air void parameters and frost resistance of portland cement concrete produced at marginal air content, and to suggest modifications, if any, to the existing specifications/guidelines for the production of frost-resistant concrete.

1.3 Research Approach

A two-phase approach was adopted for this study. Phase I of the research was to conduct an extensive literature review to identify the research needs with respect to the frost resistance of concrete made with different kinds of chemical and mineral admixtures. Phase II of the work was to develop and conduct a test program in order to determine the effects of different combinations of admixtures, water-to-cement/cementitious ratios ($W/C+P$), and curing time on the air void system and the

frost resistance of PCC. Various air void parameters were measured for each mix design, and tests were conducted to determine different freeze-thaw durability measures. A computer program developed at the University of Washington was run on data extracted from linear traverse tests to determine various air void parameters for the hardened concrete, and a statistical analysis package was used to identify and quantify relationships between the design and performance parameters.

1.4 Scope

Many types of chemical and mineral admixtures are available in today's market. It would be almost impossible to test all of these admixtures here because of time and economic constraints. Thus, the variables selected for use are representative of the admixtures and the conditions most commonly used and encountered in the production of improved PCC. Furthermore, these variables were only tested at levels that represent the current range of practice. Two types of AEA and WR/superplasticizers and four kinds of pozzolans (class F and C fly ash, CSF, and GGBF slag) were selected for the research. Curing periods of 28 and 56 days and $W/(C+P)$ of 0.40 and 0.45 were selected to be tested as nonmaterial factors. The preliminary testing was done on three levels of air content and three levels of water-to-cement ratio. In most of the cases, the test variables were kept at two levels for the reasons mentioned above; thus, a full factorial matrix design was used to determine the main and interaction effects.

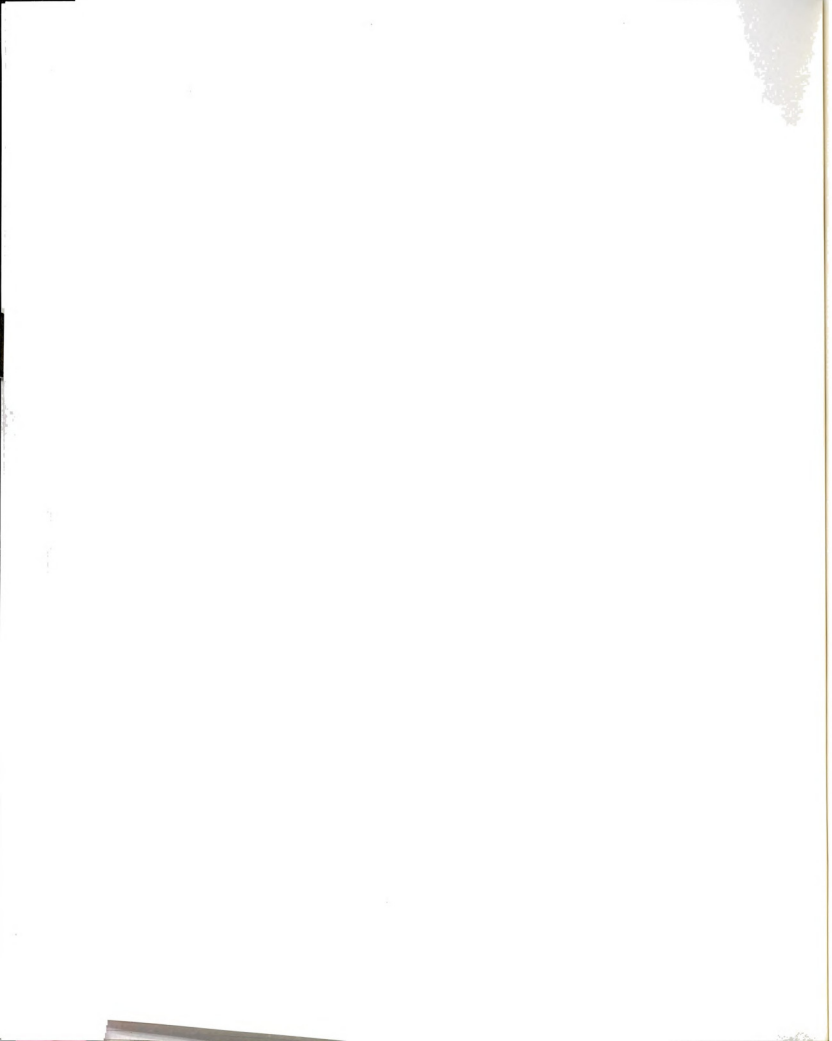
CHAPTER II

BACKGROUND

2.1 Freeze-thaw Durability of Concrete

Current designers of concrete structures in temperate regions are conscious of the freeze-thaw durability of portland cement concrete whose performance is affected by the development and increased use of different kinds of admixtures. Today, the durability of concrete is defined as its ability to resist weathering action, chemical attack, abrasion, or any other process of deterioration [24]. A durable concrete is expected to both retain its shape and quality, and render its intended service for the design period.

The research work of the past few decades has shown that freeze-thaw durability is a problem for temperate regions where structures are exposed to repeated cycles of freezing and thawing in the presence of moisture. The damage caused by freezing and thawing is considered serious since it substantially reduces the life of structures. The deterioration of concrete is normally indicated by scaling, spalling, popouts, D-cracking



(deterioration line cracking), and extensive crazing. This damage can be increased by the use of deicing chemicals (salts), which are commonly employed for the removal and prevention of ice formation.

The maintenance and reconstruction of low-durability concrete structures can consume huge amounts of effort, time, and money. However, durability problems can be considerably reduced or eliminated through the use of sound materials and proper mix designs. Extensive research has shown that concrete made with good quality aggregates, low water-cement ratio, and a proper air void system is likely to be highly resistant to frost action if it is allowed to reach maturity before exposure to aggressive environments [25]. The frost resistance of pozzolanic concrete depends on the adequacy of the air void system, the soundness of the aggregate, age, the degree of hydration (maturity), the strength of the cement paste, and the moisture condition of the concrete [26]. Frost resistance will be further discussed in the next chapter.

Aggregate is generally treated as a filler in concrete, but it often plays an important role in concrete durability. Aggregates from different sources with different chemical compositions and physical characteristics exhibit varying properties. Only a few with low absorption, adequate pore structure, and a good freeze-thaw durability record can provide a frost-resistant concrete. The use of good quality, frost-resistant aggregates constrains potential freeze-thaw problems to the paste fraction of the concrete.

2.2 Freezing and Thawing of PCC

2.2.1 General

The deterioration of hardened cement paste can be related to the combined effects of the complex microstructure of the materials from which concrete is made and the specific environmental conditions to which concrete is exposed. Thus, concrete that is frost-resistant under one set of conditions may not be durable under another set of environmental conditions. For example, a well-designed concrete structure cast without air entrainment may last a long time in Texas; the same mix will probably show signs of deterioration much earlier in Michigan, where it would experience repeated cycles of freezing and thawing.

The original hypothesis explaining the mechanism of freezing and thawing was advanced by Powers in 1945 [27]. He and his colleagues further improved upon this work in later years [28]. Although other theories have been presented, all researchers believe that damage due to frost action takes place when the concrete is frozen at or above some critical level of saturation. Therefore, it is useful to discuss the concept of critical saturation before discussing theories relating to the mechanisms of freeze-thaw damage.

2.2.2 Critical Saturation

The theory of critical saturation was first presented by Hirschwalt in 1910 [29]. Since water expands by one-tenth of its volume in changing to ice, when the pores of rock or similar material are uniformly filled with water to nine-tenths of their capacity or less, freezing may complete the filling of the pores without creating additional pressure, and the rock remains unchanged by frost action. When the saturation is carried beyond nine-tenths of the available pore volume, the ice has insufficient room for expansion and produces cracks. This theory was further confirmed by Cardon [30], who explained that one cubic centimeter (cc) of water occupies about 1.09 cc of space after freezing and any void in the aggregate or cement paste which is more than 91 percent full of water will be subjected to pressures when freezing water forms into ice, unless the excess water can be forced from the void during freezing. Thus, concrete deteriorates very rapidly with repeated freezing and thawing, if it is fully saturated [31].

Before further discussion of the mechanisms of freezing and thawing damage, it is important to understand the water pore structure of the hydrated cement paste, which plays a key role in determining the performance of concrete exposed to repeated cycles of freezing and thawing.

2.2.3 Water Pore Structure of Hydrated Cement Paste

General

A knowledge of the microstructure of portland cement paste and the roles played by various kinds of pores is essential to the better understanding of the freezing and thawing mechanism. The discussion below is based primarily on the explanations of Bruneauer [32], Copeland and Schulz [33], Brunauer and Copeland [34], Mehta [2], and Cordon [30].

Structure of the Hydrated Cement Paste

Anhydrous portland cement is produced by pulverizing clinker (a product of high temperature reactions between calcium oxide, silica, alumina, and iron oxide) with a small amount of calcium sulfate. In ordinary portland cement, the amounts of the principal clinker minerals are typically 40 to 60 percent C_3S (tricalcium silicate), 15 to 30 percent C_2S (dicalcium silicate), 6 to 12 percent C_3A (tricalcium aluminate, and 6 to 8 percent C_4AF (tetracalcium aluminoferrite, where $C=CaO$, $S=SiO_2$, $A=Al_2O_3$, $F=Fe_2O_3$, $S=SO_3$, and $H=H_2O$). The two calcium silicates comprise about 75 percent of the portland cement by weight.

Mehta [2] describes in detail the types, amounts, and characteristics of the four principal solid phases of hydrated portland cement, as resolved by the electron microscope: (1) calcium silicate hydrates (C-S-H); (2) calcium hydroxide $\{Ca(OH)_2\}$; (3)

calcium sulfoaluminates; and (4) unhydrated clinker grains. In the hydration reaction, the two silicates produce similar calcium silicate hydrates and different amounts of calcium hydroxide. Because of the resemblance of C-S-H to the natural mineral tobermorite, it is sometimes called "tobermorite gel." This gel is the most important constituent of hardened portland cement paste and, as such, of the concrete, as well. This gel plays a key role in determining the rheological properties of the fresh concrete. Tobermorite gel also plays a vital role paste in setting and hardening, and is important in determining the strength and dimensional stability of the hardened paste and concrete.

The exact structure of C-S-H is not yet known, but several models have been proposed to explain the properties of the material. According to the models of Powers [35] and Brunauer [32], the material has a layered structure with a very high surface area (on the order of 100 to 700 m²/g, depending on the technique of measurement). The strength of the material is mainly attributed to van der Waals forces, since the size of the gel pores or the solid to solid distance is typically about 18 Å. The C-S-H structure has been visualized by the Feldman-Sereda model [36] as being composed of an irregular or kinked array of layers that are randomly arranged to create interspaces of different shapes and sizes (5 to 25 Å).

In contrast to C-S-H, calcium hydroxide is a compound with a distinctive hexagonal prism morphology, which varies from nondescript to stacks of large plates and is affected by the available space, temperature of hydrogen, and impurities present in the system. The strength contribution potential of Ca(OH)₂ due to van der Waals forces is limited as a result of its considerably lower surface area. Furthermore, the presence of excess calcium hydroxide in the hydrated cement paste has an adverse effect on chemical

durability to acidic solutions due to its higher solubility than C-S-H.

Types of Pores/Voids

In addition to solid phases, the hydrated cement paste also contains various kinds of voids that have an important influence on the properties of the cement paste and the concrete. The typical sizes of these solid phases and the voids are diagrammatically explained by Mehta [2] in a very comprehensive manner (figure 2.1).

Powers and his colleagues [37] were the first to show the two physical properties of cement paste, surface area and porosity, which are instrumental in determining the two most important engineering properties, strength and dimensional stability. Inevitably, there are tiny pores of molecular dimensions between particles of tobermorite gel and somewhat larger pores between aggregations of gel particles. The former are known as gel pores, while the latter are called capillary pores. The various types of voids and their significance are discussed below.

(1) **Gel pores.** These are the interstitial cavities between the particles of tobermorite and other calcium silicate hydrates. They are also known as interlayer spaces within the C-S-H structure. Powers assumed gel pores to be 18 Å, whereas Feldman and Sereda suggested they vary from 5 to 25 Å. These pores are too small to have an adverse effect on the strength or permeability of the hydrated cement paste. However, since water in these pores is held by hydrogen bonding, its removal under certain conditions may contribute to drying shrinkage or creep [2].

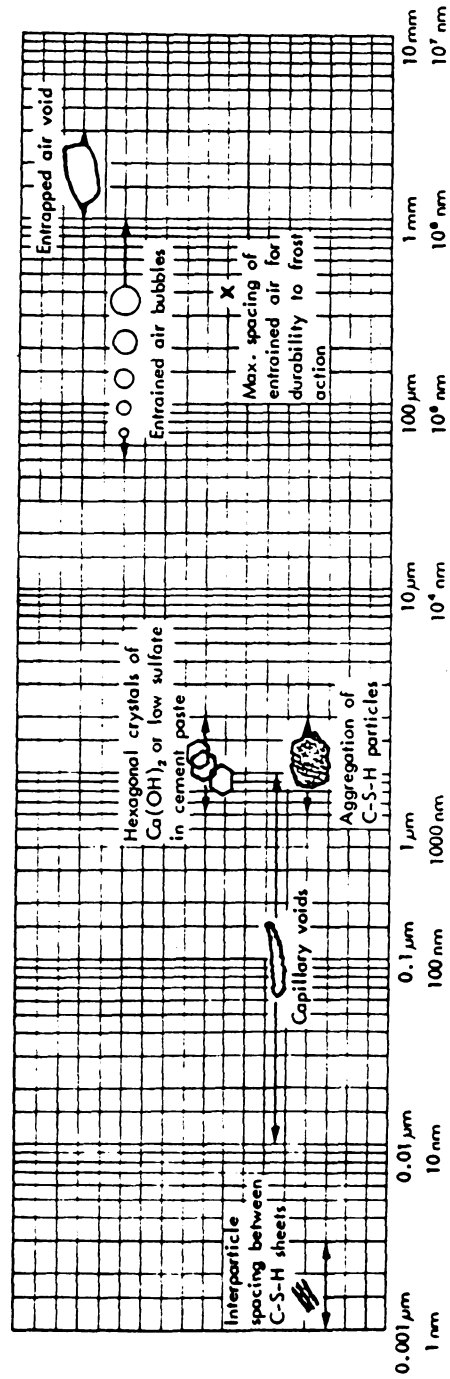


Figure 2.1. Dimensional range of solids and pores in hydrated cement paste [2].

(2) **Capillary pores.** These are also known as capillary cavities/voids. These are the unfilled, irregularly shaped spaces between the aggregations of gel particles in the solid component of hydrated cement phase. They are formed by water in excess of that required for the hydration of the portland cement. It has been shown experimentally by Powers [37] that higher water-cement ratios lead to more and larger capillary pores. Since the total amount of the hydration product remains constant for a given amount of cement, the increase in volume paste content is due to the capillary pores, which determines the porosity of the cement paste. Typical pore size distribution plots for different hydrated cement pastes found by Mehta and Manmohan [38] are shown in figure 2.2. It can be seen that the size of pores reduces with decrease in water-cement ratio and increase in hydration period. The size and number of capillary pores depend on the water-cement ratio and the degree of hydration. The capillary pores vary in size from 0.01-0.05 μm for well-hydrated cement pastes with low water-cement ratios, and are generally 3-5 μm at early stages of the hydration reaction [2]. Capillary pores smaller than 50 nm are important with respect to shrinkage and creep whereas pores larger than 50 nm are considered harmful to strength and impermeability.

(3) **Air voids.** There are two kinds of air voids in portland cement concrete: entrapped and entrained. One difference between the two is that entrapped air voids are unintentionally included in the cement paste during the mixing process, whereas entrained air voids are purposely introduced in the cement paste with the help of an AEA to protect the concrete from frost action. Entrapped air voids are usually larger than 1 mm (some researchers agree they are greater than 3 mm) while entrained air voids generally range

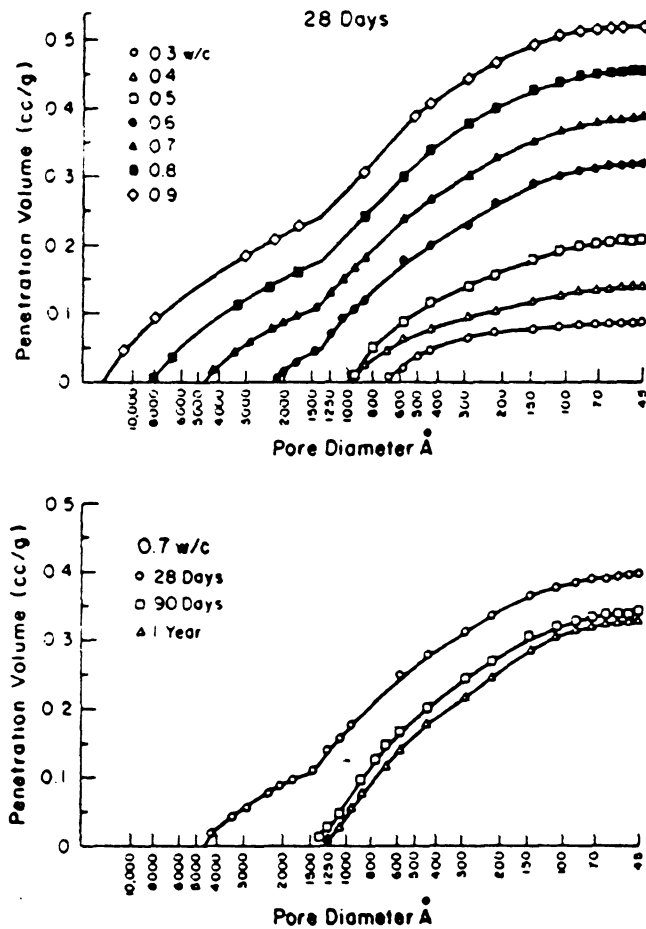
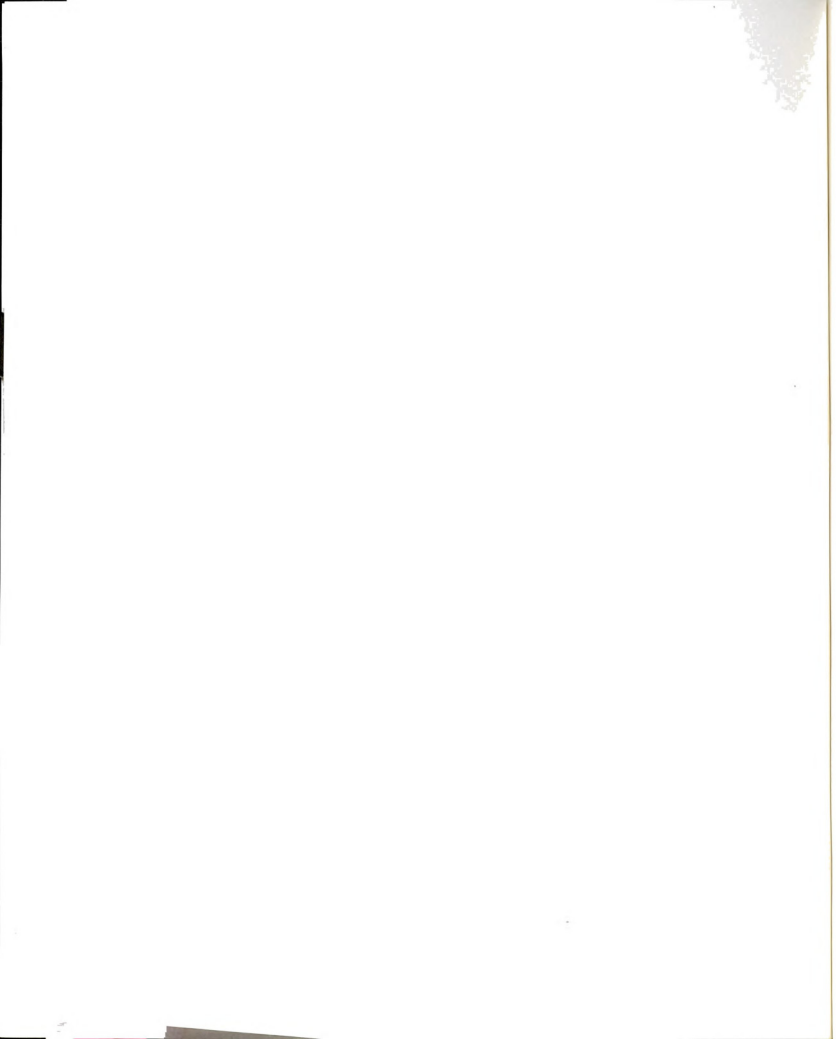


Figure 2.2. Pore size distribution in hydrated cement paste [38].



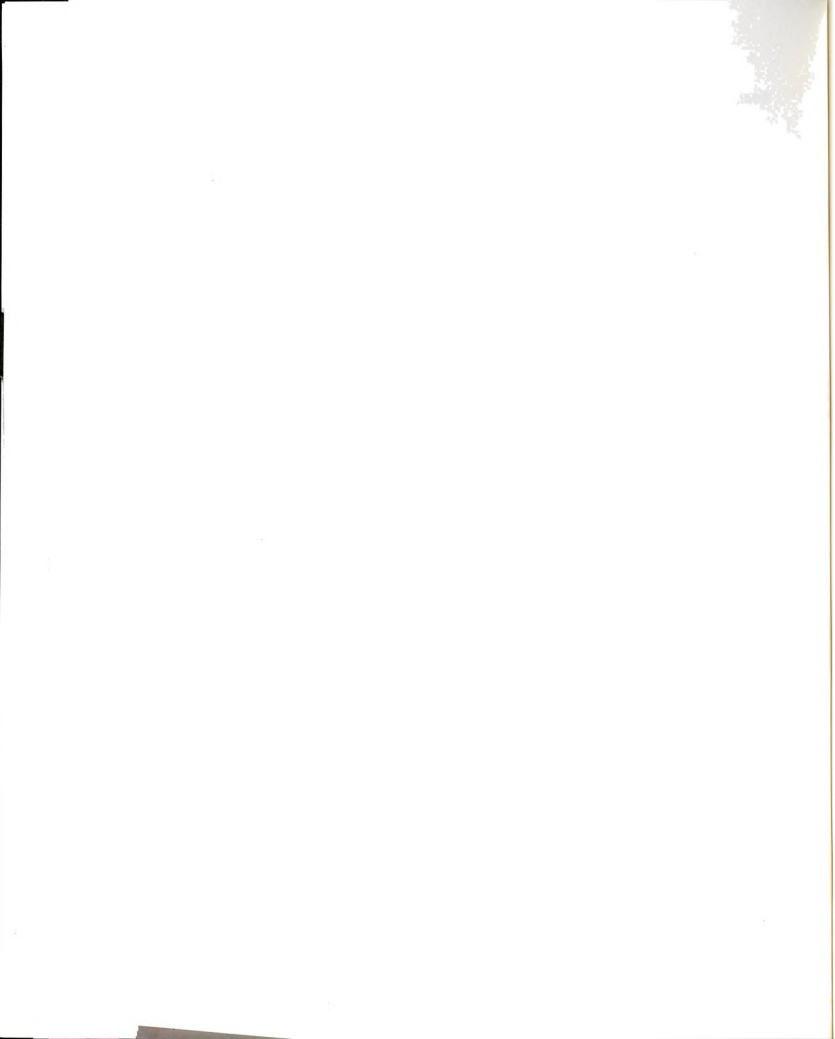
from 50 to 200 μm . Thus, both types of air voids are much bigger than the capillary pores and are capable of adversely affecting the strength and impermeability of the cement paste or concrete.

Water in the Hydrated Cement Paste

Water in the hydrated cement paste exists in many forms and its classification is usually based upon the degree of difficulty associated with its removal. As there is a continuous loss of water from a saturated cement paste in conditions of low relative humidity (RH), the dividing line between the different moisture classifications is not rigid. The different classifications are defined and discussed below:

(1) **Capillary water.** Water in capillary pores is considered "bulk water" and is not influenced by the attractive forces exerted by the solid surface. From a behavioral point of view, water in capillary pores that are greater than 50 nm in diameter is considered "free water" because its removal does not cause any volume changes. The removal of water from smaller capillaries (i.e., less than 50 nm in diameter) can cause shrinkage.

(2) **Adsorbed water.** This water is closer to the solid surface than capillary water. Under the influence of the attractive forces, the water molecules are physically adsorbed onto the surface of the solids. It is thought that up to six molecular layers of water (15 Å) can be physically held with hydrogen bonding. A major portion of the adsorbed water can be lost by drying the hydrated cement paste to 30 percent relative humidity. Its loss is



mainly responsible for drying shrinkage.

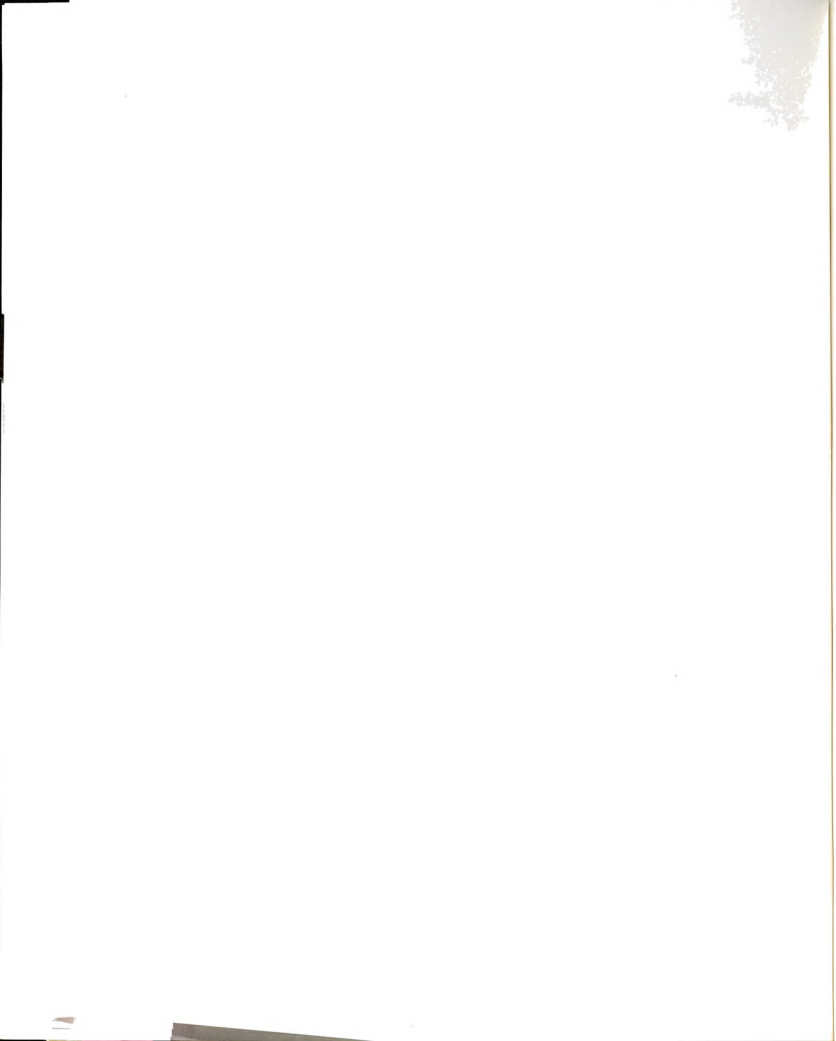
(3) **Interlayer water.** This is the nonmolecular layer of water between the C-S-H layers. This water is held strongly by hydrogen bonding, and thus the bond can only be lost under extreme drying conditions (below 11 % RH). Considerable shrinkage results from the removal of interlayer water.

(4) **Chemically combined water.** This water is an integral part of the hydrated cement paste. This water is lost only under extreme heating conditions when the hydrates decompose. It is basically considered part of the hydrated cement paste solids.

2.2.4 Freeze-Thaw Damage Theories

Hydraulic Pressure Theory

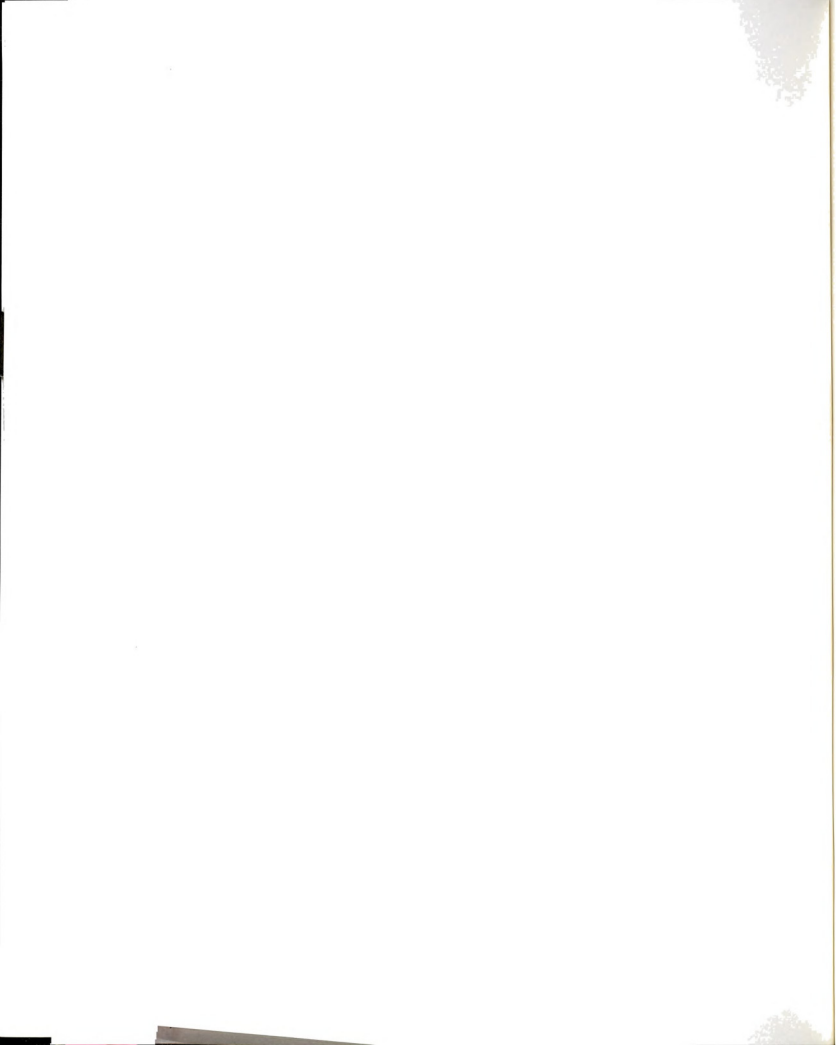
Powers first advanced the "hydraulic pressure theory" hypothesis in 1945 to explain the mechanism by which damage due to repeated cycles of freezing and thawing would take place [27]. He further amplified the hypothesis in 1949 [28]. The basic premise is that in water-soaked paste, the capillary pores and the gel pores are full, or nearly full, of water. When the temperature falls to a point where ice crystals should begin to form (possibly first in larger capillaries), the volume of the water and ice will increase. If space for expansion is unavailable, the water and the surrounding cement paste will be subjected to increased pressure until excess water in the capillary escapes



to the nearest void. Since cement paste is a porous material with an extremely low coefficient of permeability, "hydraulic pressure" will be generated. The magnitude of this pressure depends on: (1) the coefficient of permeability of the material through which the water is forced; (2) the distance to the nearest void boundary; (3) the rate at which the freezing occurs; and (4) the degree of saturation.

Theoretically, the hydraulic pressure increases in approximate proportion to the square of the distance from the air void [37]. If this pressure exceeds the tensile strength of the cement paste at any point, it will cause local cracking. Additional water will enter through this crack in wet environments only to freeze again and, with repeated cycles of freezing and thawing, there will be progressive deterioration of the concrete with each cycle. Powers concludes that every void in the cement paste is assumed to be bordered by a zone or shell in which the hydraulic pressure cannot become high enough to cause damage.

Powers and Helmuth experimentally verified the hydraulic pressure hypothesis, and as demonstrated in figure 2.3, which shows that shrinkage takes place before the freezing starts, but that expansion takes place as freezing continues. Hydraulic pressure in the capillaries first develops at the instant freezing starts, with the amount of the pressure depending upon the rate of freezing and the ease with which water is forced out of the capillary. Thus, the specimen as a whole begins to expand, as shown in figure 2.4. No other mechanism identified to date has accounted for all of the events and conditions described above [30,37].



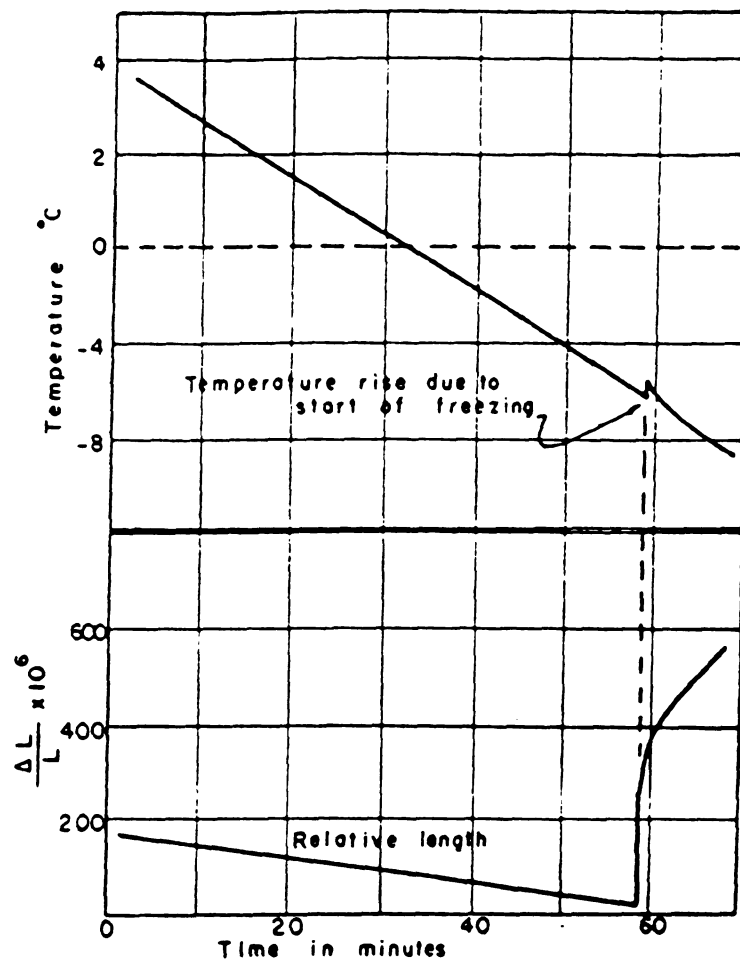
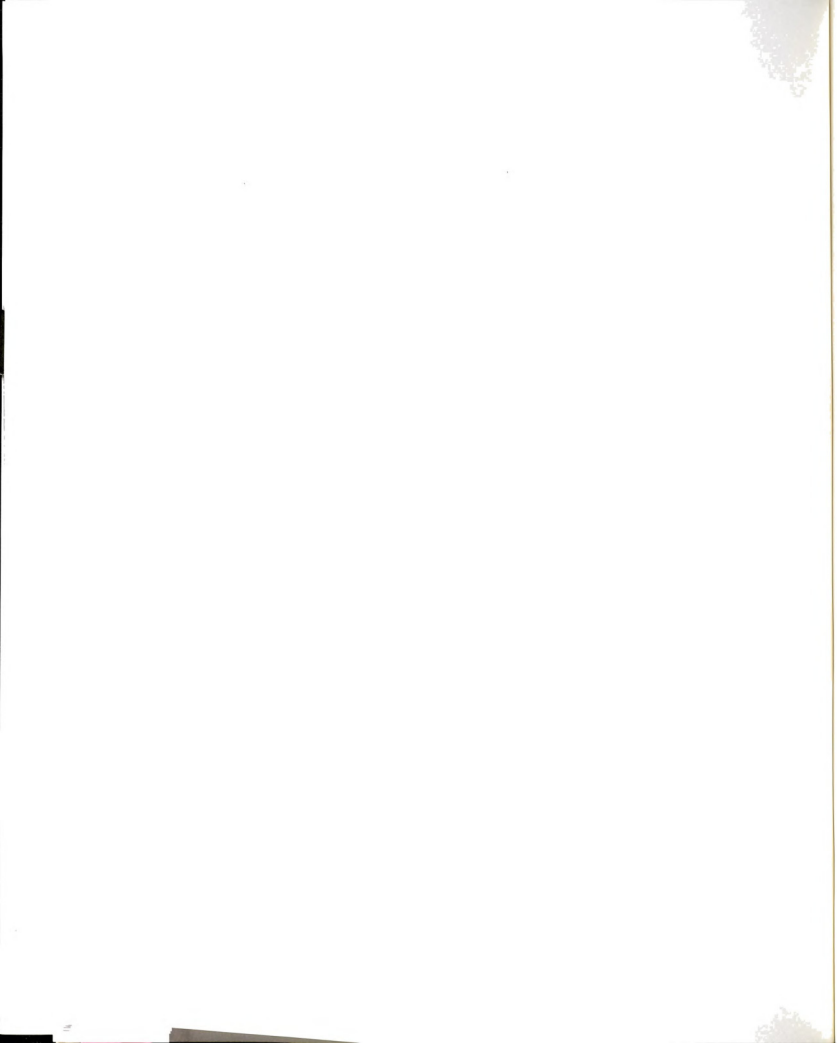


Figure 2.3. Initial expansion at the start of freezing [37].



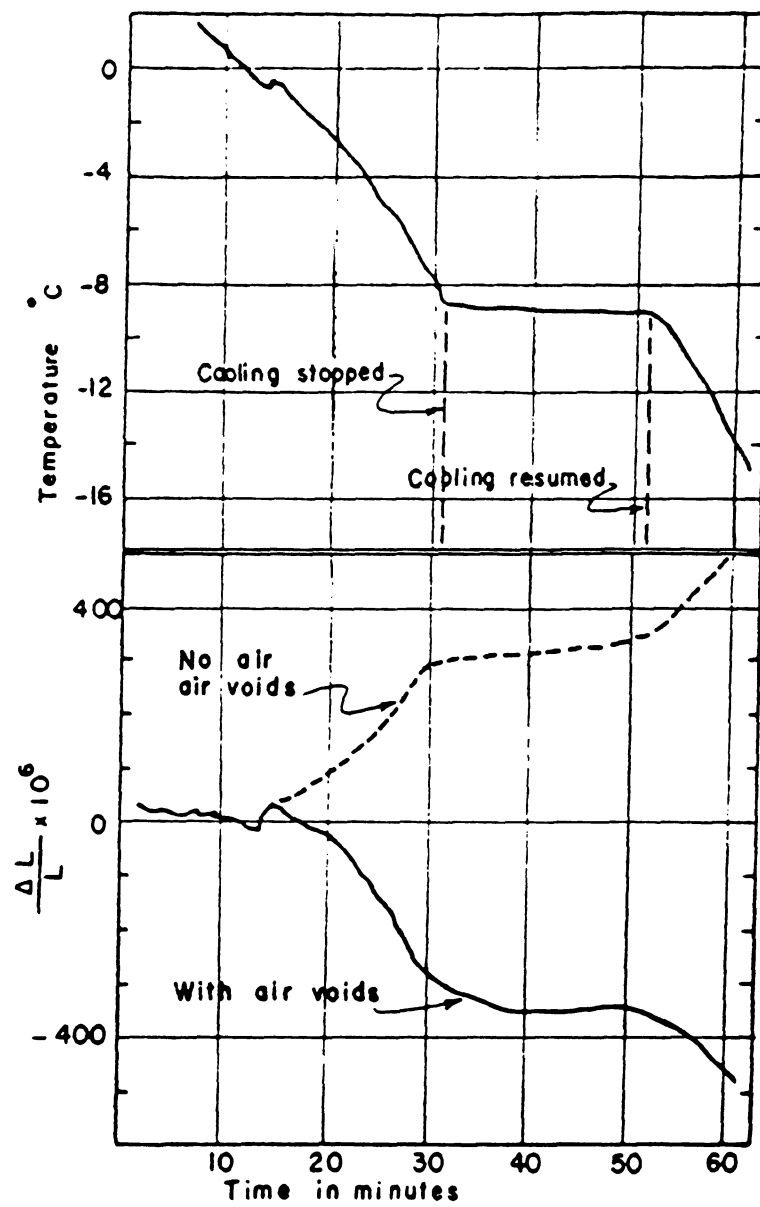
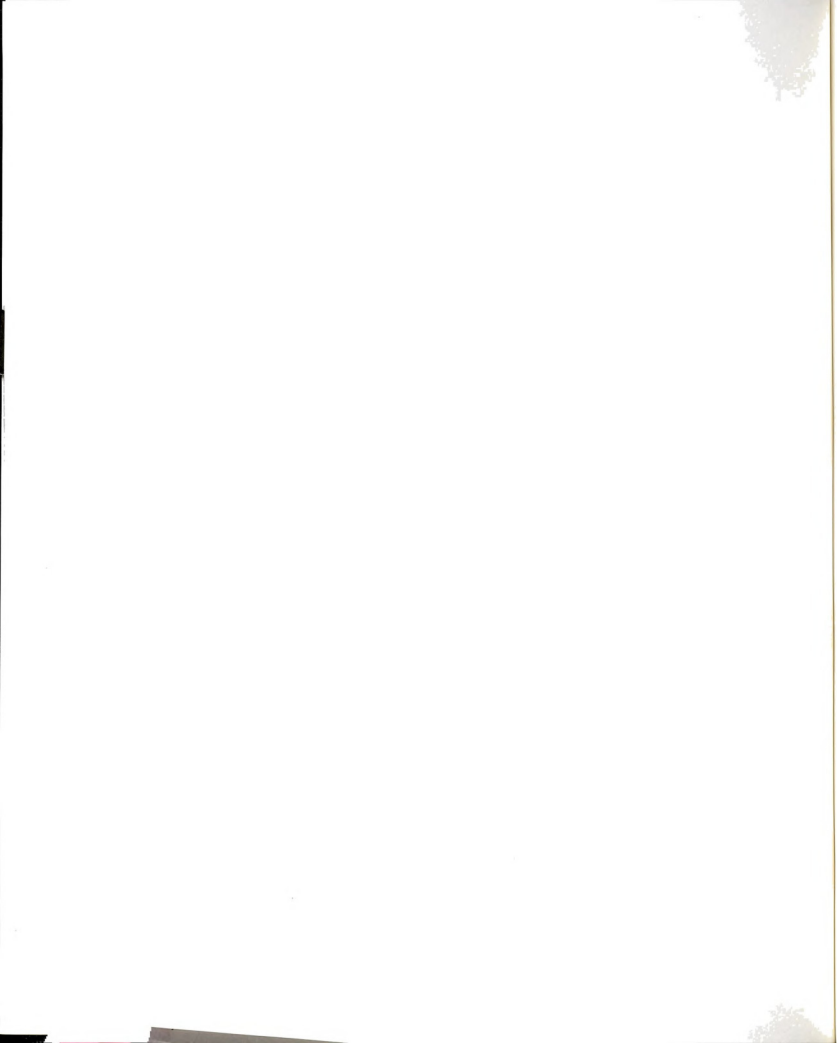


Figure 2.4. Dimensional changes in cement paste with or without air voids [37].

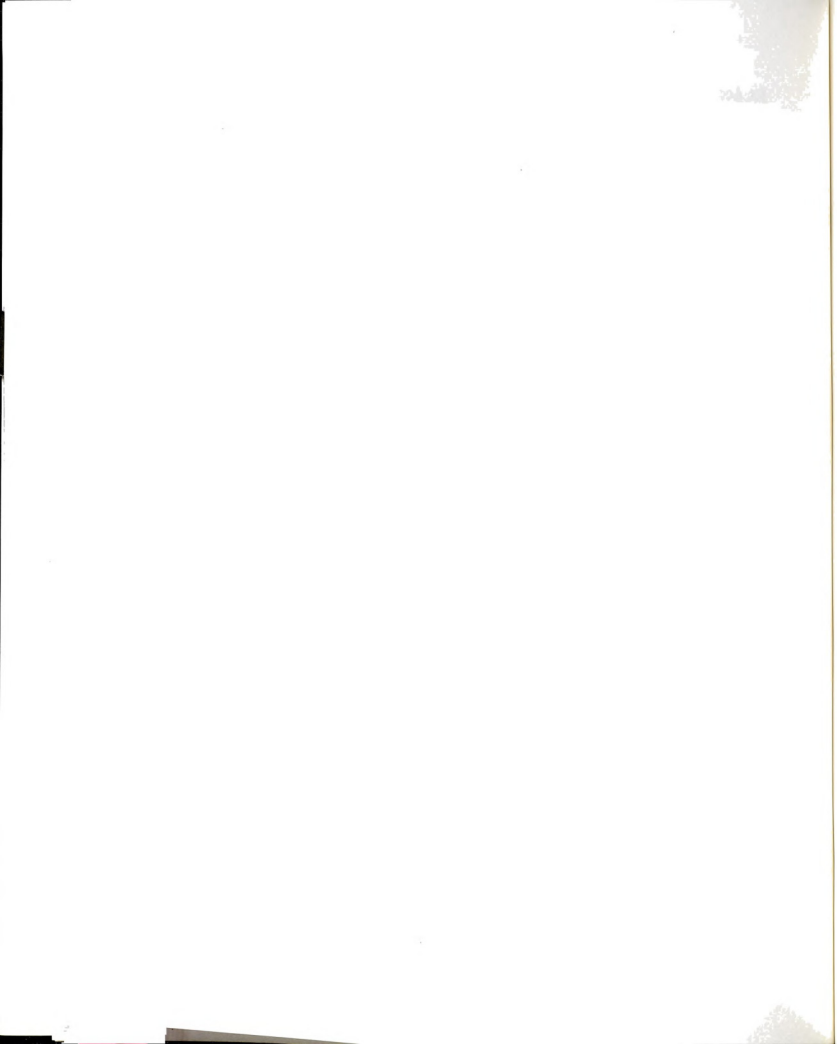


Ice Accretion/Diffusion of the Freezing of Gel Water in Capillaries

With continued experiments, Powers and Helmuth advanced the basic assumption of the hydraulic pressure hypothesis to the status of an established fact [37]. At the same time, they also realized that hydraulic pressure does not account for all the phenomena produced by freezing. Part of the effect of freezing is apparently due to the tendency of microscopic bodies of ice to grow by drawing water from the gel.

The experiments also showed that only very small amounts of water in the concrete freeze near the normal freezing point (0°C or 32°F); indeed, the amount of frozen water increases as the temperature decreases. This behavior and the other evidence show that most of the capillaries are quite small, resulting in increased surface tension and higher pore water pressure as the pore size decreases. Therefore, as pore size decreases, pore pressures will increase and the freezing point of water is depressed. Thus, ice in the capillary pores of the frozen cement paste is surrounded by the unfrozen water of the gel pores.

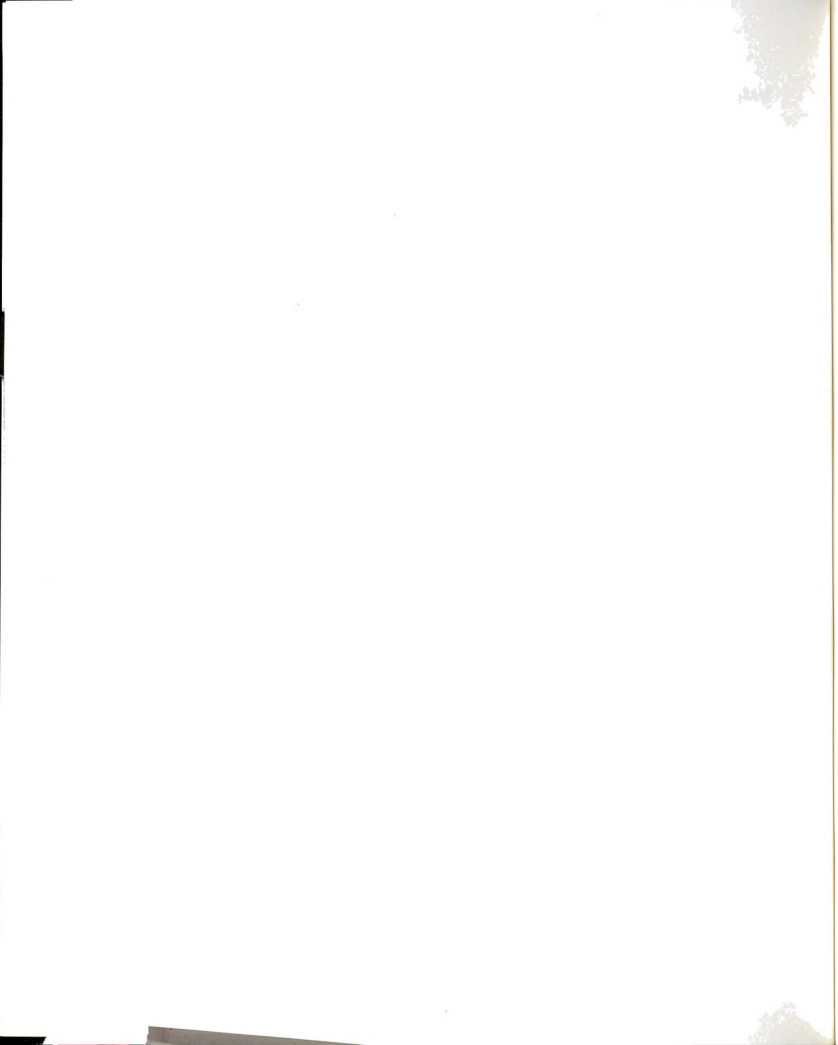
The gel water in a saturated state has the same energy as that of the normal water in bulk. There is a thermodynamic equilibrium between the gel water and the ice in the capillary pore at 0°C , assuming one atmosphere pressure for both and a capillary size large enough so that the surface tension is negligible. If the temperature drops below the freezing point of water in the capillary, thermodynamic equilibrium is destroyed and the gel water gains a higher energy state than the capillary ice. This higher energy state enables the gel water to move to the capillary where it freezes and causes the ice crystal to enlarge. With this diffusion of water, the gel has a tendency to shrink. On the other



hand, the growth of the ice in the capillary places the ice and the film around the ice under pressure, which is enough to produce dilation and expansion of the cement paste. This explains the phenomena of continued expansion in a non-air-entrained paste.

In the case of air-entrained concrete, water in the gel pores can also diffuse to the previously formed ice by the hydraulic pressure in the air void. However, the amount of ice in the air void is usually less than the void capacity. While the ice in the air void also grows, it may not be under significant pressure. Thus, the net effect of the water lost by the gel pore to the air void is shrinkage of the paste. In the case of non-air-entrained concrete, a large amount of water may diffuse to the capillary pores. Here the capillary ice can grow until thermodynamic equilibrium is achieved with the gel water. If the stress from hydraulic pressure or from the growth of capillary ice ruptured the gel and thus released the pressure on the ice, the growth is limited to the freezable water in the system. If the paste is air-entrained, the diffusion period to the capillary cavities is brief. In figure 2.3, the fast rising part of the curve shows expansion due to hydraulic pressure; expansion due to diffusion is shown by the dotted line in figure 2.4. The influence of the air voids is shown by the solid (bottom) line in figure 2.4. The replenishment of the gel water during the thawing period (through the cracks) will theoretically provide moisture for unlimited growth of the ice crystals [30,37].

It should be emphasized here that failures by hydraulic pressure and ice accretion occur due to different mechanisms and under different circumstances. Hydraulic pressure will be the greatest when the rate of freezing is rapid, whereas ice accretion progresses with time and is most likely to cause damage if the concrete remains frozen for an extended period [39].



Osmotic Pressure Theory

In addition to the hydraulic pressure caused by the water freezing in large capillaries, the osmotic pressure resulting from the partial freezing of solution in the capillaries can be yet another source of destructive expansions in the cement paste [2,30]. The water in the capillaries is not usually pure, typically consisting of soluble substances such as alkalis, chlorides, and calcium hydroxide. Solutions other than pure water freeze at lower-than-normal temperatures. In such cases the freezing point decreases as the concentration of the solution increases. If two solutions of different concentration are present, the solvent particles under such conditions move towards the solution of greater concentration, and a differential head is established between the two solutions. This osmotic action increases the hydraulic pressure in the cement paste as the freezable water is forced from the capillaries into the gel pores opposite to the direction of flow of water [30]. The pressure required to overcome osmotic pressure in the capillary is a combination of the hydraulic pressure required to force capillary water into the gel pore structure and the osmotic pressure which resists this flow.

This mechanism is considered a possible cause of scaling of concrete pavements where salts are used for the removal of ice. Use of salt increases the concentration of salt in the capillary voids near the surface and, as the salt solution freezes, osmotic pressure builds up in the capillaries. This increase in the pressure may be sufficient to cause a rupture of the cement gel near the surface of the pavement, which causes scaling. Verbeck and Klieger [40] found that increases in the concentration of the salt in freezing and thawing tests increases the disruptive effect of frost action. A two to four percent

concentration of salt appears to cause the greatest damage to concrete, due to the presence of an optimum combination of freezable water and osmotic pressure. At greater concentrations (more than 4%), there is a decrease in deterioration, since lowering the solution freezing point gives the water in the capillaries an anti-freeze effect and reduces the freezable water. The use of salt may also increase the availability of moisture for saturation at the surface due to its anti-freeze effect.

Other Theories

The mechanisms just discussed do not appear to be the only causes of expansion of cement paste due to freezing. Expansion of the cement paste has also been observed when benzene, which actually contracts on freezing, was used as a pore liquid [41].

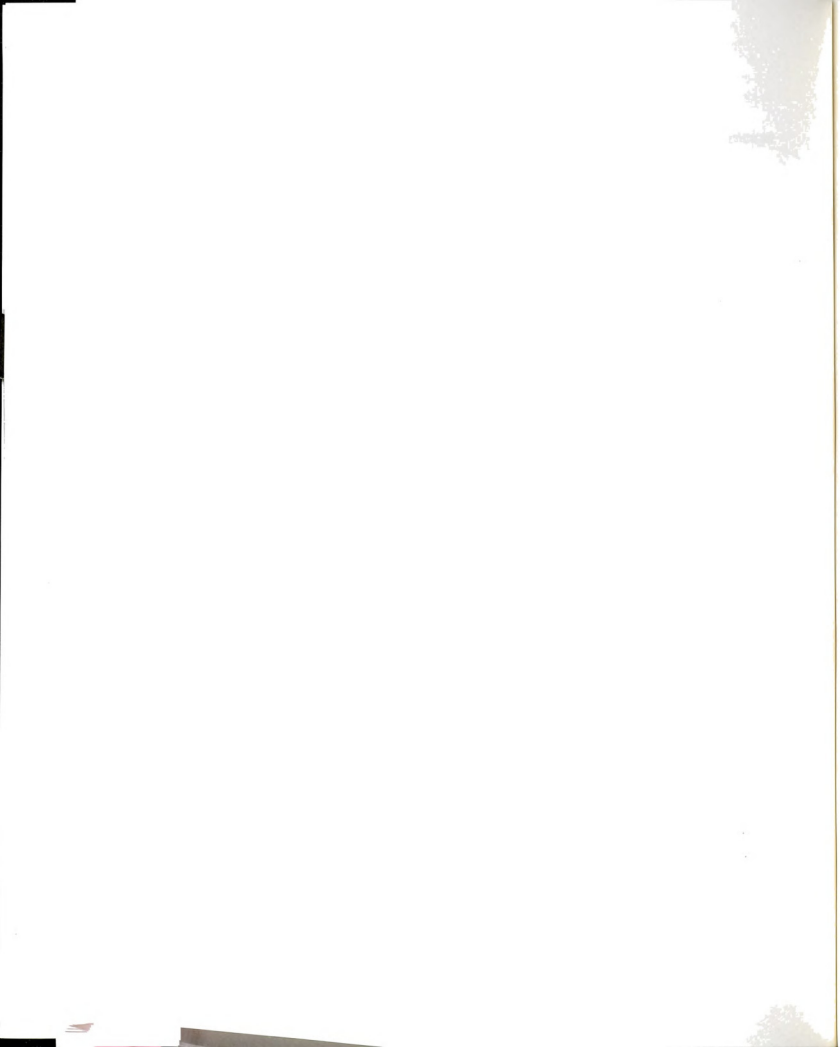
Litvan [42] explains that the rigidly-held water in the C-S-H (both interlayer water and adsorbed water in gel pores) cannot rearrange itself to form ice at the normal freezing point of water because the mobility of water existing in an ordered state is rather limited. Usually, the more rigidly water is held, the lower the freezing point. The increasing order of rigidity with which water is held in the cement paste is: (1) capillary water in small pores of 0.01 to 0.05 μm ; (2) the adsorbed water in gel pores; and (3) interlayer water. The gel pore water does not freeze above -78°C and it stays in a supercooled state while water in the capillaries freezes. Due to the thermodynamic inequilibrium, the water moves to the areas of lower energy state, the capillary pores. When there is no room in the capillary pores (i.e., they are saturated), internal pressure increases and the system expands.

Litvan also indicated that moisture transport associated with the cooling of saturated porous bodies may not necessarily lead to mechanical damage. The mechanical damage occurs when the rate of moisture transport is considerably less than demanded by the conditions such as large temperature gradient, low permeability, and a high degree of saturation.

2.2.5 Factors Affecting Frost Resistance

Air Content

As explained earlier, the total amount of air content includes both entrapped air and entrained air. The presence of entrained air is desired in concrete which is required to be protected from frost action. Cook [43], while discussing the durability of a concrete specimen under severe conditions, stated that, "Well-made concrete containing good quality materials will not ordinarily withstand the exposure for more than one winter unless the concrete contains proper amount of entrained air." It has been well established that these air voids reduce hydraulic pressure by providing a place where water flowing out of a capillary cavity can safely freeze. As a result, the hydraulic pressure within a certain radius of the void is less than the tensile strength of the cement paste; the cement paste in this area may be considered to be in a zone of protection. When the air voids are properly distributed throughout the cement paste, there will be no place where the hydraulic pressure exceeds the tensile strength of the paste, and the paste will be protected from the damage of frost action. The maximum acceptable spacing factor i.e., an

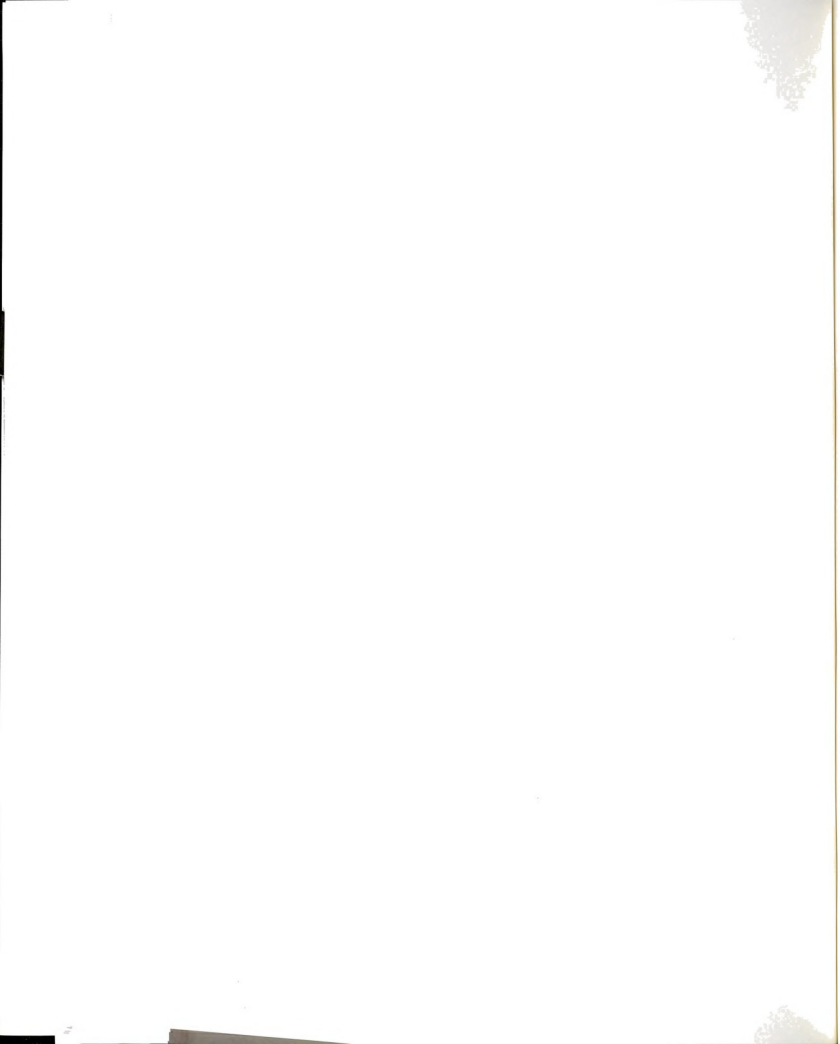


index related to the maximum distance of any point in the cement paste from the periphery of an air void, in millimeters or inches (as per current specifications) is typically considered as 0.20 mm (0.008 in.), which can be achieved by entraining quantities of air that vary with the size of the aggregate used. This will be discussed later in detail.

Powers [44] was the first to explain the role played by air content in the frost resistance of concrete. He observed that a saturated cement paste without air entrainment elongated by 1600 microstrain during a freezing cycle (-24°C) and retained a residual permanent elongation of 500 microstrain after thawing to its original temperature, as shown in figure 2.5a. Another specimen with two percent entrained air showed a maximum elongation of 900 microstrain and a residual elongation of less than 300 microstrain under similar conditions (see figure 2.5b). The specimen with 10 percent entrained air showed no elongation on freezing and no residual dilation on thawing; rather, it experienced a slight contraction (figure 2.5c), which is considered as the net effect of the different mechanisms taking place in the cement paste, as explained earlier.

Apart from the positive effects of the air content in the cement paste, reduction in strength is considered a negative side effect. Strength losses varying from two to ten percent per one percent increase in entrained air have been reported by different researchers [8,9,10,11].

Thus, proper air entrainment can be used to produce a frost-resistant concrete, but it also reduces the strength of PCC. The effect of combinations of various kinds of admixtures on the air content and other properties of concrete will be discussed in the next chapter.



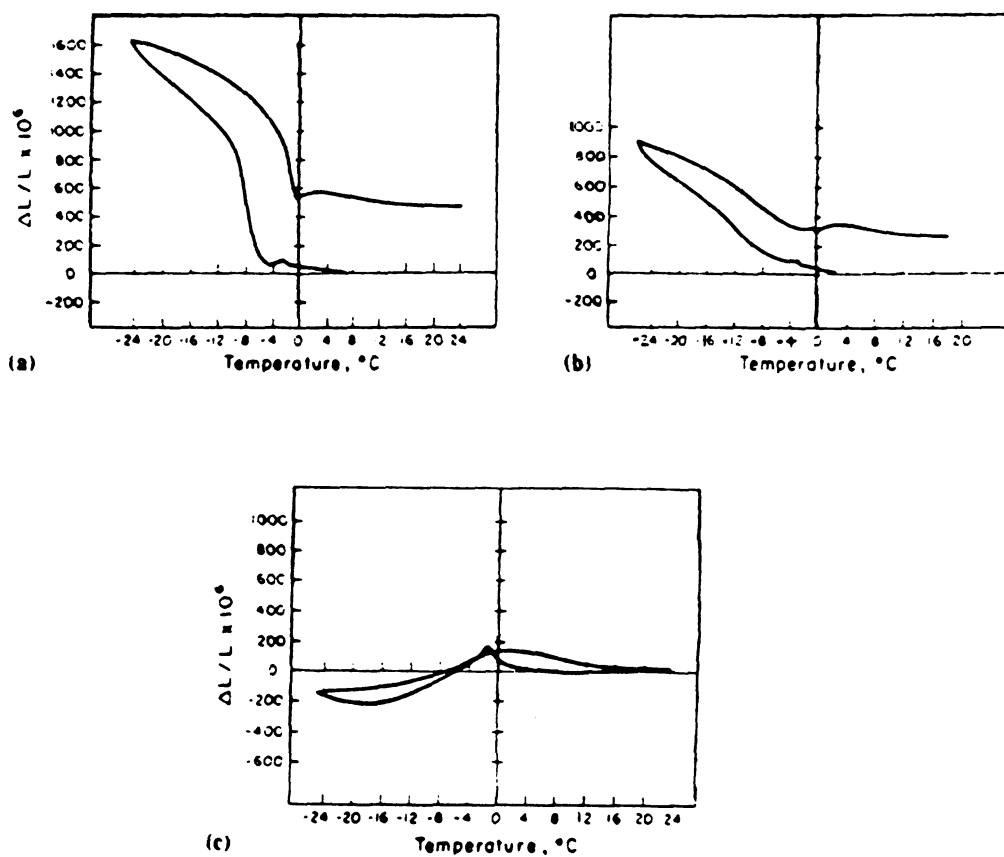
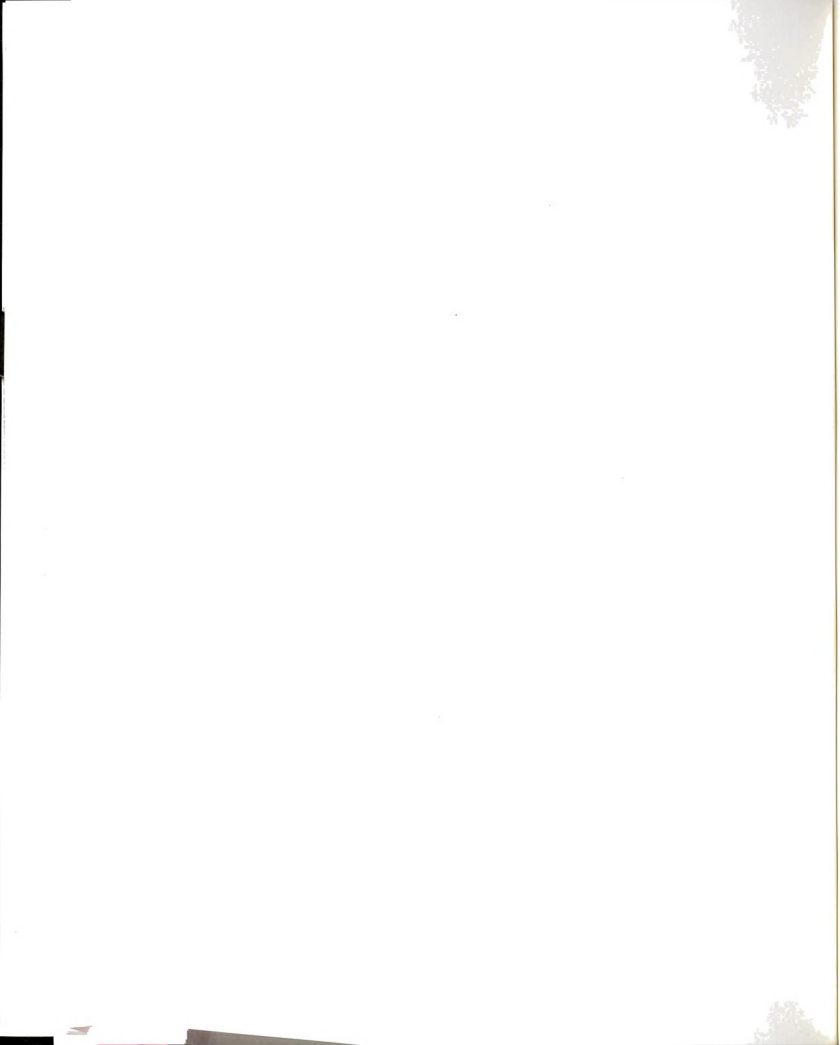


Figure 2.5. Response of saturated cement paste to freezing and thawing, both with and without entrained air [44].

- (a) Specimen without air-entrainment,
- (b) Specimen with 2% air-entrainment, and
- (c) Specimen with 10% air-entrainment.



Aggregate

Concrete with appropriate air entrainment can still be damaged due to frost action if it includes non-durable aggregate. The mechanism for the development of internal pressure in the cement paste upon freezing is also generally applicable to aggregates. Aggregate behavior under freezing and thawing basically depends on the quantity and size distribution of the aggregate pores and the continuity of the pore structure.

Verbeck and Landgren [45] classified aggregates into three categories. The first category consists of aggregates with low permeability and high strength, in which the elastic strain introduced by freezing water is accommodated without causing cracks. The second includes aggregates with intermediate permeability (i.e., with pores diameters of less than 500 nm). These aggregates can get saturated and hold water which, upon freezing, requires an escape boundary of an empty pore (like the entrained air void in cement paste) to relieve the pressure. The distance to this boundary in the case of most aggregates, is much higher than in cement paste due to higher permeability. It has also been shown by Bloen [46] that larger aggregate sizes are often less resistant to repeated cycles of freezing and thawing than smaller sizes of the same type of aggregate. This gives rise to the concept of critical aggregate size, which depends upon the rate of freezing, degree of saturation, and permeability of the aggregate. The third category of aggregates includes those with high permeability. The high permeability permits easy entry and exit of water under freezing and thawing conditions, but creates frost action problems by allowing water to accumulate in the transition zone between the aggregate and the cement paste.

It is considered advisable to avoid the use of highly absorptive aggregates in portland cement concrete [39]. It has been well-established that the use of good quality aggregate with less than three percent absorption will restrict frost action problems to the cement paste fraction of the concrete.

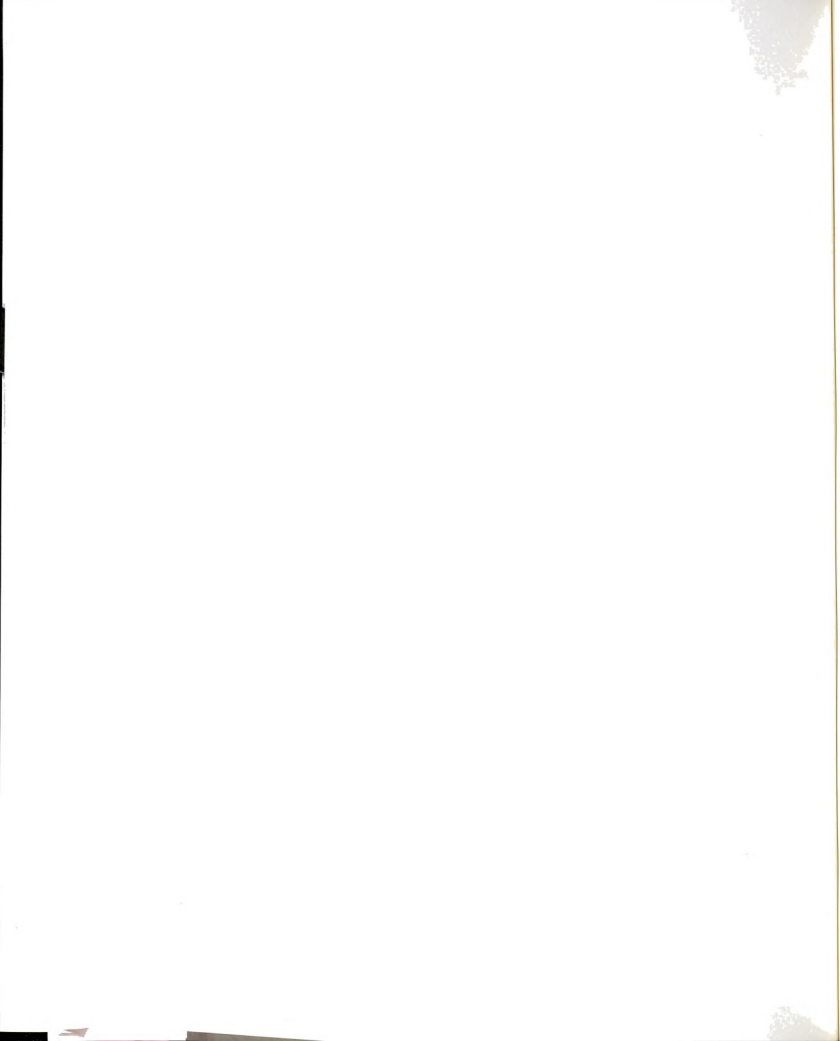
Curing and Strength of Concrete

It has been experimentally seen by many researchers that increasing the degree of hydration decreases the freezable moisture present in the pore structure and increases the tensile strength of the hydrated cement paste. Thus, it is best to allow adequate time for curing before the concrete is exposed to repeated cycles of freezing and thawing.

Greater amounts of freezable water are generally found in concretes cured at elevated temperatures, which is not desirable for concretes that will be exposed to repeated cycles of freezing and thawing. However, concrete that is allowed to dry and develop higher tensile strength before being subjected to freezing and thawing is generally less susceptible to damage than concrete that remains saturated after curing.

Generally, there is a direct relationship between strength and durability, but this does not necessarily hold true when comparing air-entrained and nonair-entrained concretes. While comparing the strength of a non-air-entrained concrete with an air-entrained concrete, the former may be higher in strength but the latter will be more frost-resistant. The incorporation of entrained air produces a reduction in strength, but increases the concrete durability.

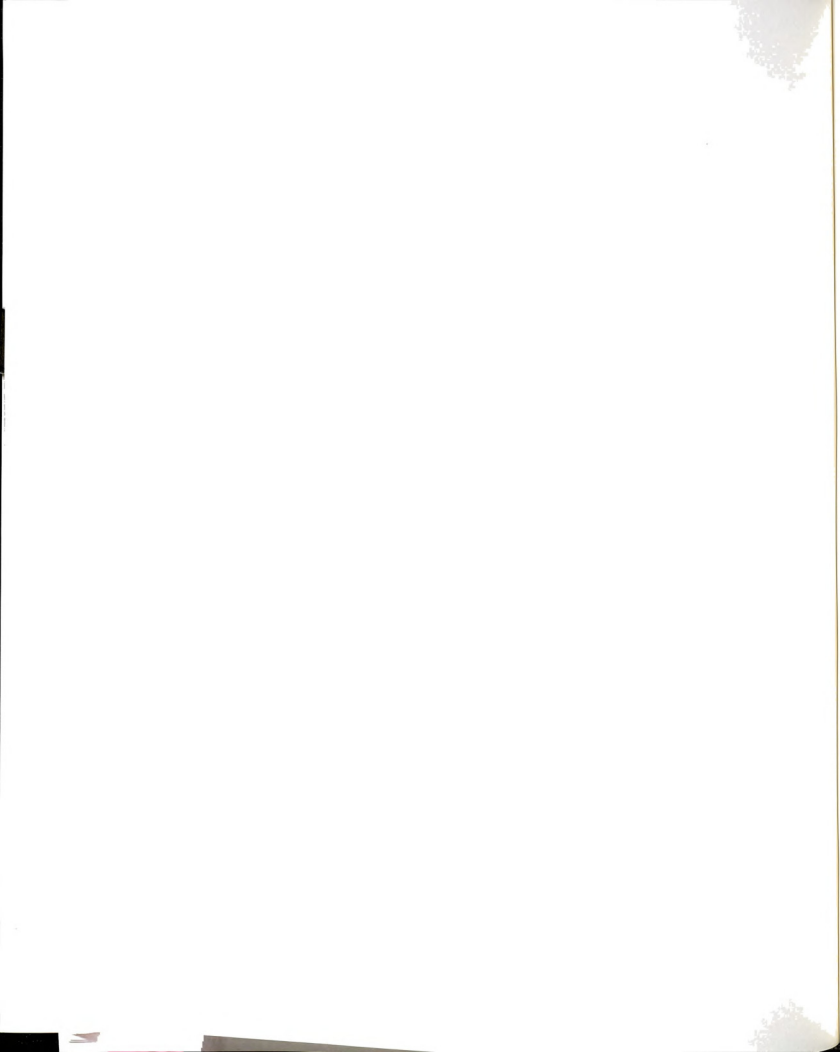
Curing is a function of time, and strength is a function of curing, water-cement



ratio and several other factors. Strength is expected to increase with an increase in the curing period due to an increase in hydration products, which also results in a reduction in freezable water. Thus frost resistance improves with increased favorable curing. The behavior of mixes with chemical and mineral admixtures related to curing is discussed in the next chapter.

Water-Cement Ratio

The water-cement ratio influences the durability of concrete in several ways and air entrainment alone cannot ensure the durability of concrete. A low ratio imparts greater strength that can withstand the tensile stress developed by the hydraulic pressure or ice accretion in a much better way. This also increases the impermeability of the cement matrix and reduces the chances of for accumulating freezable moisture because it takes a longer time to reach critical saturation [2,30,39,47]. Since the freezable water resides in large pores, it is hypothesized that, at a given freezing temperature, the amount of freezable water will be larger with a high water-cement ratio and at early stages of curing. The experiment data of Verbeck and Klieger [48] shown in figure 2.6 confirmed this hypothesis. Wood [49] estimated that if a water-cement ratio below 0.42 (by weight) is used in concrete, the small number of capillaries in the paste would not be vulnerable to freezing and thawing. But Powers [28] has shown that even where there are fewer capillaries in the portland cement paste, they must be protected by air voids, otherwise the development of hydraulic pressures in existing capillaries, although not as extensive as in the paste of higher W/C, would be sufficient to cause dilation.



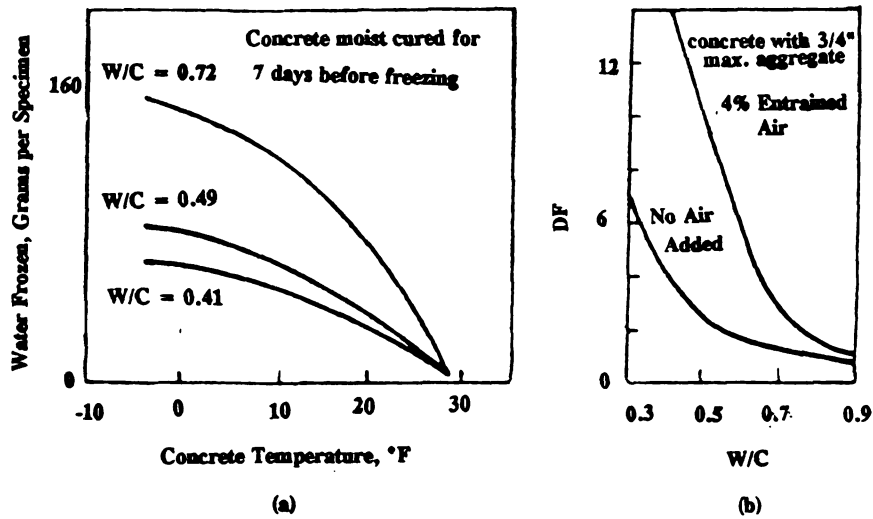
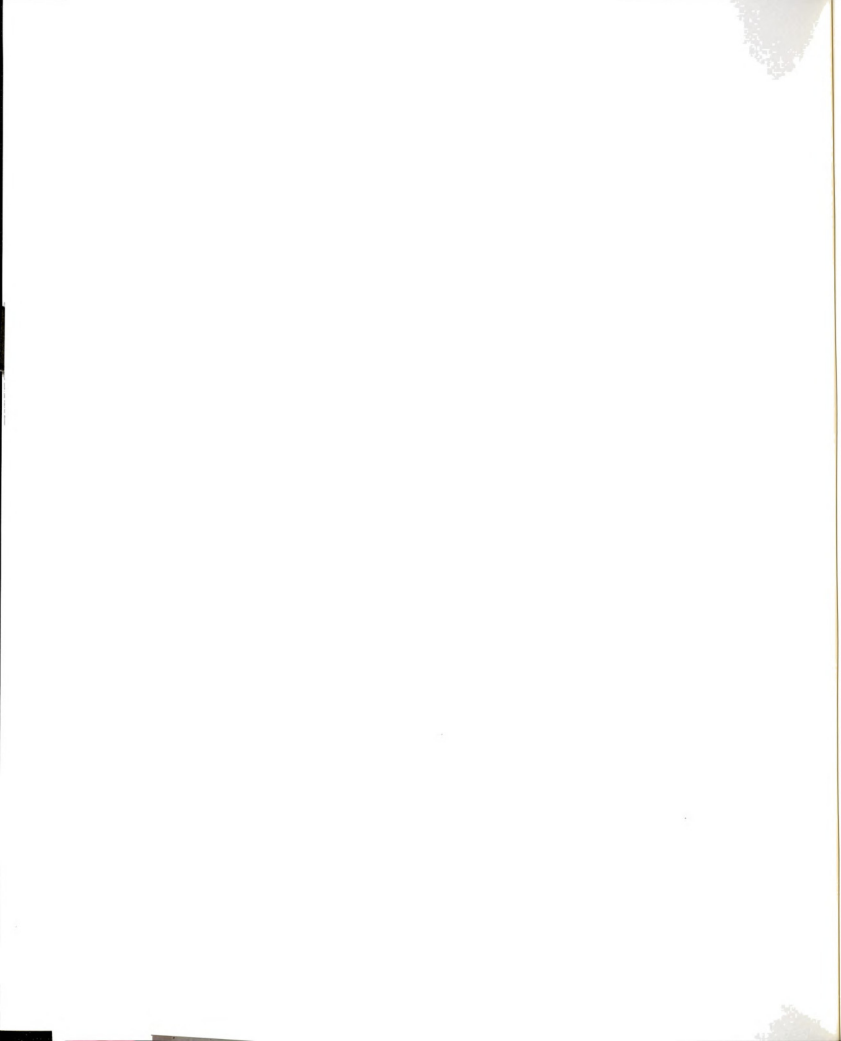


Figure 2.6. Influence of water-cement ratio and air content on durability of concrete to frost action [2,48].

- (a) The amount of freezable water in concrete, with a given water-cement ratio, increases with decrease in temperature.
- (b) High durability shown as combination of low water-cement ratio and increase in air-entrainment.



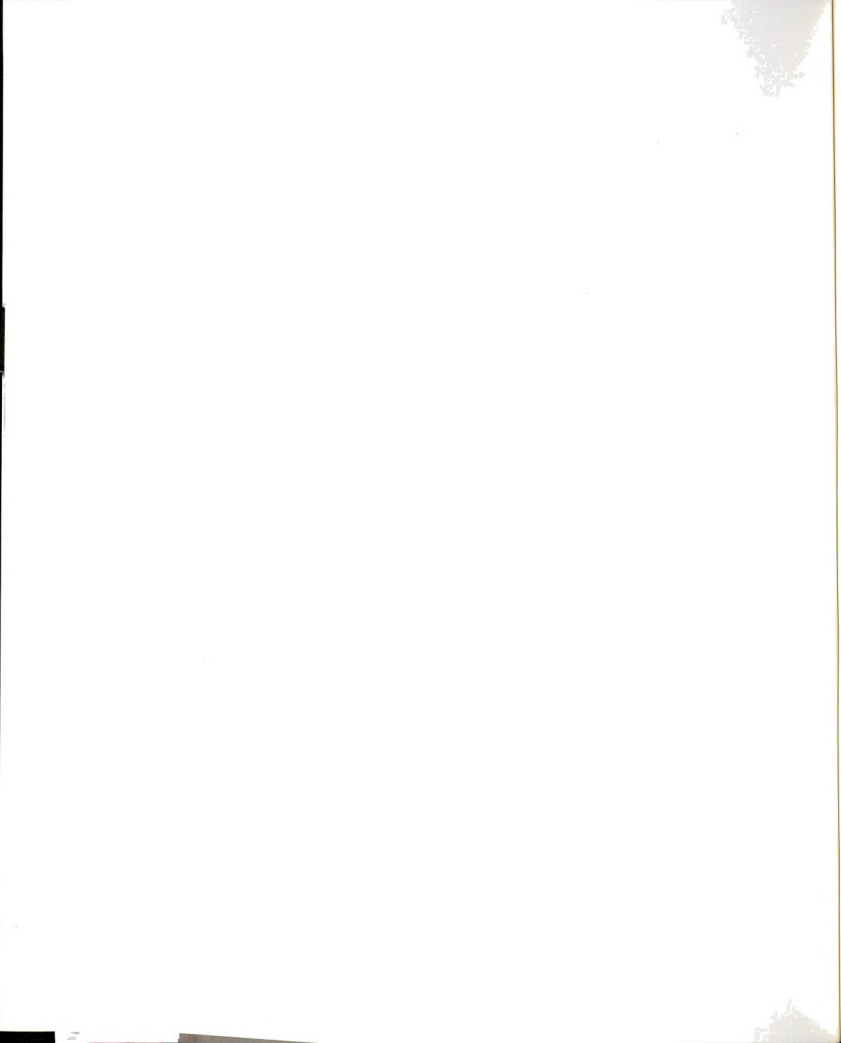
The US Bureau of Reclamation [50] showed that high quality concrete (low water-cement ratio) produces more durable concrete with air entrainment than low quality (high W/C) air-entrained concrete. But the improvement in durability due to air entrainment is of far greater magnitude than that experienced by reducing the water-cement ratio. A decrease of W/C from 6.5 to 5 gallons per sack may increase the durability of concrete by 100 percent, whereas air entrainment of the same concrete by five percent, may increase the frost resistance by 1000 percent [51].

Considering the above, the typical values of the curing period and water-cement or cementitious ratios, which are functions of strength, need to be evaluated with respect to the freeze-thaw durability of PCC.

2.3 Air Void Parameters

2.3.1 General

The greatest single factor affecting the durability of concrete in freezing and thawing is the presence of a well-distributed air void system in the paste [39]. Since the discovery of air entrainment, continuous efforts have been made to quantitatively characterize the air void parameters that are indicative of a frost-resistant concrete [52]. It was determined after early studies that air content alone was not enough to be indicative of the concrete durability. In addition to the air volume, the sizes of air voids and their distributions were also studied. It was considered necessary to expand on the air void characterization so that a clear, accurate picture of the internal composition of



concrete was available. Although some researchers have studied additional parameters, the most widely accepted air void system parameters for reliable prediction of durability are: air content, specific surface, spacing factor, and void frequency. These parameters are determined after microscopic analysis of a specially prepared specimen of the concrete according to ASTM C 457-90 [53], which will be discussed in the following paragraphs.

2.3.2 Air Void Content (A)

Air void content is defined [53] as "the proportional volume of air voids in concrete expressed as volume percent of the hardened concrete." Typically, air contents between three and six percent of the volume of concrete are considered satisfactory for producing a frost-resistant concrete [54]. The production of the desired air content is also affected by other factors, such as dosage and type of air entraining agent, degree of consolidation, water-cement ratio, and the use of chemical or mineral admixtures.

As mentioned earlier, the incorporation of entrained air adversely affects strength, which may not be desirable. On the whole, it is desirable to use the minimum air content necessary to produce a durable concrete [55].

2.3.3 Specific Surface (SS)

The specific surface is defined [53] as "the surface area of the air voids divided by their volume, expressed in compatible units so that the unit of the specific surface is

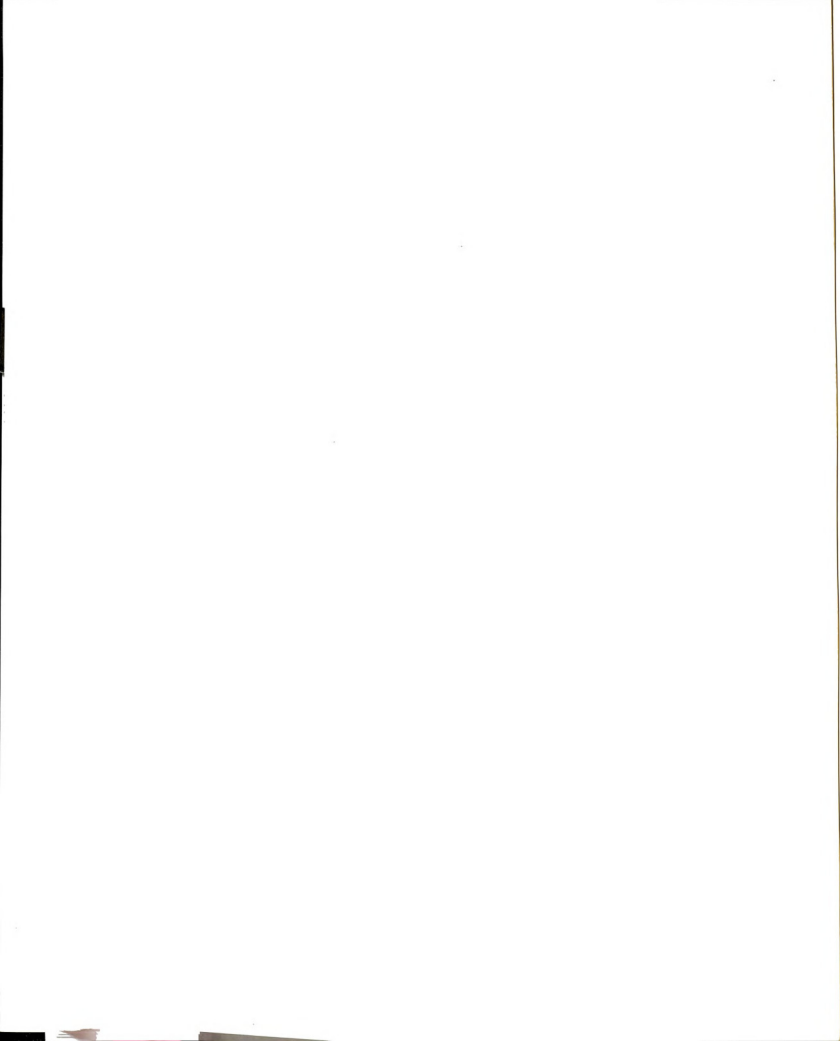
reciprocal length."

When other conditions are kept constant, the specific surface decreases very quickly with an increase in the water-cement ratio because the average void size increases. It is also obvious that, as the proportion of small bubbles in given volume of air increases, the specific surface will also increase. Bruere [55] indicates that a high specific surface allows the production of frost-resistant concrete with low air contents, since the spacing factor is inversely proportional to the air content and surface area of the bubbles. Moreover, at equal air contents, the safety margin against rapid freezing and variations in surface area due to variable mixing, mixtures, or materials will be greater for a concrete with higher specific surface.

There have been a number of recommended ranges for the production of frost-resistant concrete. Powers, for example, initially suggested a range of 300 to 800 in^2/in^3 , whereas Mielenz et al. stated that values of specific surface may be expected between 600 to 1100 in^2/in^3 . Most authorities now recommend that specific surface should not be less than 600 in^2/in^3 (24 mm^2/mm^3) [47,56].

2.3.4 Void Frequency (n)

Void frequency is defined as "Voids per unit length of traverse; the number of air voids intercepted by a traverse line divided by the length of that line." It is a critical parameter in determining the specific surface and the spacing factor. If other conditions are kept constant, the void frequency decreases rapidly with increase in water-cement ratio. American Concrete Institute (ACI) guidelines recommend that the void frequency



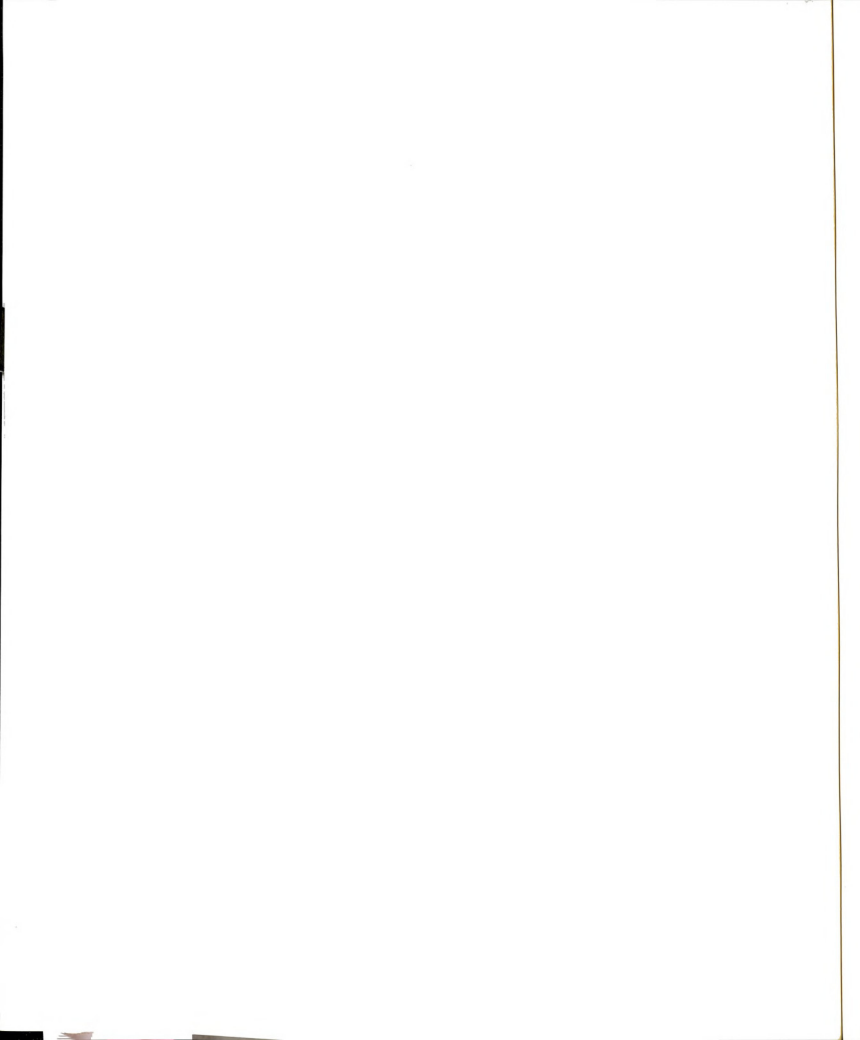
(voids per unit length) should be considerably greater than the air content.

2.3.5 Spacing Factor (SF)

The spacing factor is often believed to be the most important indicator of concrete durability with respect to freezing and thawing. It is defined [53] as "an index related to the maximum distance of any point in the cement paste from the periphery of an air void, in millimeters or inches." This distance must be small enough to allow the unfrozen water, expelled from a capillary under freezing conditions, to reach a "protective" air void. Klieger [8] added that "if this distance is relatively large, water moving through the paste during freezing may develop pressures sufficient to cause failure before the water can reach an air void." Therefore, the smaller the spacing factor, the more durable will be the concrete.

Powers initially estimated that a spacing factor of 0.01 in. (0.254 mm) or less was required to produce a frost-resistant concrete [28]. Mielenz et al. recommended that spacing factor should be limited to 0.006 to 0.008 in. (0.15 to 0.20 mm) for extreme exposure. Many specifications today [3,53] recommend a value of 0.008 in. (0.20 mm) or less for durable concrete subjected to moderate exposure, although somewhat larger values may be allowed for concretes subjected to mild exposures, and smaller values may be needed for severe exposures, especially when deicing chemicals are used.

The specification of a spacing factor of 0.008 in. (0.20 mm) has been a subject of debate between researchers of concretes made with different kinds of admixtures. Tynes [15] studied concretes with (W/C of 0.45) and without (W/C of 0.34 and 0.37)



HRWR. He found spacing factors of 0.08 mm for concrete without admixtures and 0.2 to 0.3 mm for concretes with admixtures, which produced durability factors of 84, and 15 to 55, respectively. He attributed the poor performance of concrete with HRWR to the inability of the AEA to produce a proper air void system in the presence of HRWR. Mielenz and Sprouse [57] and Perenchio [58] determined that, although concretes with HRWR produced higher spacing factors than the conventional values, they did provide durable concrete.

The theory of spacing factor was initially developed for relatively high water-cement ratios; some researchers have now begun to study the fact that, for high strength concretes, the required spacing factor might be a function of low water-cement ratio. In this context, Okada et al. [59] tested air-entrained concretes with W/C ranging from 0.25 to 0.55 in accordance with ASTM C 666 Procedure A [52]. Their results are shown in figures 2.7 and 2.8, which indicate that the spacing factor required to produce durable concrete increases as the W/C decreases. The horizontal portion of the curves for W/C above 0.50 at an ordinate 0.2 mm (0.008 in.) indicates the validity of the constant spacing factor for higher W/C. Philleo [60], referring to the results of Okada et al., draws the inference from these figures that there appears to be no need for a maximum allowable spacing factor below a W/C of 0.50. However, these authors had previously concluded that some air entrainment is required, even for low W/C concretes. They obtained durability factors below 50 for concretes with W/C of 0.25 and 0.30, which was in contradiction to previous work. The results of Kobayashi et al. [61] shown in figure 2.9 also suggest that higher spacing factors produce durable concrete for lower W/C. These authors also believed that some air entrainment is necessary for low W/C, but

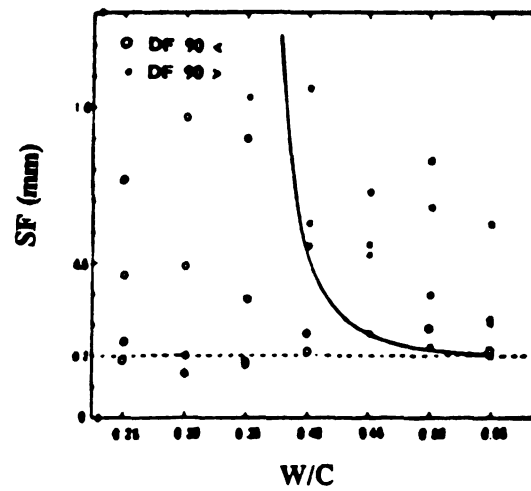


Figure 2.7. Relation of durability, water-cement ratio, and spacing factor at 300 freeze-thaw cycles [59].

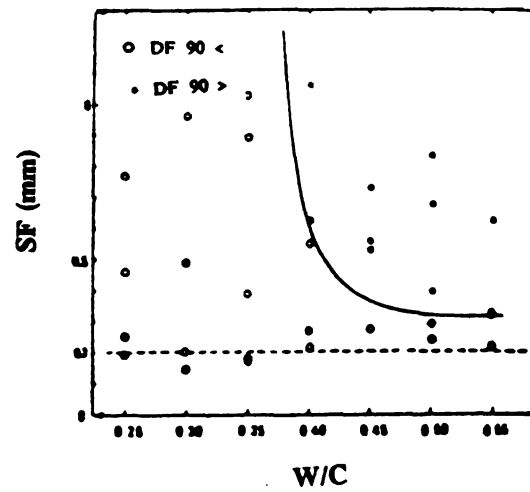


Figure 2.8. Relation of durability, water-cement ratio, and spacing factor at 1000 freeze-thaw cycles [59].

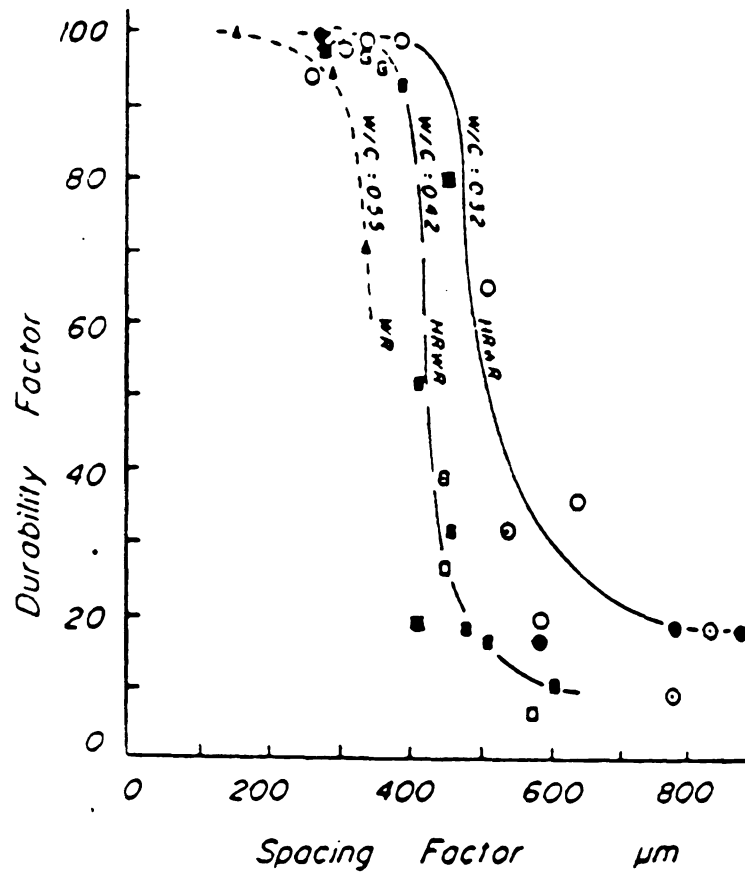


Figure 2.9. Relationship between air void spacing factor and durability factor in concrete containing HRWR [61].

speculated that no air entrainment may be necessary below W/C of 0.25 . In the next chapter, the interaction between the spacing factor and the use of different mineral admixtures in the presence of chemical admixtures is explored.

2.3.6 Philleo Factor

The calculation of Powers spacing factor is based on the assumption that all of the air bubbles in the concrete paste are of the same size and equally spaced. In practical situations this is not the case. The Powers spacing factor is calculated from measurements of the paste content, air content, and specific surface. Powers equations (ASTM C 457-90 [53] paragraph 14) take into account equal spheres of the same specific surface area and each sphere is assumed to be at the center of a cube of paste [28]. The sum of such cubes is considered to be equal to the total paste content in the concrete. While calculating the expression for permissible bubble spacing from the paste characteristics, Powers himself recognized the shortcoming in the theoretical calculations [28]: "Eqs. 13, 14, and 17 apply only to a material in which the air voids are of the same size. Therefore, these theoretical equations would not be expected to hold exactly for a material in which the void sizes cover a wide range. Nevertheless, we may expect the equations to give the correct order of magnitude of pressure intensity and permissible spacing." In a continuation of the discussion he writes, "The theoretical equations... indicate that the maximum permissible spacing will differ according to differences in paste characteristics and to differences in rate of cooling. The equations for hydraulic pressure involve simplifying assumptions, and the computation for L_{max} (spacing factor based on

maximum air content) will apply strictly only to pastes in which the air voids are equal in size." For this he recommended an empirical establishment of the spacing factor based on an extensive experimental program of tests. His calculations of the spacing factor (ASTM C 457-90 [53] paragraph 14) based on linear traverse results are based on the assumption, "...that the voids are equal-size spheres, each sphere having the same specific surface as the measured specific surface."

Philleo [62] suggested a new parameter which he termed "The Protected Volume Concept." This offered promise in overcoming the limitations of Powers spacing factor, "...its merits had never been tested because of the difficulty in obtaining the necessary data and perhaps also because of the somewhat involved mathematics used" (Larson et al. [63]). Philleo's concept required an accurate estimate of the number of air bubbles per unit volume of paste as an input. "This requirement was partially met through improved linear traverse equipment. It also led to additional study of air bubble size distribution." To determine the bubble size distribution, it was necessary to know two things: (1) the relative frequency distribution of the spheres; and (2) the total number of spheres. Larson et al. [63] studied Philleo's concept and derived a mathematical expression, termed the "Philleo Factor". This factor may be thought of as the thickness of the spherical shells with randomly distributed air voids such that the volume contained in a unit volume of paste constitutes a given percentage of paste. In order to determine the Philleo Factor (PF), one needs to [64]:

- (1) Obtain an air void chord distribution; and
- (2) Determine the total number of voids per unit volume of paste.

Larson et al. evaluated the protected paste volume concept through a laboratory

program which involved evaluation of limited data using a single probability factor, while the results of the program did not warrant an unqualified acceptance of the Philleo spacing factor as superior indicator of frost resistance of concrete. However, the evidence was considered sufficient to justify further studies of this kind and to continue improving the techniques for collecting and processing the necessary data.

In a written discussion, Philleo himself congratulated the authors for the development of equipment, collection of data, and analysis of results. He also said that the approximation of the chord distribution function by an exponential function was a workable method for overcoming the difficulties inherent in the Lord and Willis [65] method, yet he considered it "unfortunate" that they found it necessary to resort to the exponential function. Larson, et al. responded to Mr. Philleo's comments and justified their approach.

The Philleo factor is considered by many to be a more reliable parameter for predicting the frost resistance of concrete than the spacing factor.

2.3.7 Attiogbe Mean Spacing

Attiogbe [66], referring to Powers [28,67] said that his equations did not give the actual mean spacing of air voids in hardened concrete: "The equations inherently give spacing factors that exceed the actual mean spacing due to the assumptions made in derivations." He concluded from his discussion that the actual air void spacing in the hardened concrete could be much less than indicated by the calculated spacing factor, and, as such, this may not be a consistent predictor of freeze-thaw durability.

Regarding the Philleo factor, Attiogbe mentioned that it depends on a knowledge of the size distribution of air voids in the hardened concrete. Moreover, existing methods for determining the void size distribution were not considered suitable for routine analysis. Thus, "As such, the Philleo spacing factor cannot be easily and/or accurately determined for routine characterization of air void system."

Using probability concepts and stereological principles, he derived an equation (which will be discussed later) for estimating the mean spacing of air voids in the concrete, which he compared with Powers spacing factor and found to be a better predictor of freeze-thaw durability than the standard spacing factor.

2.4 Summary

The above discussion indicates that use of sound aggregates, proper air entrainment, low water-cement ratio, and adequate curing are the key factors for making of frost-resistant concrete. The most important requirements of a frost-resistant concrete are the development of favorable air void system and water pore system.

There are numerous air void system and water pore system parameters which can be used to characterize the frost resistance of PCC. Powers spacing factor is considered the single most important indicator and is widely in durability specifications, but there are problems with its applicability for all concretes due to some inherent limitations. The applicability of a universal spacing factor criteria has also been questioned. Philleo factor is thought by some researchers, to be a more accurate predictor of durability, but is difficult to calculate. Attiogbe's mean spacing offers an alternative and is believed to



overcome problems associated with the other two, but needs to be evaluated for different kinds of mix designs. The problem becomes even more complex when the selected evaluation criterion is applied to concretes prepared with chemical and mineral admixtures (which will be discussed in the next chapter). This needs to be resolved or at least further clarified for the guidance of the users and researchers working in the area.

CHAPTER III

EFFECTS OF ADMIXTURES ON FROST RESISTANCE: PREVIOUS RESEARCH

3.1 General

An admixture for concrete is defined by ACI 116 R [24] and ASTM C 125 [68] as "a material other than water, aggregates, hydraulic cement, and fiber reinforcement, used as an ingredient of concrete or mortar and added to the batch immediately before or during mixing." The development of admixtures in the past four and a half decades has brought significant changes in the properties of concrete. Tremendous amounts of research by the advanced users of portland cement concrete (e.g., USA, Japan, Germany, United Kingdom, Australia) has been, and is still, directed towards improving its properties through the use of different kinds of admixtures.

Admixtures vary in composition from surfactants and soluble chemicals to insoluble materials. Improvement of workability, acceleration or retardation of setting

time, control of strength development, reduced cost, and conservation of energy, as well as enhancement of resistance to frost action, thermal cracking, and the actions of acidic and sulfate solution, are some of the major purposes for the use of admixtures. The use of admixtures in concrete CAN also have a significant affect on the properties of PCC exposed to repeated cycles of freezing and thawing. The following sections discuss admixtures that have been used in this research work.

3.2 Chemical Admixtures

3.2.1 Air Entraining Agents

The research work of the past few decades has indicated that the greatest single factor in producing a durable concrete that will be resistant to freezing and thawing is the presence of a well-distributed air void system in the cement paste. This can be achieved with the proper use of a good quality air entraining agent (AEA).

Air entraining admixtures are surfactants that consist of a non-polar hydrocarbon chain with an anionic polar group. Lea [69] explained that at air-water interfaces the polar groups are oriented towards the water phase, thereby lowering surface tension, promoting bubble formation, and counteracting the tendency of the dispersed bubbles to coalesce. At solid-water interfaces, where directive forces exist in the cement surface, the polar groups become bound to the solid with the non-polar groups oriented towards the water, making the cement surface hydrophobic (water repellent). These polar groups are electrically charged so that air can displace water and remain attached to the solid

particles as bubbles [69]. In other words, the negative charge is attached to the positively charged cement particle, which helps in stabilizing the bubbles. The AEA forms a tough, water-repelling film with sufficient strength and elasticity to contain and stabilize the air bubbles and prevent them from coalescing. This film keeps the positively charged water particles away from the bubbles [47].

For a durable and frost-resistant concrete, the required amount of the air entrainment is dependent on the aggregate size as well as the severity of exposure. As the aggregate size decreases, the surface area increases. This, in turn, requires greater amounts of paste to cover the aggregate. As a net result, air content increases. The air contents recommended by ACI Committee 201 [3] for frost-resistant concrete as a function of aggregate size are shown in table 3.1.

Table 3.1. Recommended air contents for frost-resistant concrete [3].

Nominal maximum aggregate size, in. (mm)	Average air content, percent*	
	Severe exposure	Moderate Exposure
0.375 (9.5)	7.5	6
0.5 (12.5)	7	5.5
0.75 (19)	6	5
1.5 (38)	5.5	4.5
3 (75)	4.5	3.5
6 (150)	4	3

* A reasonable tolerance for air content in the field conditions is ± 1.5 percent. The tolerance limits according to reference [47] are -1% and +2%.

According to some studies, most known types of AEAs, especially wood resin-based varieties, have not been entirely satisfactory with respect to stability of the number

and/or volume of voids they have produced [11]. That is, they show increased or decreased air content tendency as the mixing time increases.

The type and the quantity of the AEA being used in a particular environment has specific effects on the development of a stable air void system. For example, Wood [7] showed that the incorporation of five to six percent air content using five different types of AEAs produced 24000, 49000, 55000, 170000, and 800000 air voids per cubic centimeter of hardened cement paste. The corresponding concrete specimens survived 29, 39, 82, 100 and 550 freeze-thaw cycles, respectively, before exhibiting 0.1 percent expansion.

After a lengthy literature review, the National Cooperative Highway Research Program Report 258 [70] categorized different variables influencing control of air content. According to this survey, the most prevalent problems affecting control of entrained air content in concrete are the batching procedure and the chemical admixtures. This report concludes that up to ten times the normal dose of air entraining agent is sometimes needed to obtain specified air contents in low slump, dense overlay mixtures. With a particular AEA, it may not be possible to achieve specified air contents even at high dosage rates. Once the specified air content has been achieved, the concrete is assumed to exhibit an excellent air void system and is expected to offer long term durability, provided the concrete is adequately consolidated.

Klieger [71] found that the strength reduction due to air content depends on the cement content, aggregate size, and amount of AEA. He found that six percent of air content resulted in a reduction of 2.7 percent of flexural strength and a compression strength reduction of 3.9 percent per percent of air. Litvan reports [13] that substantial



loss of mechanical strength is unnecessary and can be avoided without loss of freeze-thaw durability. Good frost resistance appears to be possible by increasing the volume of small pores, thus avoiding the loss of mechanical strength.

The US Bureau of Reclamation found that air-entrained pastes with high water-cement ratio were more durable than nonair-entrained pastes with low water-cement ratios, which means the relative improvement in durability due to air entrainment is greater than the increased durability obtained by decreasing the water-cement ratio [50].

In the above discussion it was noted that frost resistance of concrete is achieved not only with increased air content but also through a well-distributed air void system, which can be obtained with the use of an AEA. On the other hand, all AEAs do not provide the well-distributed air void system necessary for frost resistance, and the admixture dosages also vary. According to Klieger and many others, the incorporation of air entrainment also results in a reduction of strength. Litvan, on the other hand says that strength can be maintained by increasing the quantity of small pores. This suggests the possibility of making frost-resistant concrete through the use of mineral admixtures that affect the pore structure of concrete. This is discussed in the following sections.

A great deal of research has been conducted to study the effects of chemical and mineral admixtures on the amount and type of AEAs, and the resulting air void system. This research is summarized in the succeeding paragraphs.

3.2.2 Water Reducers/Superplasticizers

Typical water-reducers reduce the requirement of water content by approximately five to ten percent whereas superplasticizers reduce water content demand by twelve to thirty percent [47]. ASTM C 494-90 [72] divides the water-reducing and/or set controlling chemicals into seven types. The water-reducing and high-range water-reducing admixtures, which are of interest from this research point of view, will be discussed.

There are basically four ways to use WR and HRWR, but numerous combinations of these are also possible [2,5]:

- (1) To produce high strength concrete. The invention of superplasticizers has opened new avenues for making high strength (15000 to 20000 psi) workable concretes with low water-cement ratios. Japan is the prime user of this technique.
- (2) To produce concrete with low cement contents. The cost of concrete can be greatly reduced by producing concretes with the same workability and water-cement ratio at low cement contents.
- (3) To produce "flowing concrete". Slump can be increased from three in. (75mm) to more than eight in. (200 mm) without changing the cement content and water-cement ratio. While this type of concrete is generally expensive in production (due to the large demand for expensive admixtures), the economic advantage lies in the reduction of placement costs. Concrete made using with this technique can be placed with greater assurance of freedom from honeycombing in congested forms or around steel reinforcement, and requires less vibration.

This is the method of choice in Germany.

(4) HRWRs provide an economical means of providing high early strength concrete. This appears to be the most popular application in the USA and Canada.

The water reducers and high-range water reducers, also known as "superplasticizers" or "super-water reducers", generally belong to one of four types [5]:

Sulfonated melamine-formaldehyde condensates;

Sulfonated naphthalene-formaldehyde condensates;

Modified lignosulfonates; and

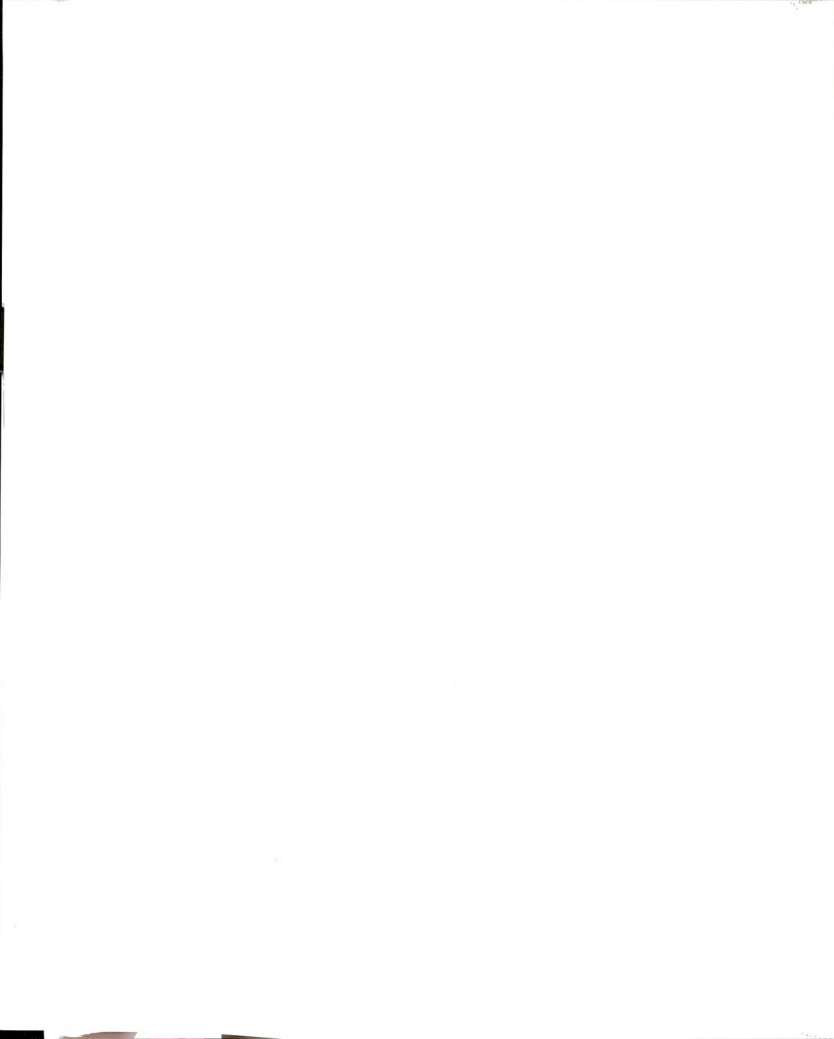
Polycarboxylate derivatives.

The last two are sodium salts with high molecular weight condensates and may be augmented by set-controlling chemicals. All four types are compounds of complex, high molecular weight groups.

In 1958 Japan was the first country to develop the naphthalene group, while the melamine group was discovered in Germany in about 1970. The modified lignosulfonates are most closely associated with recent North American practice. The research into and use of HRWR in United States began in about 1974 [25].

The effect of water reducers/superplasticizers with respect to the freeze-thaw durability of portland cement concrete is still a controversial issue. The basic concern is that when water reducers/superplasticizers are used with an air entraining agent, they often fail to produce air void systems that are considered essential for frost-resistant concrete.

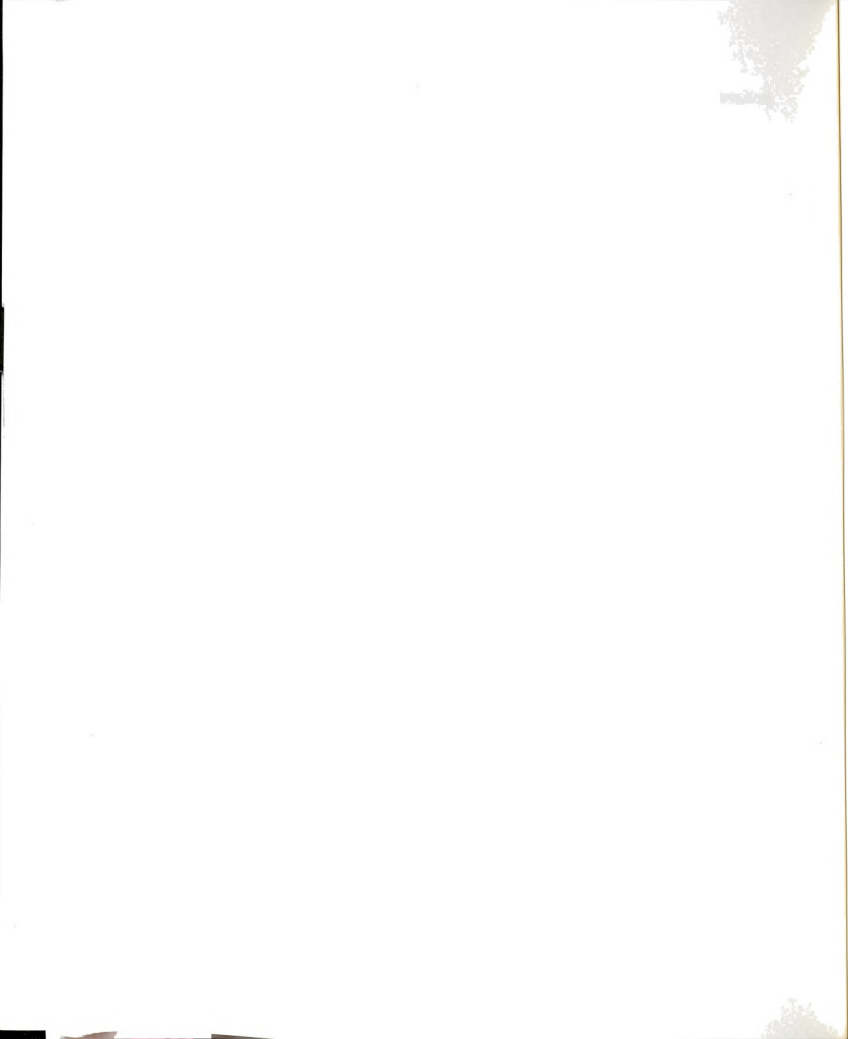
Giamietro and Cangiano [14] found that the presence of superplasticizers resulted in the production of a less stable air void system, as compared to the air void system



produced by the air entraining admixture alone. Microscopic examination of the hardened concrete showed that the air bubbles produced in the presence of superplasticizers are about two to three times larger than those caused by AEA. It appears that superplasticizers would produce a system of bubbles not "bound" to the cement particles, with consequent possible coalescence phenomena. This is unlike the bubbles produced by AEAs, which are generally bound to the cement and aggregate particles.

Philleo [73] hypothesized that HRWR do not significantly alter the pore structure of the low water-cement ratio pastes. Moreover, he indicated that the freeze-thaw durability of concrete is directly related to the freezable water. Litvan [13] explained that the superplasticizers eliminate large air voids visible under microscope but do not significantly interfere with the action of the air entraining agents in forming of small pores. Such concretes have a considerable percentage of pores in the range of 0.3 to 2 microns, which are believed to improve frost resistance characteristics despite exhibiting higher values of the spacing factor (in the range of 0.008 to 0.017 inch (0.2 to 0.43 mm)). Lane [74] concluded that the superplasticizers are compatible with fly ash concrete and produce no detrimental effect. Water reductions for equal slump did not exceed 15%, which improved this characteristic only slightly over the standard water reducers. Low water reduction was attributed to the lower water requirement for the fly ash concrete as compared to ordinary concrete with equal consistency.

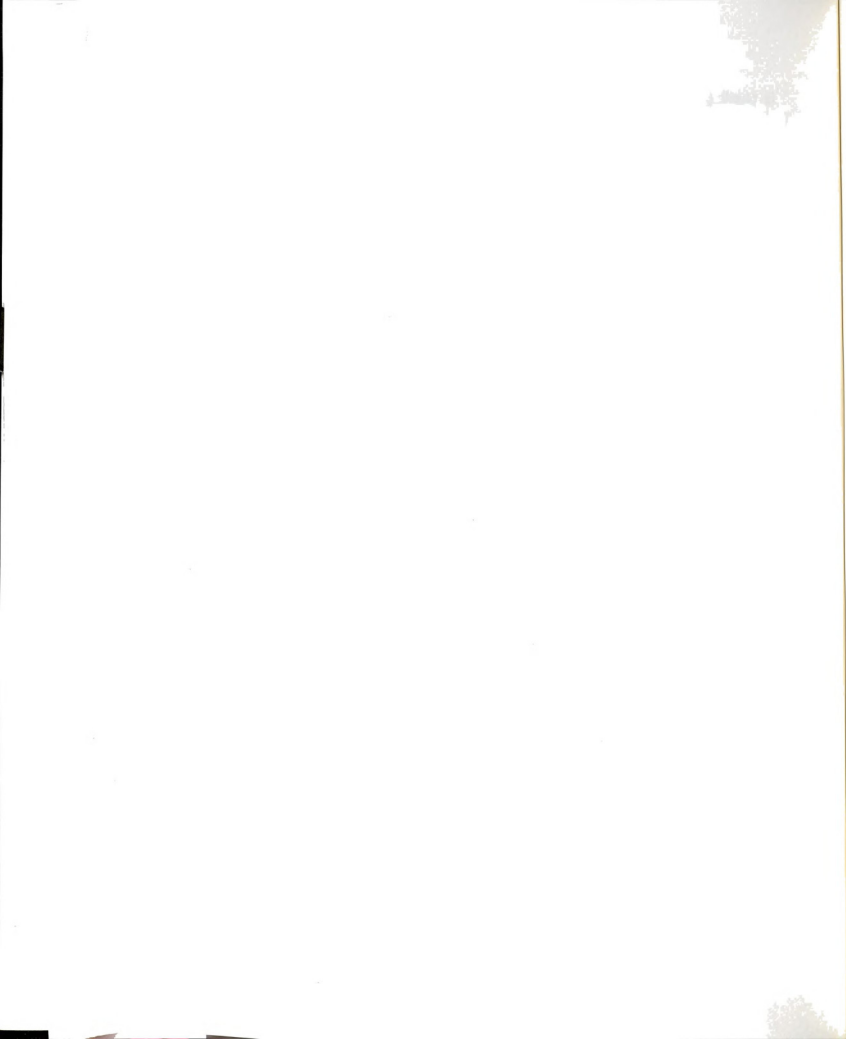
Early research in the US was carried out by Tynes at WES [21], Malhotra at CANMET [22], and Whiting at Portland Cement Association [23]. All of these researchers generally agreed regarding the effects of the admixtures in terms of water reducing ability, improved workability, increase in compressive strength, and reduction



in bleeding and shrinkage. However, they reported major differences on the frost resistance of concrete made using these admixtures. Early users of these admixtures, had concerns regarding the ultimate durability of concrete. Most of the concerns with respect to the durability of concrete were based on the discrepancies in the air void characteristics measured according to ASTM C 457 [53] and the results of freeze-thaw testing using rapid procedures [25]. Most of the studies reported air void characteristics inferior to the standard specifications. It was also observed that, in spite of these discrepancies in concretes using HRWR, the frost resistance was, in general, satisfactory. Whiting found that air-entrained concretes made with water-reducers produced excellent results when exposed to repeated cycles of freezing and thawing and deicing salts, although the spacing factors were greater than recommended values [23].

When superplasticizers are used to produce concretes with low water-cement ratio, reduced permeability may play an important role in the assessment of the long term durability of concrete. This is because the concrete requires greater time to become critically saturated. Olkada et al. argued the need for a spacing factor of up to 0.01 in. for water-cement ratios greater than 0.45 [59]. They also concluded that concretes with low water-cement ratio can be durable even with higher spacing factors. Kobayashi et al. [61] found a sudden drop in the durability of concretes with a water-cement ratio of 0.55 when the spacing factor increased to 0.01 in., whereas concrete with water-cement ratios of 0.42 and 0.32 showed similar performance up to spacing factor values of 0.015 and 0.018 in. Whiting [25], showed that high strength concretes with water-cement ratios of 0.31 will be durable up to a spacing factor of 0.012 in.

Whiting [75], while studying superplasticizers for highway applications, reported



that the spacing factor was correlated with increasing coarseness of air void distribution. He found that the coarseness of an air void system was common to all superplasticizers and their combinations with air entraining agents. He also found that an increase in air content in fresh concrete beyond eight percent allowed sufficient air to be retained in hardened concrete so as to mitigate the distribution shift effect and decrease the spacing factor below 0.008 in. [25]. However, extended vibration reduced air content and increased spacing factors. Reduction in air content of hardened concrete containing HRWR below five percent showed poor resistance to freezing and thawing.

Whiting et al. [25] provide field performance data of concretes containing HRWR in highway pavements and bridge decks. The overall goal of this work was to study the effects of HRWR, if any, on the long term durability of concrete exposed to severe freeze-thaw environments. It was concluded that the HRWRs in themselves have no significant deleterious effects on the surface durability of PCC exposed to freeze-thaw environments and deicing agents. The characteristics which lead to durable conventional concrete (i.e., low water-cement ratio and proper air entrainment), are also applicable to concrete containing HRWR. It was also noted that, although the spacing factor and the specific surface in many HRWR concretes fail to meet minimum established guidelines, other factors, namely water-cement ratio and amount of entrained air removed from the near surface zone, have greater influence on durability than do air void characteristics measured in bulk of the concrete.

The above discussion illustrates the controversies in the use of HRWR with respect to frost resistance of concrete. These differences are basically about the interaction of superplasticizers with AEA, and its failure to produce the air void system

considered essential for frost resistance (according to the existing specification) or providing frost-resistant concrete even if out of specification. This leads to the questions about the validity of current spacing factor criteria being applied to concretes with chemical and mineral admixtures, which must be addressed.

3.3 Mineral Admixtures

3.3.1 General

Mineral admixtures, also known as pozzolans or fillers, are currently being used very widely. They are expected to gain even more prominence because of their extensive production, cost effectiveness, and their beneficial effects on properties of PCC when used in appropriate proportions. The most common types of mineral admixtures being used are fly ashes, ground blast furnace slag, and silica fume. They impart different type of characteristics to portland cement concrete. These are briefly discussed in the following paragraphs.

3.3.2 Fly Ash

General

The possible use of fly ash as a pozzolanic ingredient was first recognized as early as 1914, but the annotated bibliography prepared by Abdun-Nur [76] indicates that the



work by Davis in 1937 is the earliest substantial study performed on this subject in the United States [77]. Romans, about 2000 years ago, used volcanic ash, called "pulvis puteolanus" (later changed to "pozzolana") with lime to produce mortar and concrete [1]. Since the late 1930s continuous work has been done on the use of fly ash as a concrete ingredient. Today it has become more significant due to economical and environmental factors. Although statistics are not available from the former USSR, the USA, the former USSR, China, India, the UK, and South Africa are considered the largest producers of fly ash, with at least 10 million tons per annum [78]. The use of fly ash by the cement and concrete industry varies from a maximum of 20% in China to a minimum of 1% in South Africa. The annual world consumption of coal in electrical power plants is 3000 million tons (20% in the US), which results in the precipitation of about 300 million tons of fly ash [79]. The annual cement production in the world is about one billion tons, which is used in about six billion tons of concrete. These figures are expected to double by the year 2000 [79,80]. These data indicates that the potential for using fly ash is still far from being realized.

Production of Fly Ash

During combustion in modern power plants, powdered coal passes through high temperature furnaces where the volatile matter and carbon are burned off. Most of the impurities (e.g., quartz, clays, and feldspar) melt at high temperatures. The fused matter is then immediately taken to the lower temperatures zones where it solidifies as spherical particles of glass. A small portion of the mineral matter forms the bottom ash. However,

most of it flies out with the flue gas and, as such, is called "fly ash". This fly ash is later removed from the gas by electrostatic precipitators [81]. In the United Kingdom it is known as "pulverized fuel ash".

Since the production of fly ash is much cheaper than the production of cement, it holds significant promise. As such, it is the focus of current research in the United States and elsewhere. Moreover, with better understanding and development of proper specifications, the utilization rate of fly ash concrete is likely to be much higher in future.

Types of Fly Ash

ASTM C 619-91 [82] and the Canadian Standards Association (CSA) [83] recognize two classes of fly ash: Class C, usually produced from lignite or sub-bituminous coals; and class F, usually produced from anthracite or bituminous coals. The most significant difference between the two is that class C ash contains high levels of calcium (> 10 percent) and is also known as high calcium ash, whereas class F ash is also known as low calcium ash.

Class C fly ash is low in carbon and high in calcium when compared to class F fly ash. Class C fly ash, apart from being pozzolanic, is also self-hardening, which means that it hardens like portland cement when mixed with water. Its initial hardening is relatively fast; its cementitious degree varies with the content of calcium hydroxide (i.e., higher the value of the calcium hydroxide, the higher the cementitious properties). Unlike class C ash, class F fly ash is not self-hardening. It has pozzolanic properties, which means



that the fly ash particles react with calcium hydroxide in the presence of water to form cementitious products that are very similar to those present in hydrated portland cement. All types of fly ash in the United States before 1975 were of this category.

The main constituent in low calcium (fly ash due to high proportions of silica and alumina), is aluminosilicate glass. When the large spheres of the molten glass do not get cooled rapidly and uniformly, sillimanite or mullite may crystallize as small needles in the interior of the glassy spheres. This basically accounts for the presence of crystalline aluminosilicates. It has been confirmed by X-ray diffraction analyses [78] that the principal crystalline minerals in low calcium fly ashes are quartz, hematite or magnetite, and mullite. As these are crystalline and non-reactive at ordinary temperatures, their presence in large proportions at the cost of the noncrystalline component or glass in fly ash tends to reduce the reactivity of the fly ash. The high calcium fly ashes are in general more reactive because most of the calcium is in the form of reactive crystalline compounds, such as C_3A , CS , and C_4A_3S [3]. There is also evidence that the main constituent (i.e., the noncrystalline phase) contains enough calcium ions to enhance the reactivity of the aluminosilicate glass. Most fly ashes (low and high calcium) contain 60 to 85 percent glass, 10 to 30 percent crystalline compounds, and up to 10 percent carbon (which is reduced to a maximum of two percent in modern furnaces for high calcium fly ashes). Larger amounts of carbon are considered harmful in PCC due to their increased demand of water for a given consistency and a higher air entraining admixture requirement.

It has also been determined from micrographic examinations of fly ash that most of the particles are solid spheres of glass; but sometimes a few hollow spheres, which



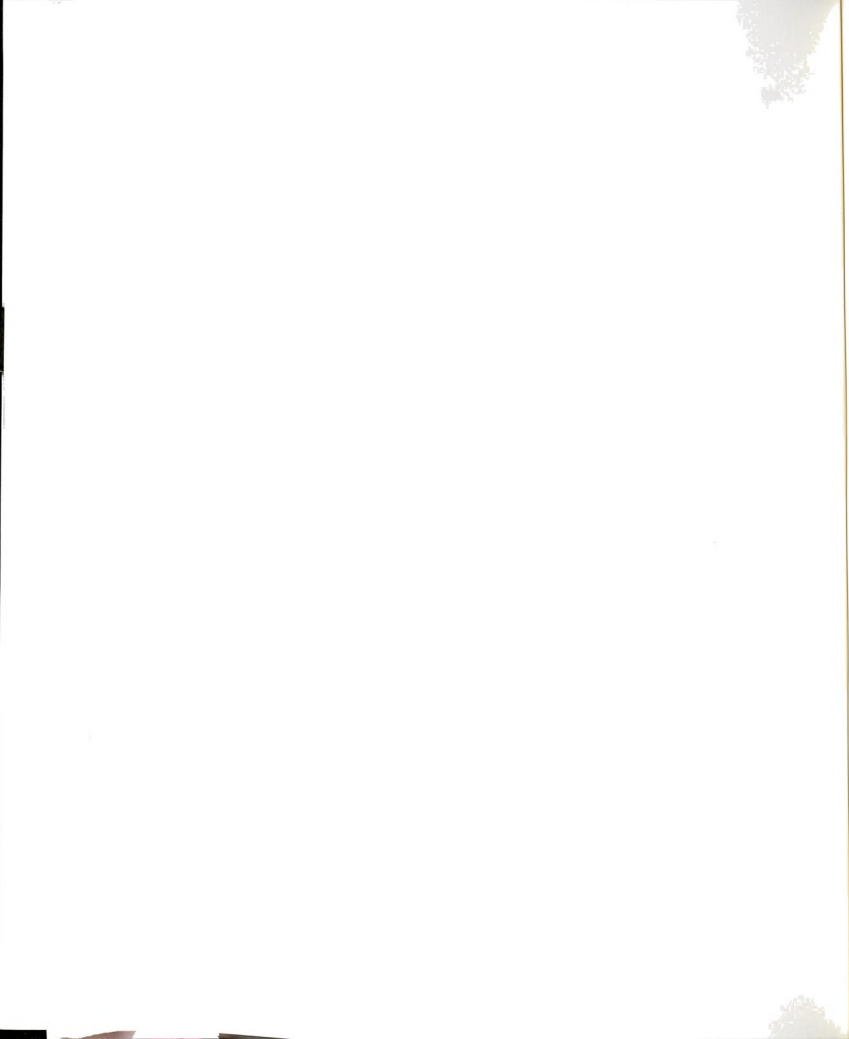
are called cenospheres (completely empty) and plerospheres (packed with many small spheres), are also present. These spheres in the low calcium fly ashes are cleaner than the spheres of the high calcium fly ashes. The particle sizes usually vary from less than $1\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$ in diameter with greater than 50 percent smaller than $20\text{ }\mu\text{m}$. Figure 3.1 provides a good comparison of the particle size distribution of two types of fly ashes, portland cement Type I, and condensed silica fume. The particle size distribution, morphology, mineralogy, and surface characteristics of the fly ashes play an important role in the water requirement, development of a refined pore structure, and the strength development of the PCC.

Methods of Use

Fly ash is currently used in concrete in two ways: (1) blending a fixed quantity with any type of the cement depending on the intended use or, (2) mixing the required quantity by the volume or weight of cement at the time of preparation of the concrete. Both methods present their own advantages and disadvantages, but generally greater flexibility is available in the second method, and the concrete can be conveniently prepared consistent with project requirements.

The Concept of Pozzolanic Activity

Fly ashes exhibit both cementitious and pozzolanic activity. A pozzolan is defined [80,84,85] as "a siliceous or siliceous and aluminous material, which in itself possess



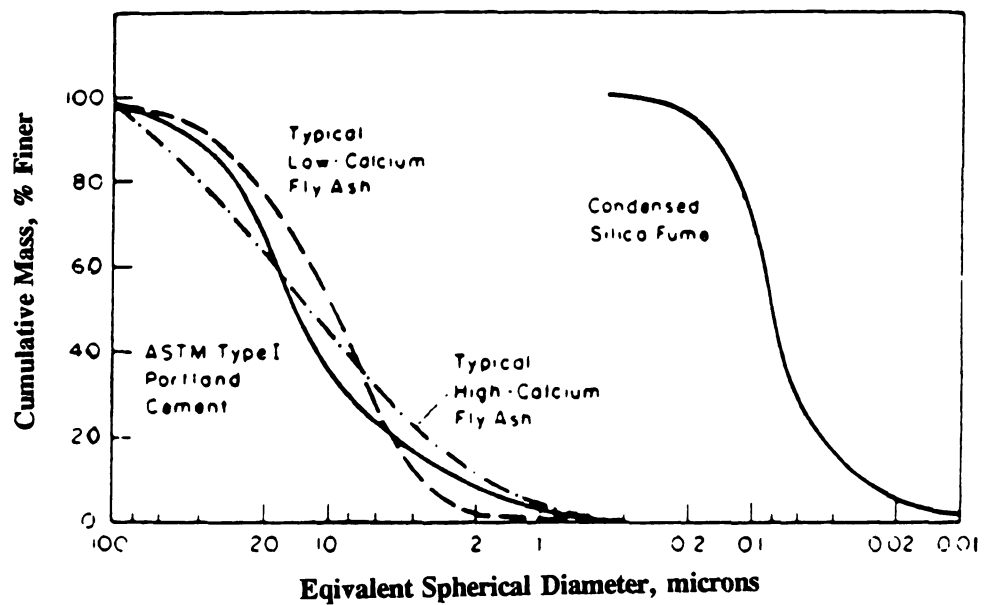
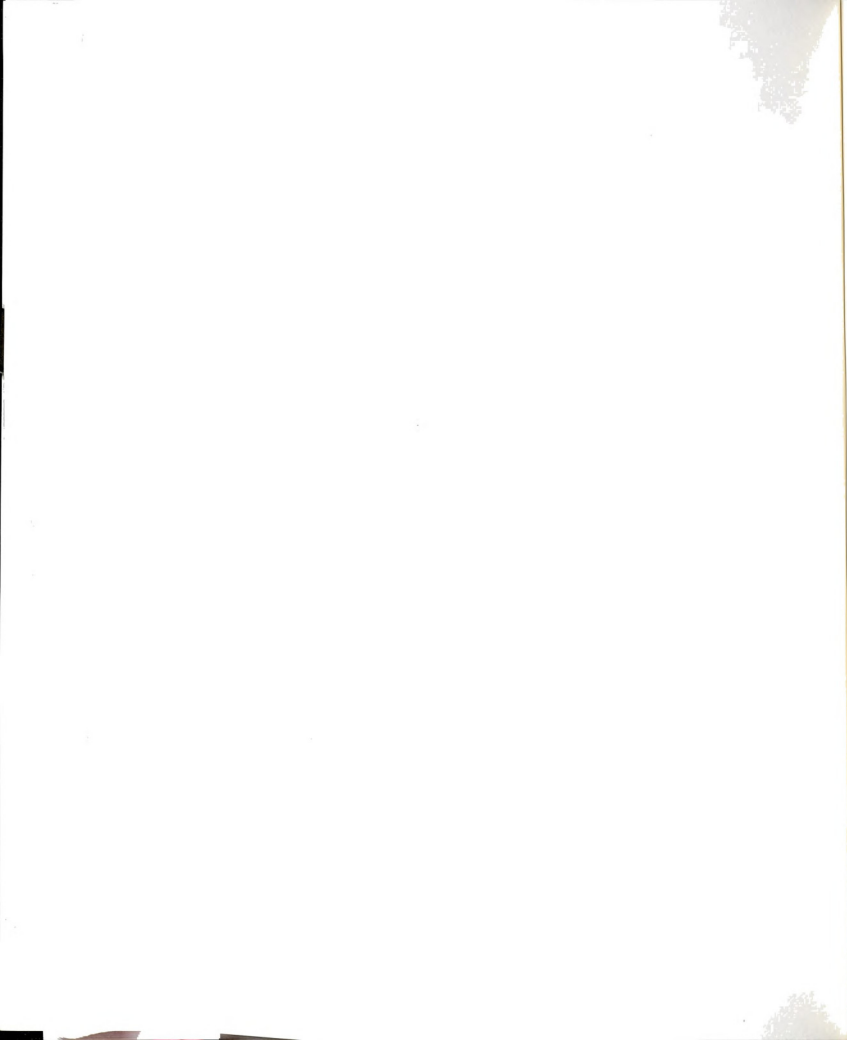


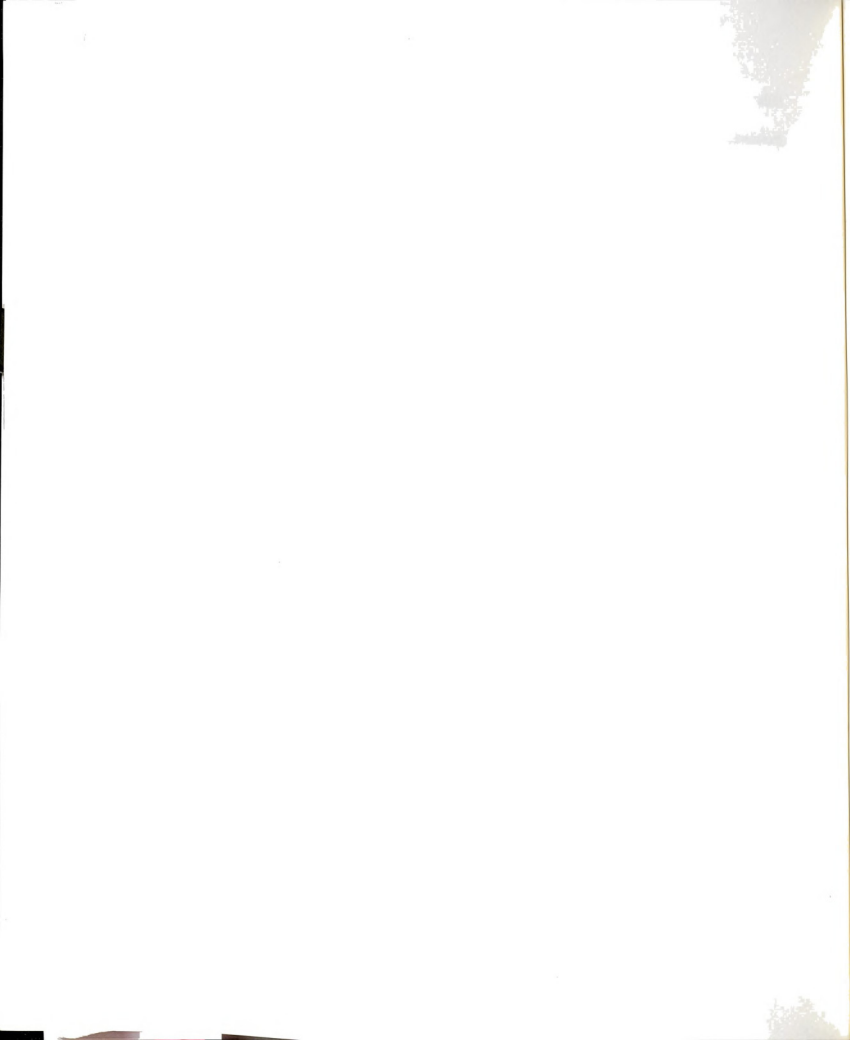
Figure 3.1. Comparison of particle size distribution of portland cement, fly ashes, and condensed silica fume [2].



little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties." "Use of Fly Ash in Concrete" [26] gives a very comprehensive explanation of the two aspects of the concept of the pozzolanic activity, which are briefly explained here.

Many types of calcium silicates and calcium aluminates are formed due to the reaction of water with cementitious compounds in the cement. These products form a structure around the aggregate, which leads to the setting of the concrete. Calcium hydroxide is one of the by-products at the initial stages. The calcium hydroxide in the solution reacts slowly with the pozzolanic materials, and the product is basically of the same type and properties as that of the initial cementitious reaction. In this way, as time passes, an additional bonding product is available. As a result of this, the initial strength development of fly ash concrete is slower than plain concrete, depending on the characteristics and the degree to which cement has been replaced, but ultimately equal or higher strength will develop.

The other aspect of pozzolanic activity is that, in concrete where the water to cement ratio exceeds 0.22 to 0.25 by weight [47], there is more water available than is required for the hydration reaction. Generally, the water is added to improve upon workability, but this unhydrated water stays in the capillary pores. Once the concrete is properly cured, the calcium hydroxide dissolved in the water is available to react with the fly ash. Now the solid reaction products that have been formed will fill or partially fill the capillary channels, resulting in a reduction of the permeability. In this way, aggressive fluids such as chlorides or sulfate solutions can not get into the concrete, and,

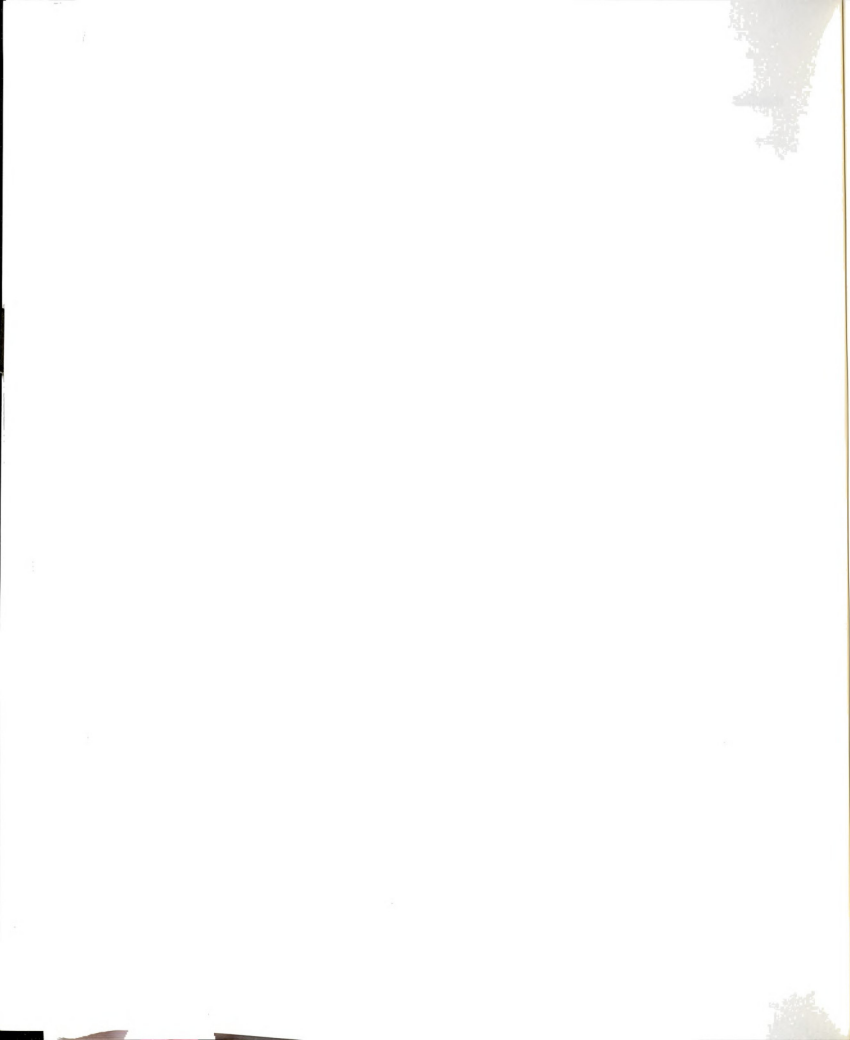


therefore, its durability increases.

Moreover, in fly ash concrete, since the pozzolanic reactions are slow, the heat generated during the hydration process can easily dissipate. In this way, the thermal stresses developed are low, and the concrete is prevented from cracking.

Research on Fly Ash

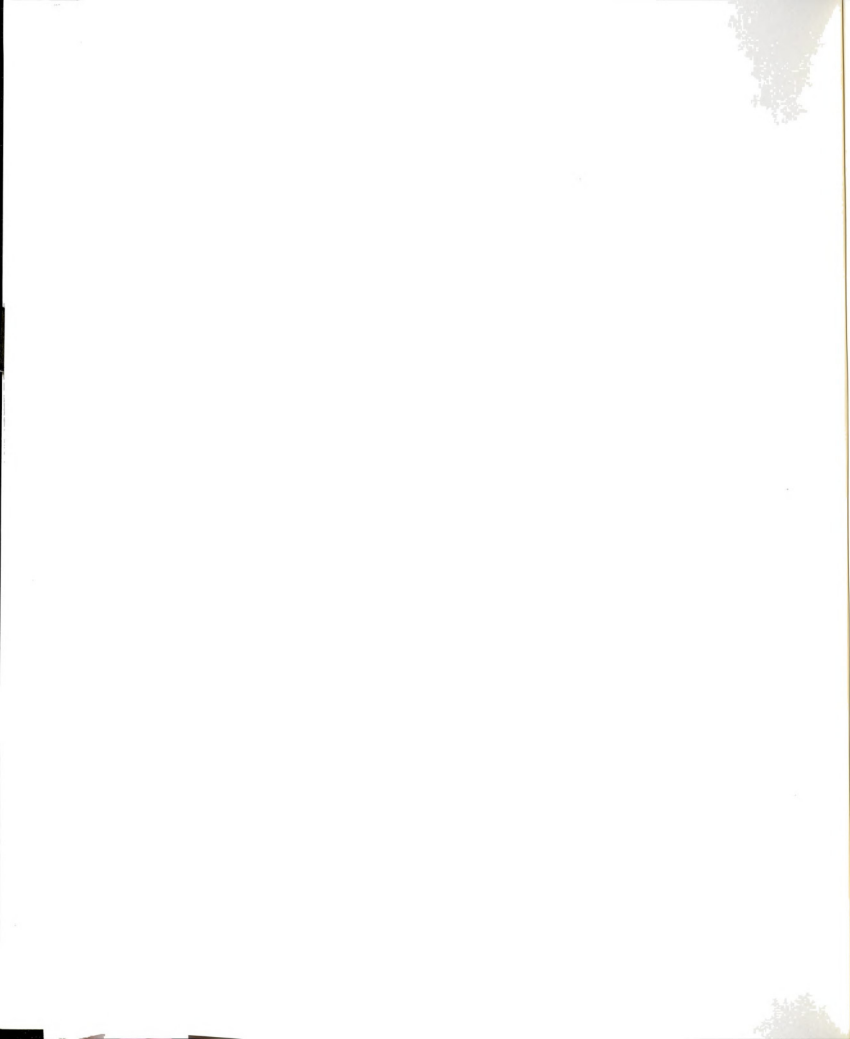
Tremendous amounts of research have been done in the past few decades on the use of mineral admixtures to better understand the various properties of fly ash so that it can best be utilized. The effects of pozzolans on the properties of freshly mixed concrete vary with the type and fineness, as well as the chemical, mineralogical and physical characteristics of pozzolan; the fineness, composition and constituents of cement; and the quantity of cement plus pozzolan used per volume of concrete [76,77,86,87,88]. A review [89] of the use of fly ash based on 275 papers shows that a good fly ash, used in optimum quantities, does not increase the unit water requirements of concrete but does improve workability and plasticity, reduces segregation and bleeding, slows setting time slightly, and reduces heat of hydration. The effect of fly ash on water content and the amount of air entraining agent required to maintain a constant air content and workability varies with the type, quantity, and fineness of fly ash used. As fly ash reduces the water requirement for workability, so it increases the ultimate strength, reduces permeability, and improves resistance to sulfate attack [90]. It appears to enable concrete to better resist acid waters, sulfate-bearing waters, and sea water, especially when Type I cement is used [69,76,91,92,93,94,95,96].



The resistance of fly ash concrete to damage from freezing and thawing is considered to depend upon the adequacy of the air void system, the soundness of the aggregates, age, degree of hydration, strength of water-cement paste, and moisture condition of the concrete [26]. Some reports have indicated that fly ash concretes, even if properly air-entrained, have shown comparatively lower resistance to freezing and thawing than the concrete without fly ash at equal ages. But when the comparisons were made when the fly ash concrete had developed adequate strength, no significant differences were observed.

It has also been recognized that test conditions in the laboratory are generally more severe than actual field conditions to which the concrete is exposed. Quite a few fly ash concretes have performed satisfactorily for several years with no evidence of scaling. At some experimental sites where greater scaling has been observed, it has been seen that the internal structure and integrity of the concrete has not been affected [97,98].

In plain concrete, water soluble calcium hydroxide formed during the hydration process can generally be leached out with time, leaving available channels for the ingress of water. In fly ash concrete, the calcium hydroxide reacts with the fly ash and forms insoluble calcium silicate hydrate of the same or similar type as produced in normal hydration products. This reduces the chance of formation of channels as was possible during the leaching of calcium hydroxide. Moreover, the reaction products also fill up, or at least reduce the size of, the capillaries, and thereby reduce the permeability for the ingress of aggressive solutions. This process can save steel from corrosion and may increase resistance to frost action. It has been seen that even if the calcium hydroxides are reduced in fly ash concrete, adequate alkalinity remains to preserve the passivity of

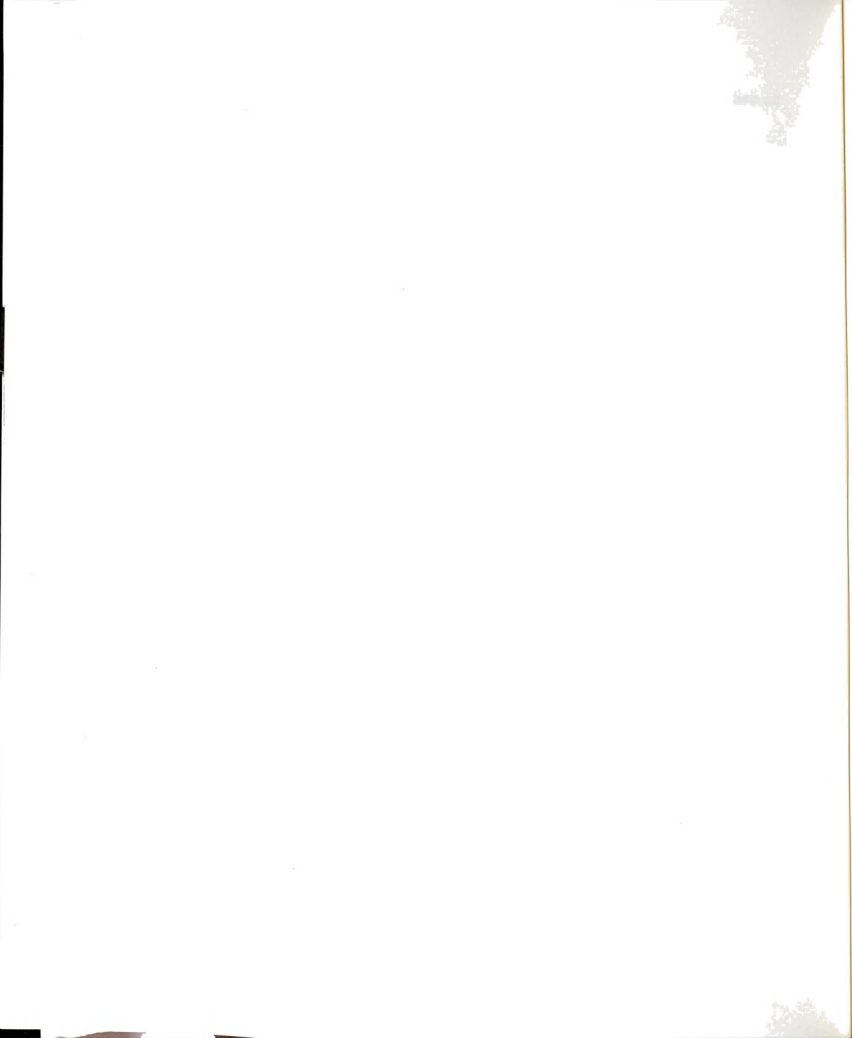


the steel necessary to prevent corrosion [26].

Fly ashes are generally characterized with regard to parameters that may influence their behavior and suitability for use in concrete. These parameters include (1) methodologies of characterization; (2) morphology, composition, and mineralogy; (3) chemical composition and physical properties; (4) classification; and (5) reactions with cement and concrete components [99]. The chemical and physical properties are specified in ASTM C 618-91 [82] and C 311 [100], but the methodologies are not limited to these relatively simple procedures. It has been generally found that the results of the standard procedures are themselves inadequate to explain the behavior. In view of the complexity and the variability of fly ashes, this is not surprising. It is, therefore, necessary to consider long lists of methodologies until the standard procedures are agreed upon.

The nature of the glass present in fly ashes, a predominant phase constituting about 60 to 90 percent of most fly ashes, is becoming the focus of studies. It has now been determined that differences exist in the structure of class F (low calcium) and class C (high calcium) fly ashes [101,102,103,104]. The glass structure of low calcium fly ashes is of a siliceous type [102,105,106,107], while high calcium ashes are likely to form calcium aluminate type glass or sometimes a mixture of glass types. Calcium aluminate glasses are believed to be more reactive in concrete.

C_3A (tricalcium aluminate) is another common component of high calcium fly ashes is frequently present and in fairly substantial amounts. This compound can rapidly react with any anhydrite present to make ettringite (a stable hydration product only while there is ample supply of sulfate available and on absence, it transforms to calcium sulfoaluminate hydrate), that links and binds adjacent spheres [106]. C_2S and C_3S are



sometimes present in high calcium fly ashes but only in small amounts. Their eventual hydration may contribute slightly to the formation of cementitious products. In some fly ashes, crystalline MgO (periclase) is present in small amounts. Based on the experience with portland cement where $\text{Mg}(\text{OH})_2$ formation leads to unsoundness, ASTM C 618-91 [82] limits the analytical MgO content of fly ash to five percent or less.

Unburned coal particles are also present in many fly ashes, and are common in those prepared under poor burning conditions [108]. The particles generally form the major portion of the coarsest fraction of many fly ashes, although these are also found in fine sizes. Irregular large size particles of vesicular glass are also common and are difficult to be distinguished from unburned coal particles. The unburned carbon particles are relatively inert in cement hydration reactions [101] and usually act as a diluent to the system. If these are present in substantial quantity, they can adversely affect the workability and lead to lower concrete strength [108]. Generally, the low calcium fly ashes have more variability and a greater percentage of carbon particles, compared to the high calcium fly ashes. These particles represent loss of ignition (LOI) and are restricted in ASTM specifications to 0.6% or less for both types of fly ashes.

Table 3.2 shows the variability in chemical composition for most of the fly ashes of the US [99]. The ranges given in this table are, however, generally broader than the ones given by Mehta [78], and should cause concern over the performance of fly ash in cement and concrete [82,100]. For example, reaction of sulfates with hydrating aluminates can result in delayed setting time and lower concrete strengths. Thus ASTM C 618-91 [82] limits the SO_3 contents to five percent in both type of fly ashes.

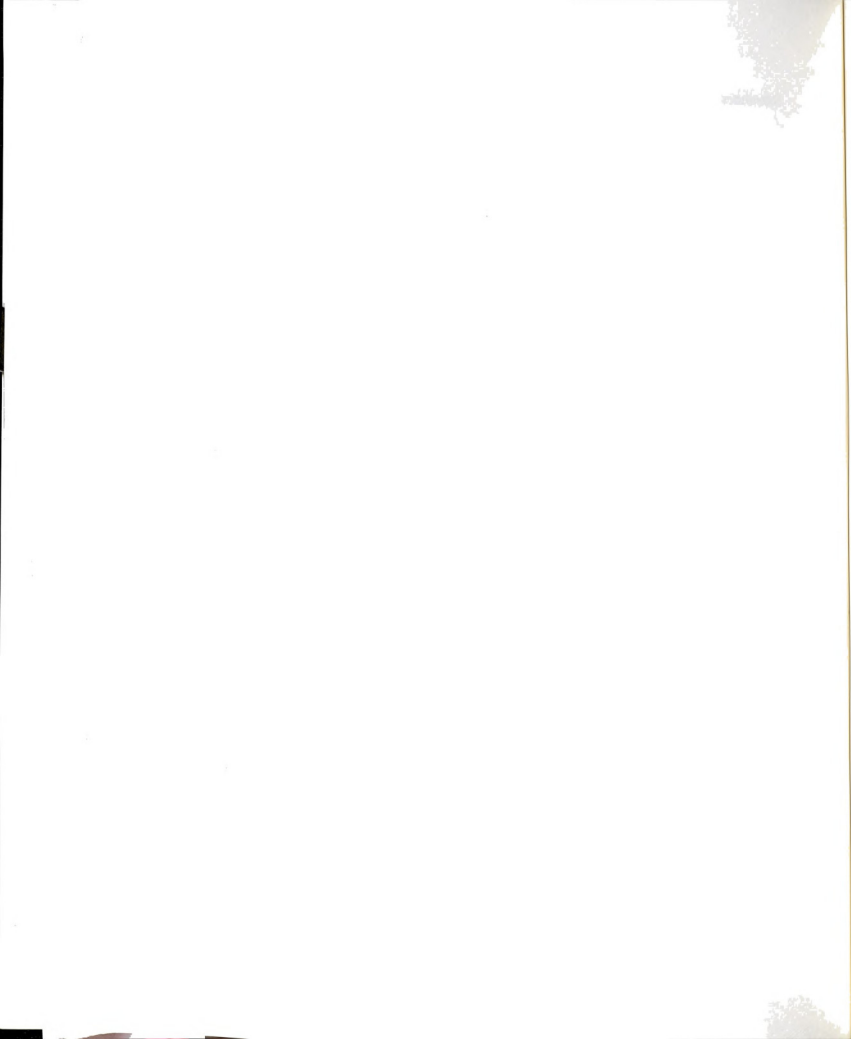
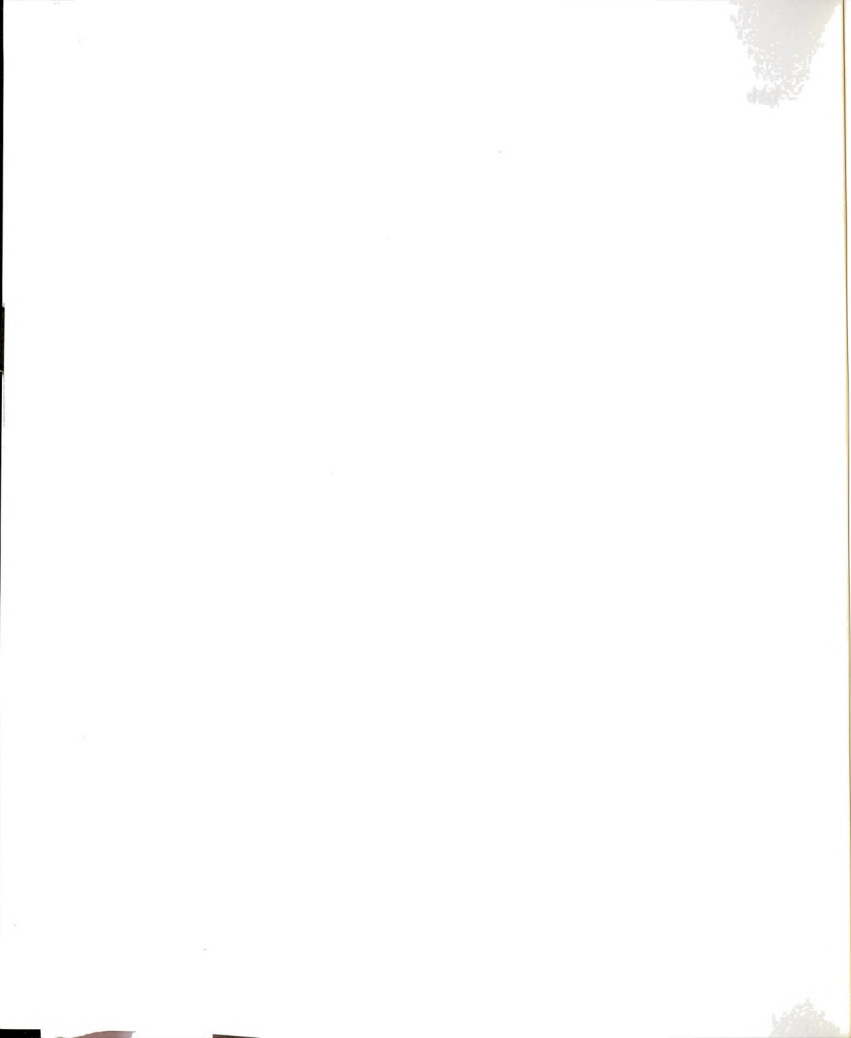


Table 3.2. Typical U.S. fly ash chemical composition, percentage ranges [99].

Oxide	Class F	Class C
SiO ₂	38-65	33-61
Al ₂ O ₃	11-33	8-26
Fe ₂ O ₃	3-31	4-10
CaO	0.6-13.3	14-37
MgO	0-5	1-7
Na ₂ O ₃	0-3.1	0.4-6.4
K ₂ O	0.7-5.6	0.3-2.0
TiO ₃	0.7-5.6	0.9-2.8
SO ₃	0-4	0.5-7.3
LOI	0.1-1.2	0.2-1.4

The specific gravity of fly ash varies from 1.6 to 2.8 and is related, in part, to its chemical composition and morphology. Generally, fly ashes with high iron content have high specific gravity, and those with low carbon content have low specific gravities. Fly ashes with high calcium have few cenospheres and generally have specific gravities of 2.4 to 2.8. These also tend to have finer particle sizes than low calcium fly ashes. Typical ranges of particle size of high and low calcium fly ashes as presented by Roy et al. [99] are shown in figure 3.2.

The use of fly ash induces changes in cement hydration rates [99]. The early strengths of the concrete are generally reduced, whereas the strengths at very late stages are increased. The age at which the strength curves cross each other varies a lot with the system being considered, and this period is reported to vary between 28 days and six



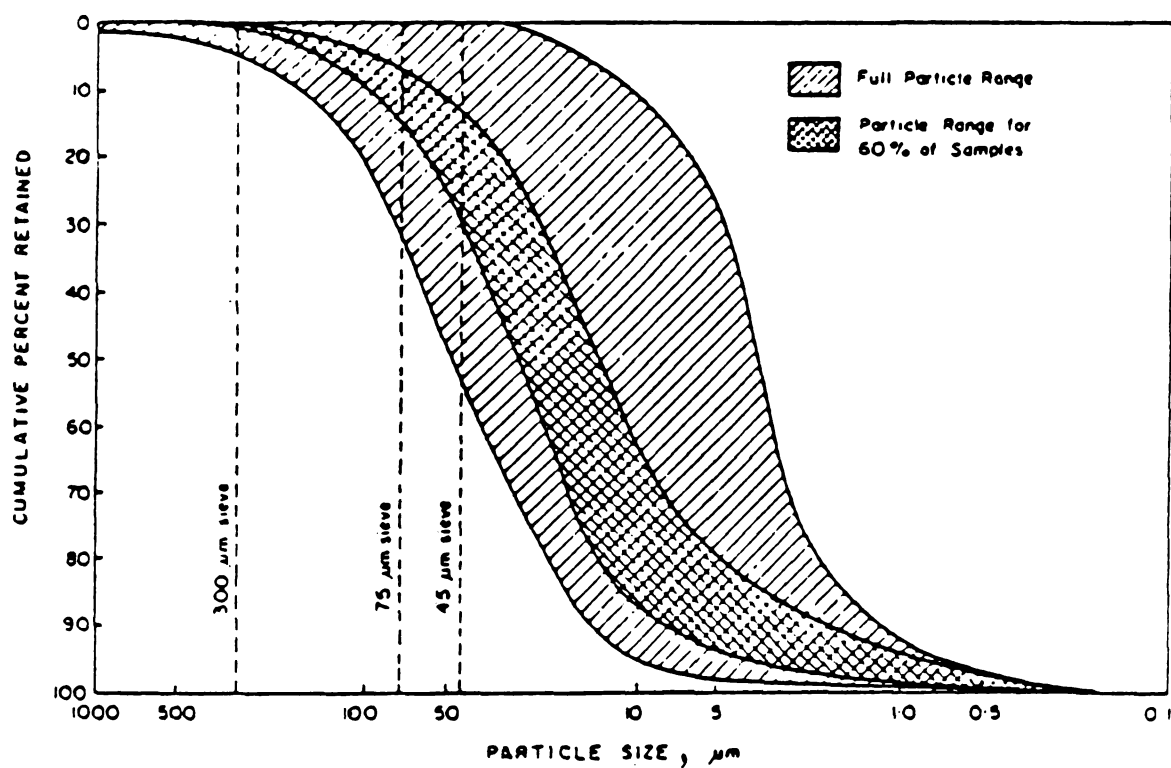


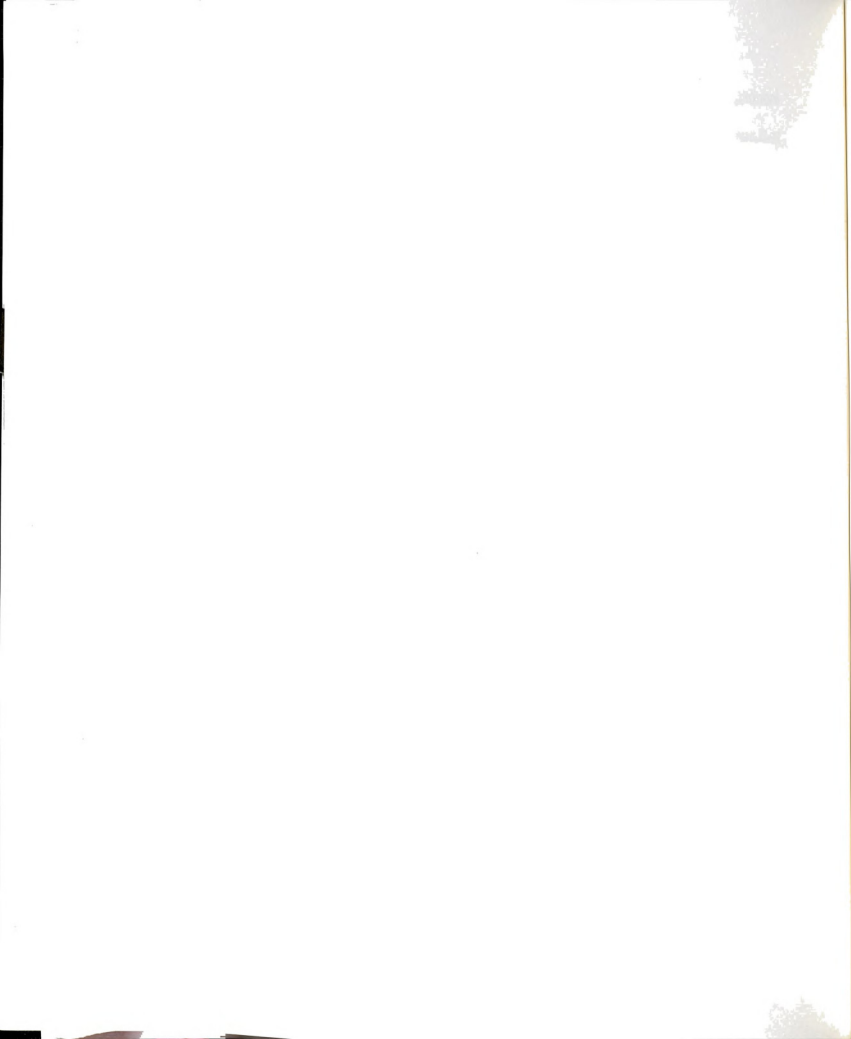
Figure 3.2. Particle size analysis of high-Ca and Low-Ca fly ashes [99].



months, depending partially on the curing conditions [80,109,110]. Some studies also indicate that fly ash concretes may also influence the initial hydration rates [111]. It has been seen that the presence of fly ash retarded the hydration of C_3S . It was concluded by Ghose and Pratt [112] that the presence of fly ash influences cement hydration, but the reaction of fly ash itself is slow and varies between fly ash particles. In some instances, reactions occurred in one day while in others there was no reaction even after five months. Mehta [113] showed concern with his test results of low calcium fly ash showing low strength. He observed that when accelerated curing was done at 43°C for seven days, the strengths for low calcium fly ashes were nearly as high as for high calcium fly ashes, and that the accelerated test results at seven days were equivalent to normal curing of 28 days. He also made similar comparisons between 28 days accelerated curing and 90 days room temperature curing.

Mehta [78] describes the hydration of fly ash in the presence of cement as a three stage reaction. "Immediately after mixing with water, reaction rims of impermeable coatings surround the fly ash particles. No further reactions occur until alkali or calcium hydroxide and sulfates ions are available in sufficient concentration in the solution phase. Thus during the second stage, it is primarily the hydroxide ions that activate the hydration of glasses in fly ash. The third, and the main reaction involving fly ash hydration is the slow pozzolanic reaction, which continues to consume calcium hydroxide and calcium silicate hydrates as long as calcium and hydroxyl ions are available".

Water plays a vital role in the development of physical and chemical properties of the portland cement concrete. The quantity that is needed for the hydration process and the target workability is considered desirable and any amount in excess of that will



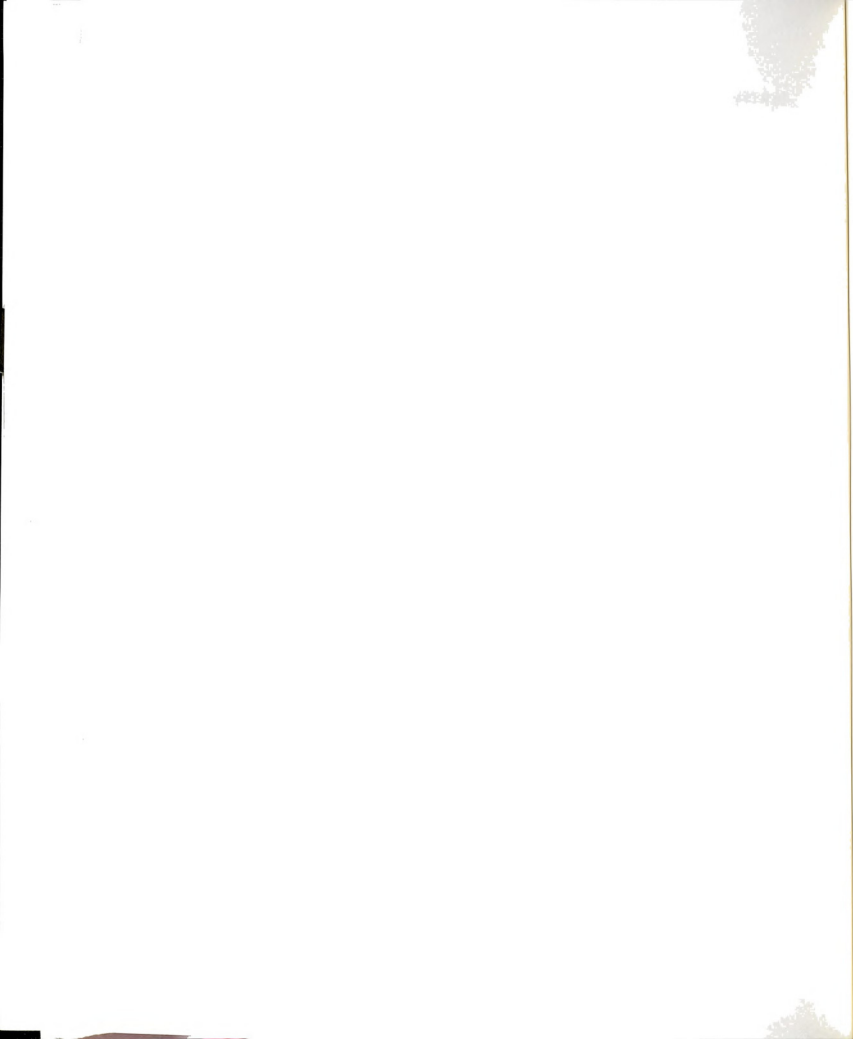
be undesirable due to its detrimental effects and loss of strength. Since water is involved in concrete deterioration, it is the permeability of concrete to water that generally controls the rate of deterioration [114]. After the capillary pores, the microcracks in concrete are the principal source of permeability. So by reducing the capillary sizes and microcracks from a variety of physical and chemical causes, the mineral admixtures can play an important role in enhancing the durability of concrete.

Berry and Malhotra [115] have reported in their review (data shown in table 3.3 referring to a study conducted by Davis [116]) that concrete pipe containing 30 and 50 percent fly ash as a cement replacement reduced permeability about five times at six months curing, as compared to a control concrete without fly ash.

Table 3.3. Relative permeability of concretes with and without fly ash [115].

Fly Ash		W/(C+P) By Wt. of Cement	Relative Permeability	
Type	% By Wt		28 Days	6 Months
None	-	0.75	100	26
Chicago Fly Ash	30	0.70	220	5
	50	0.65	1410	2
Cleveland Fly Ash	30	0.70	320	5
	50	0.65	1880	7

The imperviousness developed was attributed to the pozzolanic influence of fly ash. Elfert's data showing the comparison of permeability rates of 100% portland cement concrete and concrete made using a 30 percent replacement with fly ash is shown in figure 3.3 [116], which also show similar results.



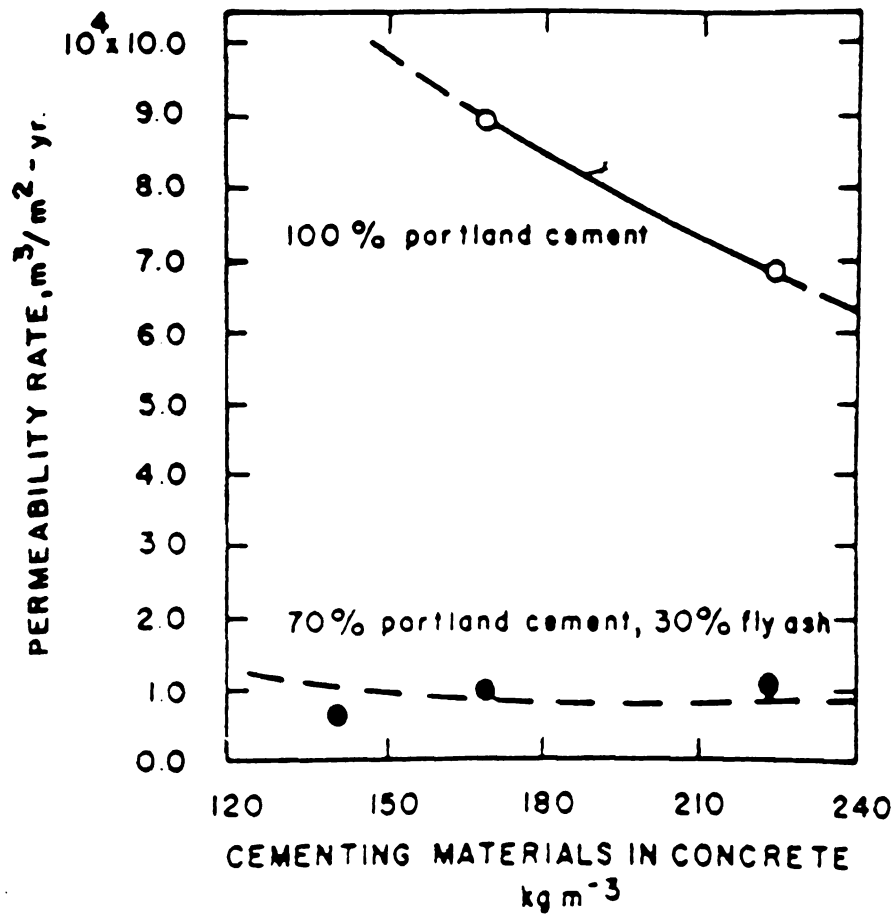
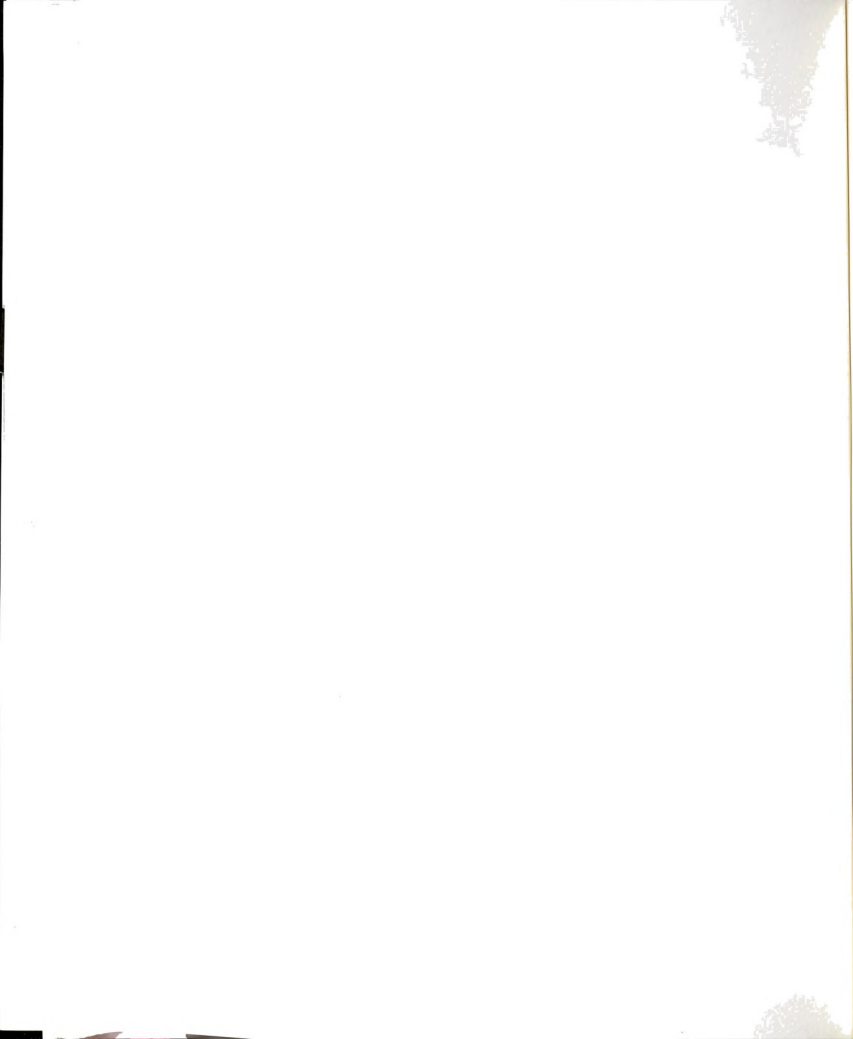
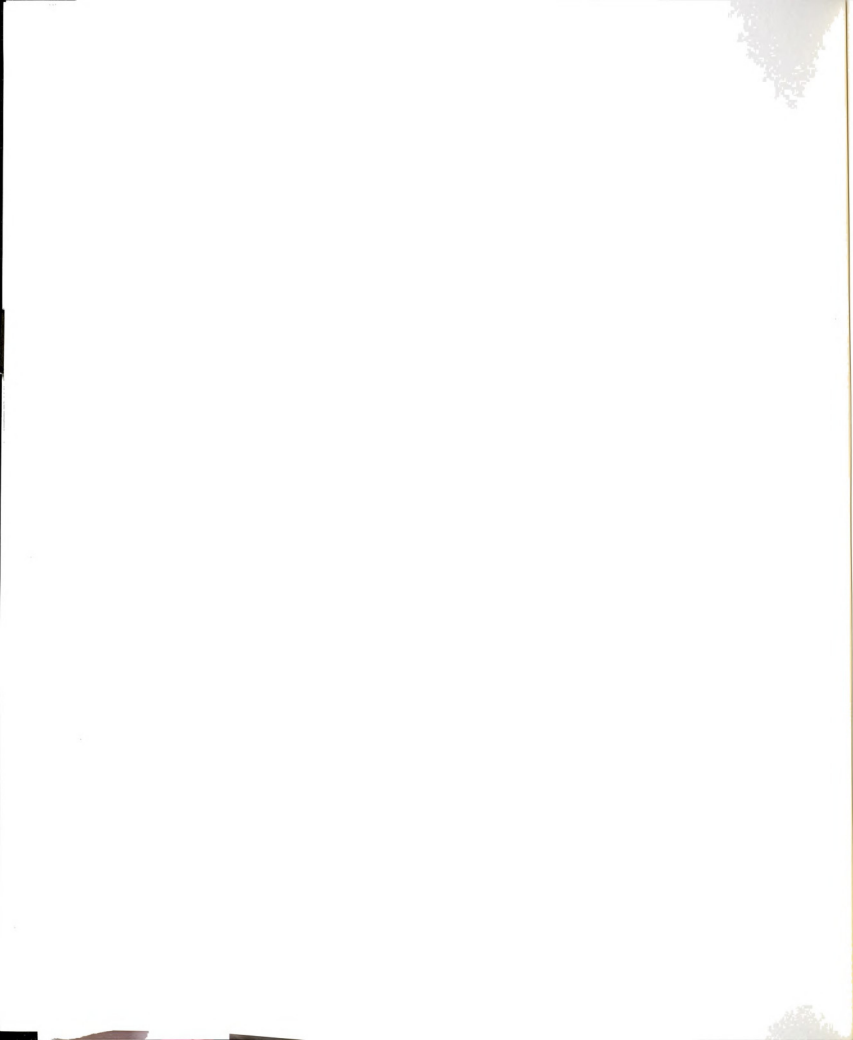


Figure 3.3. Permeability of concrete with and without pozzolan [116].



Ukita et al. [117] conducted their tests at 15 and 30 percent replacement levels of fly ash concretes with particle sizes up to 20 microns. The results of their water permeability tests, are shown in figure 3.4 [117]. Lower permeability was observed for concrete containing finer particles and 15% fly ash at 28 and 91 days of curing while samples with 30% fly ash showed higher permeability than the control concrete. Pozzolanic action was expected to be responsible for these different permeability values. It was concluded that water tightness depends upon the proportion and particle size of the fly ash. No distinctive differences in compressive strengths were noted between the fly ash and non-fly ash concretes at 7 and 28 days of curing, although higher strengths from fly ash concretes had been expected. At 91 days, significantly higher strength of 30% fly ash was achieved (as compared to the control). The reason for this was attributed to a "more compacted structure" and "accelerated hydration of cement in the presence of fine classified fly ash particles".

Repeated cycles of freezing and thawing are extremely destructive to concrete that is not specifically proportioned and carefully placed to withstand such conditions [116]. As proper air entrainment is important in all normal portland cement concretes when the concretes are exposed to freezing and thawing environments, it is also considered essential for protecting concrete containing mineral admixtures [78]. Virtanen [118], in his study on relative the frost resistance of concretes with and without mineral admixtures, found that nonair-entrained concrete incorporating slag, fly ash, and condensed silica fume showed poorer durability than the reference concrete, while properly air-entrained concrete with the same mineral admixtures showed better resistance than the control concrete. Larson [119], while presenting his work and



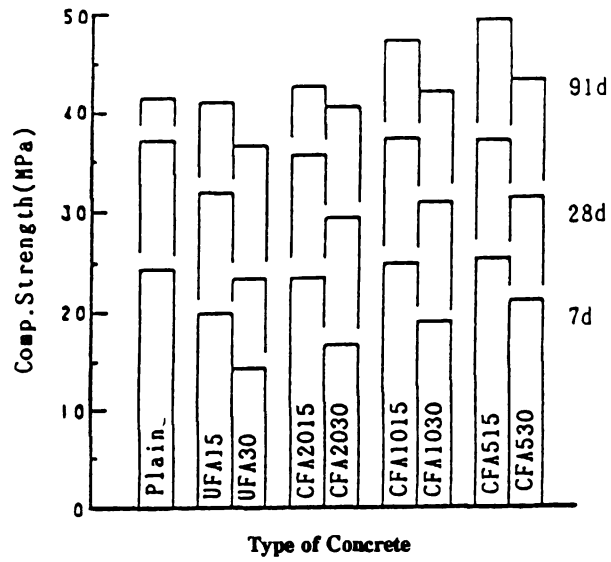


Figure 3.4a. Results of compressive strength [117] .

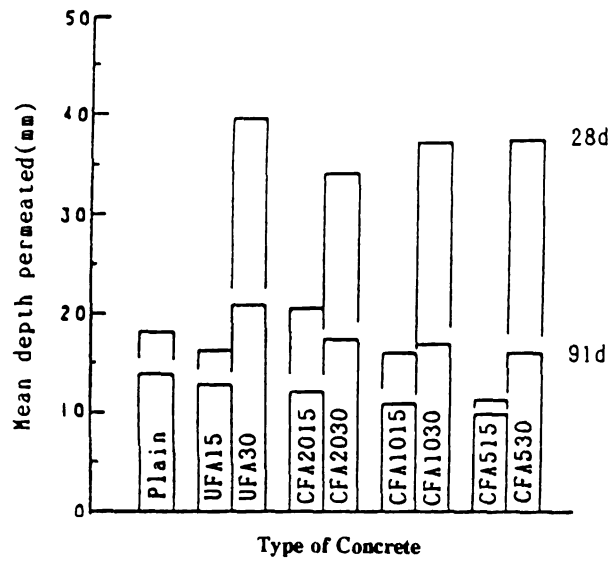
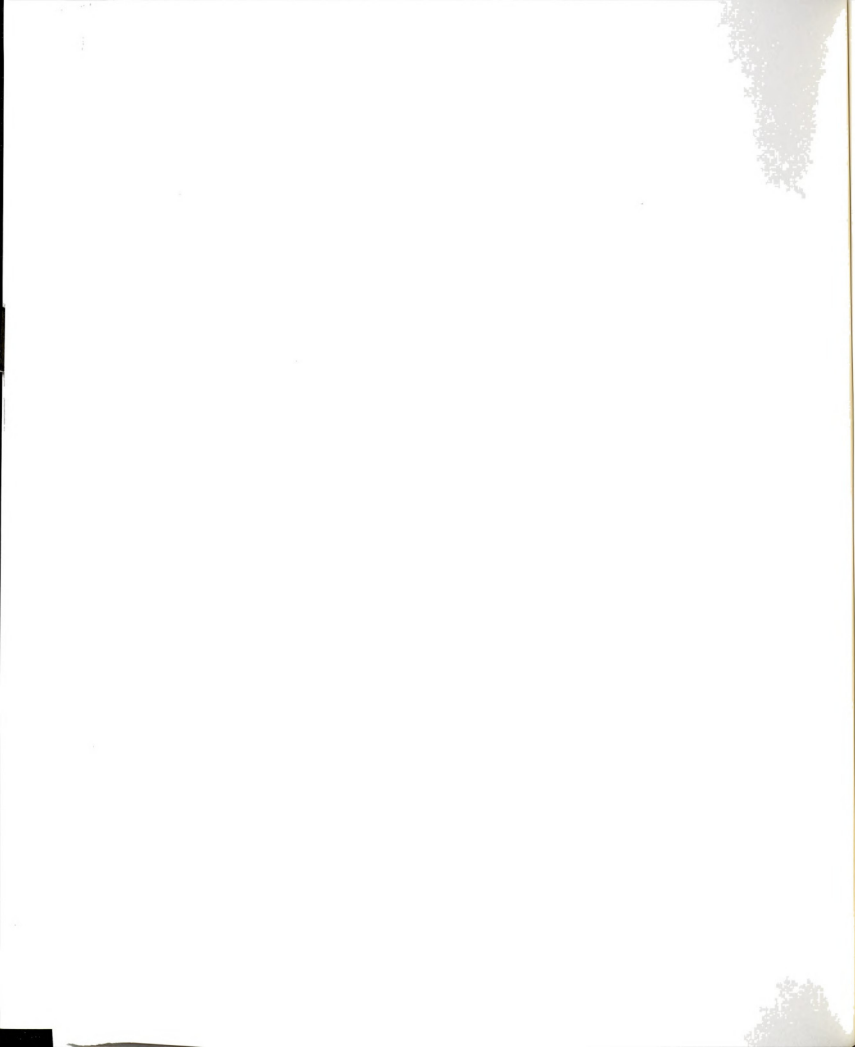


Figure 3.4b. Results of water permeability [117].

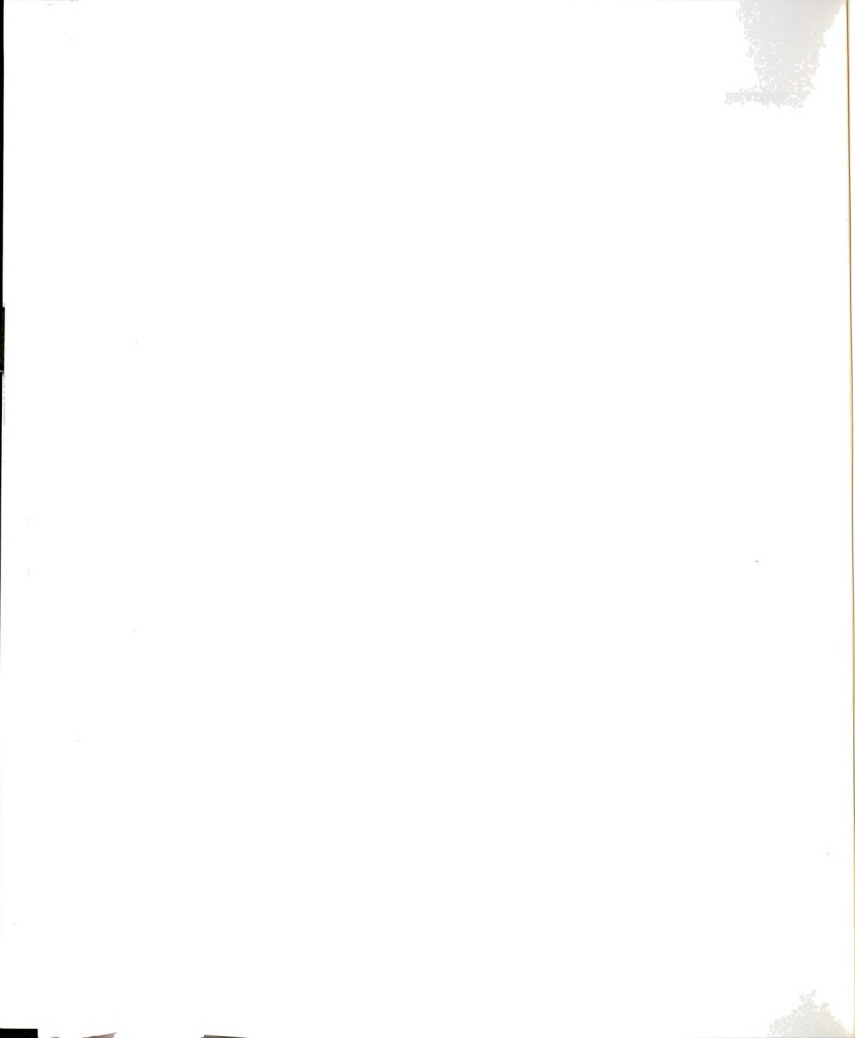


reviewing the work of other researchers on the use of fly ash concrete [120,121,122,123,124,125], concluded that the primary effect of fly ash was on air entraining agent demand, rather than air entrainment as such. He observed that fly ash had no apparent ill effects on the air voids in the hardened concrete. When the proper volume of air was entrained, the air void characteristics generally met the accepted criteria. Perenchio and Klieger [97] experimented with six types of IP cements and found that the air entraining agent requirements were 15 to 210 percent higher for all the cases of Type IP cement than for comparable Type I cements.

Brown et al. [126] found that when the blended cements are tested according to the ASTM C 666-73 procedure, inferior frost resistance was observed. This was attributed to the initiation of a test after a short curing period which does not make proper allowance for the generally lower rate of strength development of the blended cements. When freeze-thaw studies were initiated after longer curing periods and the blended cements had developed equivalent or superior strengths to that of normal portland cements, superior frost resistance was observed for blended cements.

Sivasundaram et al. [127] conducted freezing and thawing tests on two types of low calcium fly ashes, which were properly air-entrained and moist cured for 14, 21, and 28 days. These showed no significant distress and had a durability factor of 99 after 300 cycles, although considerable scaling was observed.

In summary, there are two major types of fly ashes, class F (low calcium, high carbon) and C (high calcium, low carbon), available as waste by-products, are commonly used in concrete. The physical and chemical characteristics depending on type and amount of fly ash affect the workability, strength development, and permeability of

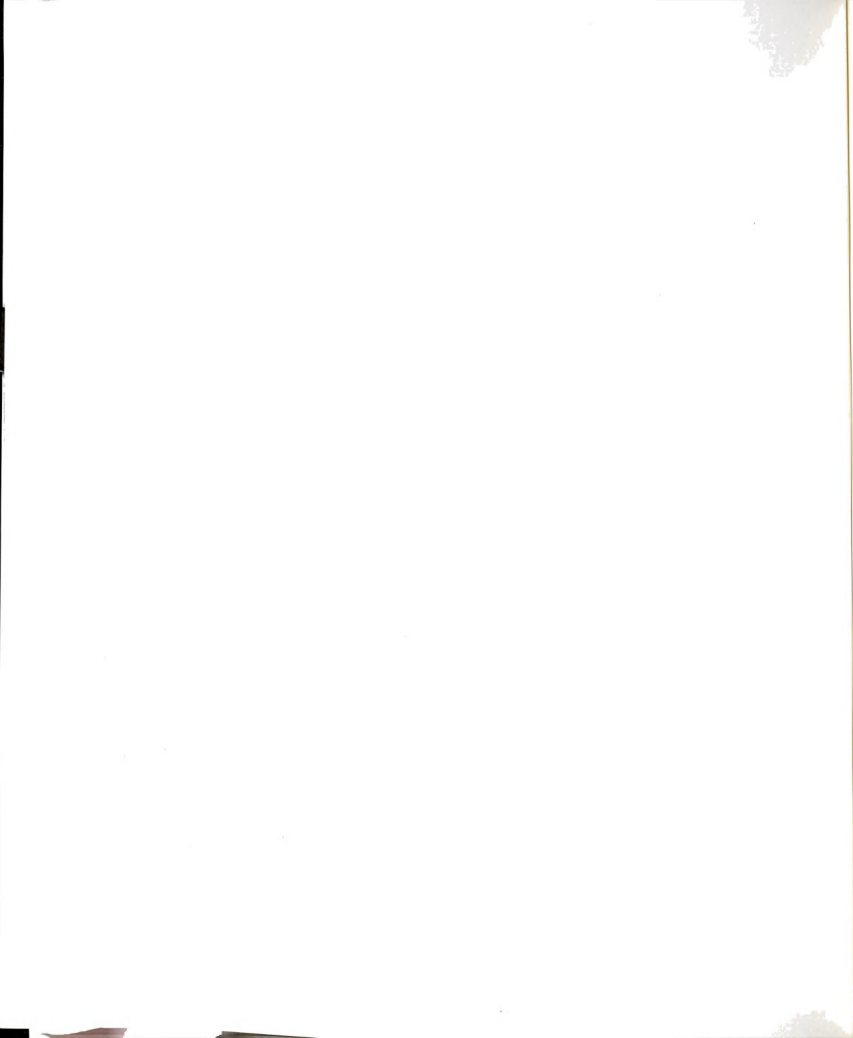


concrete differently especially with respect to frost resistance. This becomes more complex in the presence of water-reducing admixtures. Spacing factors are observed that are higher than the recommended values although durability may still be excellent if strength is allowed to develop. However, many fly ash concretes exhibit severe scaling.

3.3.3 Slag

General

The history of the use of ground, granulated blast furnace slag as a cementitious material dates back to 1774 when it was used in combination with slaked lime [17]. Later Pasow introduced the process of air granulation, which played a key role in the development of iron blast furnace slag as a hydraulic binder [128]. The United States began the production of granulated blast-furnace slag in 1905, whereas Germany started the commercial production of slag-lime cements in 1892, and France used it for the Paris underground Metro System in 1889 [128,129]. The separate grinding of blast-furnace slag and its use as a cementitious material since the 1950's has been an accepted method in Australia, Canada, Japan, United Kingdom and many other countries. It has distinct advantages: (1) each material (i.e., portland cement and slag), can be ground to its own optimum fineness; and (2) the proportions of the two can be adjusted to particular project requirements [130].



Slag-Definition

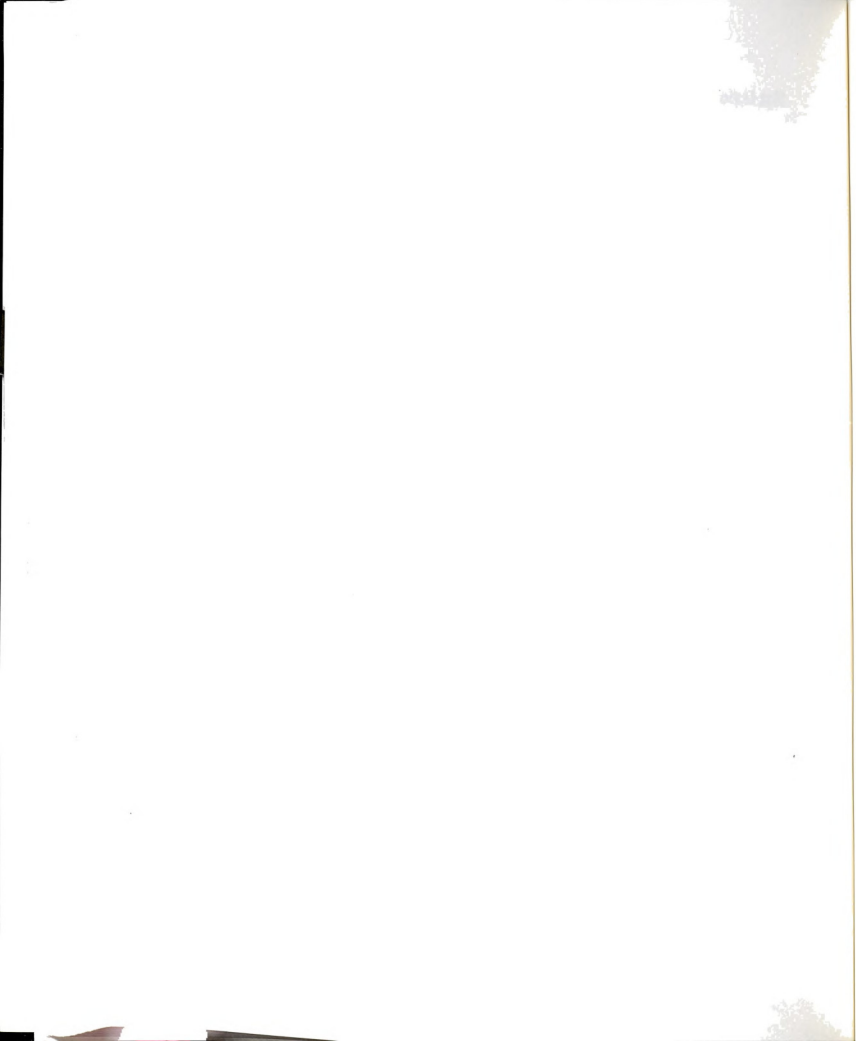
Blast-furnace slag is defined [24,130] as "The nonmetallic product, consisting essentially of silicates and aluminosilicates of calcium and of other bases, that is developed in a molten condition simultaneously with iron in a blast furnace." Granulated blast-furnace slag is "The glassy granular material formed when molten blast-furnace slag is rapidly chilled, as by immersion in water."

ASTM C 989 [131], the "Standard Specification for Ground Iron Blast-Furnace Slag", was first adopted in 1982. Canadian Standards Association A 363 [132], "Cementitious Hydraulic Slag," and CSA A 23.5 [133], "Supplemental Cementing Materials and Their Use in Concrete," differentiate between GGBF slags that react hydraulically with water and those that require an activator to develop their cementitious properties quickly [130]. ASTM C 595 [134] covers blended hydraulic cements, and divides the blended cements into three categories: (1) slag-modified portland cement (Type I [SM]), in which GGBF slag is less than 25 percent of the total weight; (2) portland blast furnace slag cement (Type IS), in which GGBF slag is 25 to 70 percent of the total weight; and (3) slag cement (Type S), in which GGBF slag comprises 70 percent or more of the total weight.

ASTM C 989 [131] classifies slag in three grades (120, 100, and 80) based on the slag-activity index (SAI), which is influenced by the type of the cement used and defined as follows:

$$\text{SAI} = \text{slag-activity index, (percent)} = (\text{SP/P} \times 100)$$

SP = average compressive strength (psi) of slag-reference cement mortar



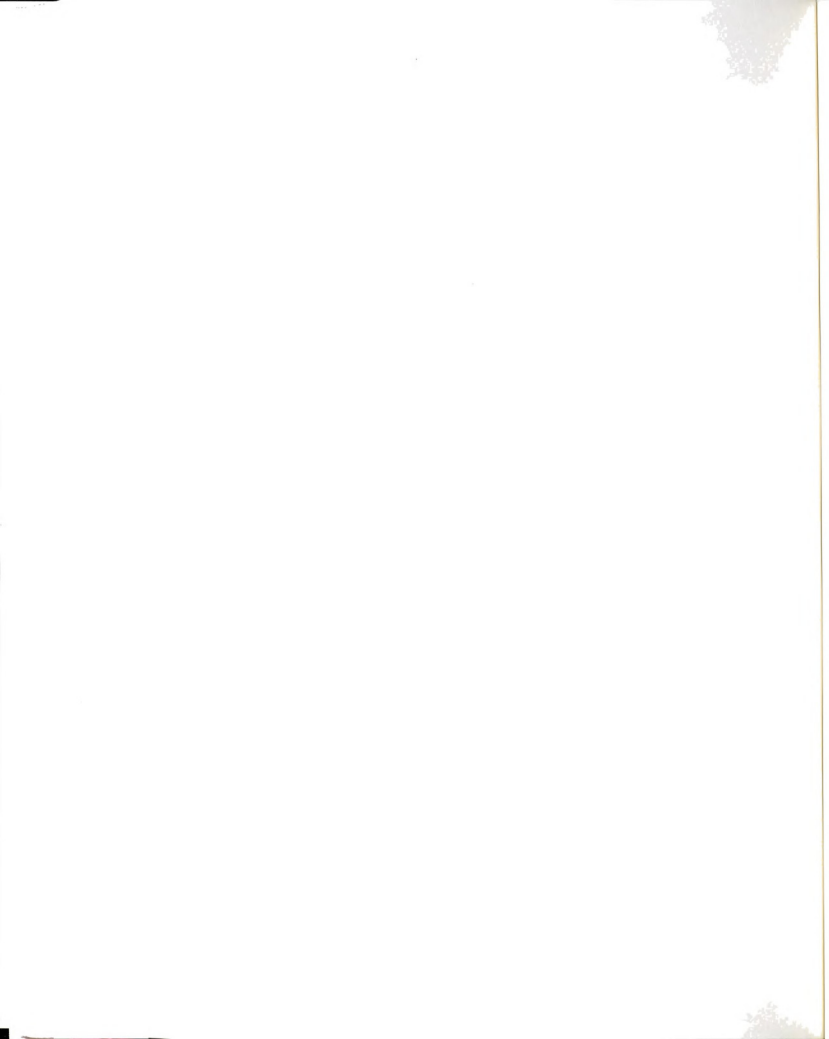
cubes,

P = average compressive strength of reference cement mortar cubes, (psi)

Prior Research

GGBF slag is usually used in proportions of 25 to 70 percent by mass of the total cementitious material [130]. In South Africa, it is generally used as a 50 percent replacement of cement due to convenience [135]. The requirement of water for a given slump is generally three to five percent lower than that of concrete made without GGBF slag [136] because the use of ground blast-furnace slag is reported to produce increased slump [137], and improved workability and placability [136]. Better particle distribution and higher fluidity of the pastes and mortars is reported both with and without water-reducers [136]. An increase in the setting time is observed at normal temperatures of placement and curing [21]; however, at lower temperatures, significant retardation can be experienced, which may warrant the use of accelerators.

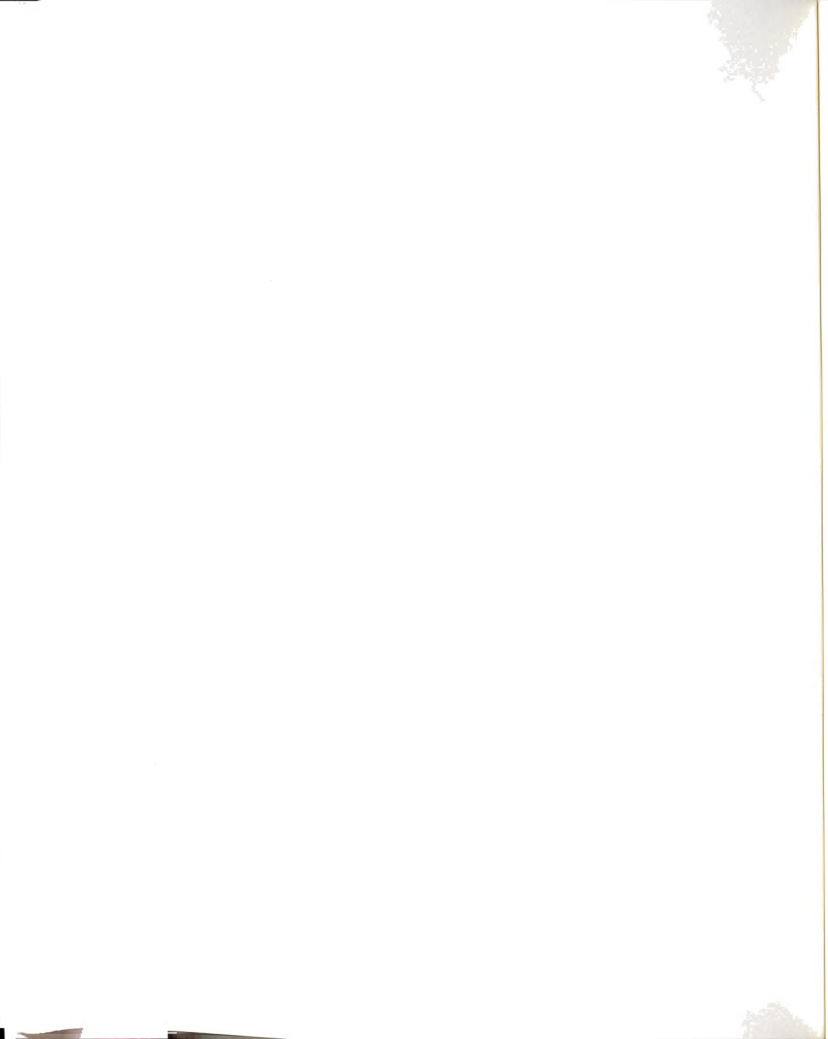
The performance of slag is affected by water-cementitious material ratio, physical and chemical characteristics of the portland cement, and curing conditions. Hagan and Meusel [16] found concrete with 50 percent slag and proper air entrainment to be frost-resistant although measurable differences in weight were observed. The effect of chemical admixtures on the properties of GGBF slags is generally reported to be similar to that of PCC. However, small increases of the required dosages of air entraining admixtures have been observed [130]. The required amount of the water reducing admixtures to produce flowing concrete is usually 25 percent less than for normal [136]. Reductions



in strengths have been reported with higher slag contents [16,138]. The strength of GGBF slag concrete is dependent on the slag activity index and the amount of slag used in the mix. The use of Grade 120 GGBF slag imparts reduced strength at early ages (one to three days) and increased strengths after seven days [16]. Results illustrating this are shown in figure 3.5. Higher strength gains for Grade 120 GGBF slag and 50 percent blends have been noted (versus PCC) for higher water-cement ratios. Results reported by Meusal and Rose [137] are shown in figure 3.6. The greatest 28 day strengths are found with blends of 40 to 50 percent slag when highly active GGBF slags are used [16,18,137].

The permeability of mature concrete containing GGBF slag is greatly reduced when compared with PCC. According to Baker [139], and Roy and Idorn [140] it was found that the pore structure of the cementitious matrix changed through the reaction of GGBF slag with calcium hydroxide and alkalis released during the portland cement hydration. Pores containing calcium hydroxide are normally filled with calcium silicate hydrate [140,141,142]. A reduction in pore sizes has been noted in concretes with GGBF slags prior to 28 day after mixing.

Studies on the frost resistance of concrete containing varying levels of GGBF slag generally indicate that their resistance to freezing and thawing in water is essentially the same as for PCC [17,18,19]. As in the case of normal concretes, proper air entrainment and air void characteristics are also essential for the production of a frost-resistant concrete. Hogan and Meusel [16] reported that properly air-entrained concretes containing 50 percent GGBF slag were found resistant to frost action even though a measurable difference in weight loss was observed. Malhotra [138] found similar results



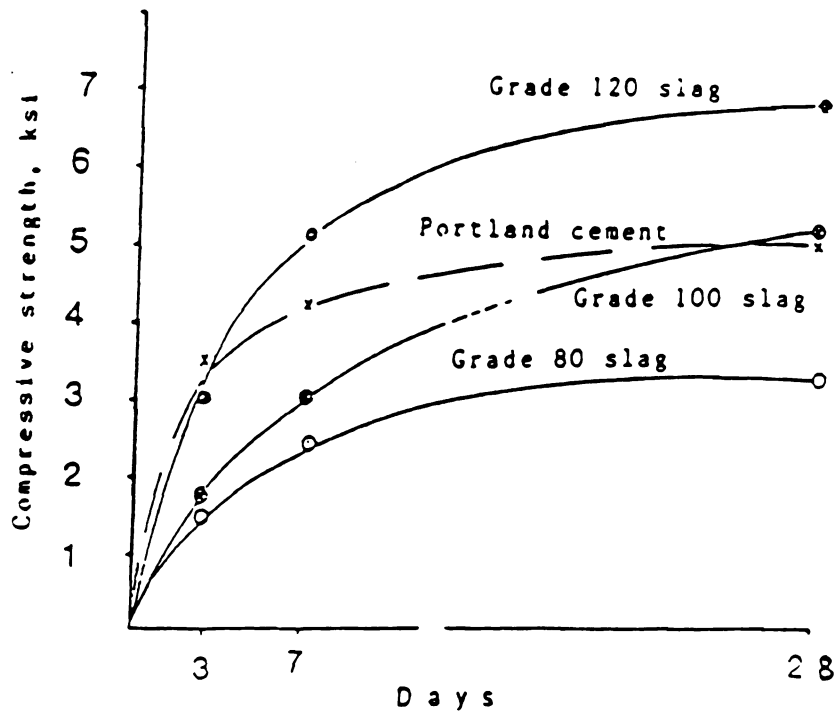
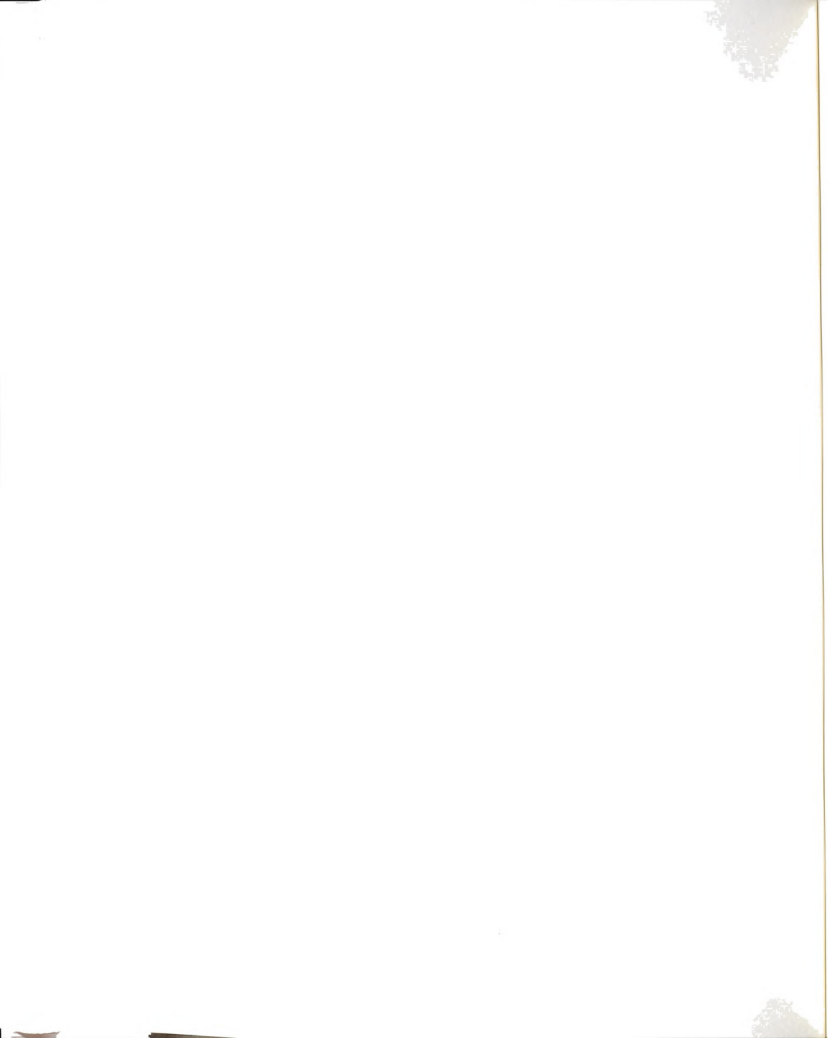


Figure 3.5. Strength relationship of mortar containing typical GGBF slag meeting ASTM C 989 requirements, compared to portland cement mortar [16].



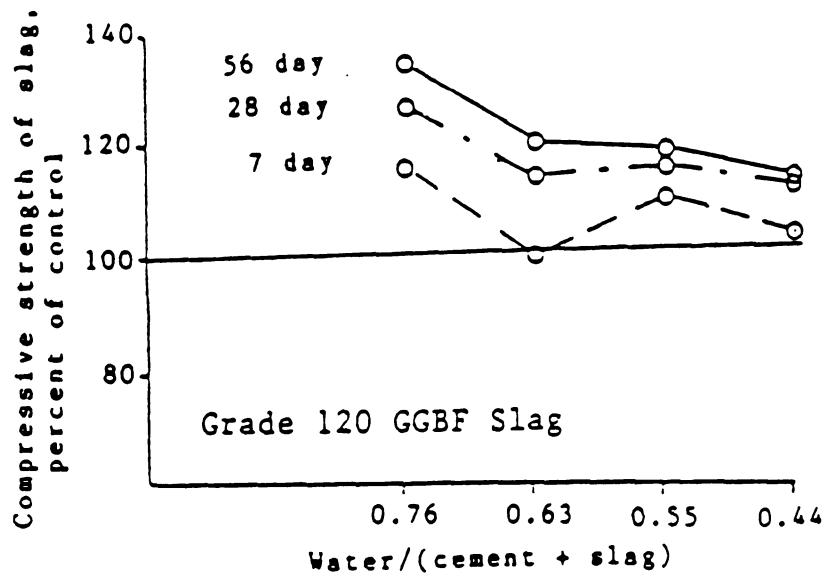
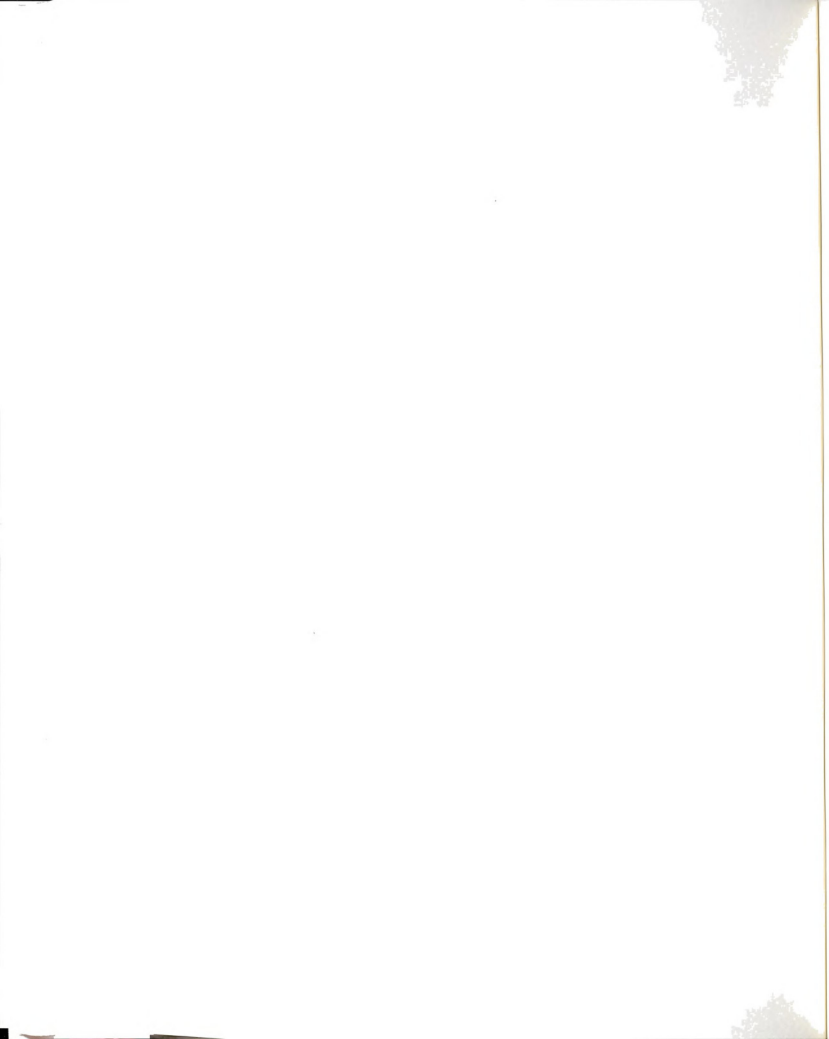


Figure 3.6. Effect of water-cementitious material ratio on compressive strength of GGBF slag levels, expressed as a percentage of mixtures made with portland cement [137].



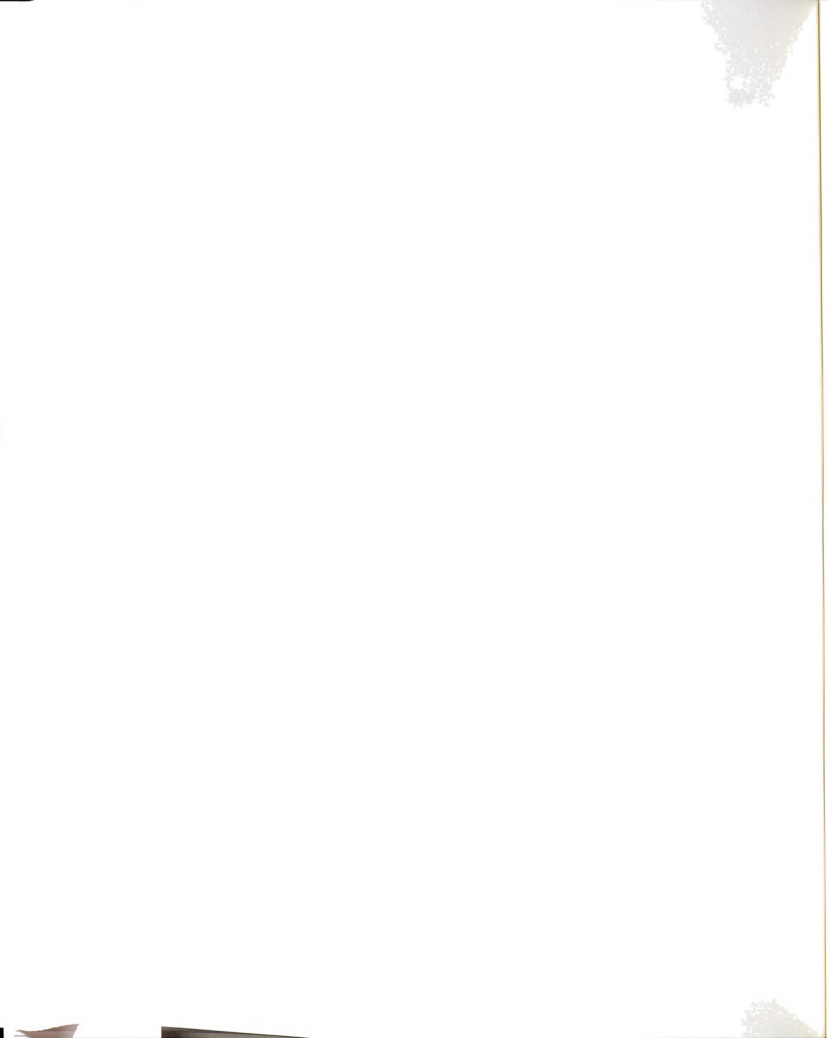
with different percentages of GGBF slags except that he did not characterize the weight loss to be significant, possibly due to comparing concrete with unequal strengths. Nagataki et al. [141] conducted detailed studies on 31 samples of GGBF slags with varying fineness and gypsum (SO_3) content, zero to three percent to access various properties of fresh and hardened concrete. Based on these experimental results, the Japanese Society of Civil Engineers (JSCE) standard for "Ground Granulated Blast-Furnace Slag for Concrete" and the JSCE "Recommendation for Design and Construction of Concrete Containing GGBF Slag" were prepared and published in 1986 and 1988, respectively. They determined that the water requirement was low, whereas the requirement for dosages of air entraining agents increased as the quantity of the slag increased and/or fineness of GGBF slag increased (see figure 3.7). It was also concluded that when the slag cement concrete is properly air-entrained and sufficiently cured, excellent freeze-thaw resistance can be expected, (see figure 3.8).

3.3.4. Silica Fume

General

Silica fume is a by-product resulting from the reduction of high purity quartz with coal in electronic arc furnaces in the production of silicon and ferrosilicon alloys.

Silica fume is also referred to in the literature as "condensed silica fume" (CSF), "microsilica", "ferrosilicon dust", "arc furnace silica", "silica flue dust", "amorphous silica" or "volatilized silica", and is a comparatively new pozzolan. A typical silica fume



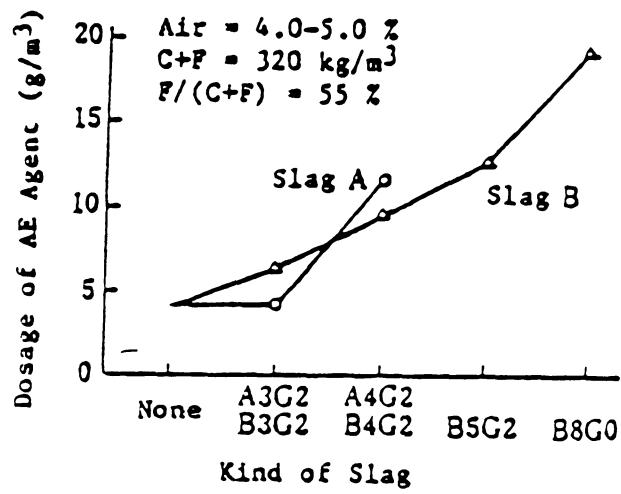
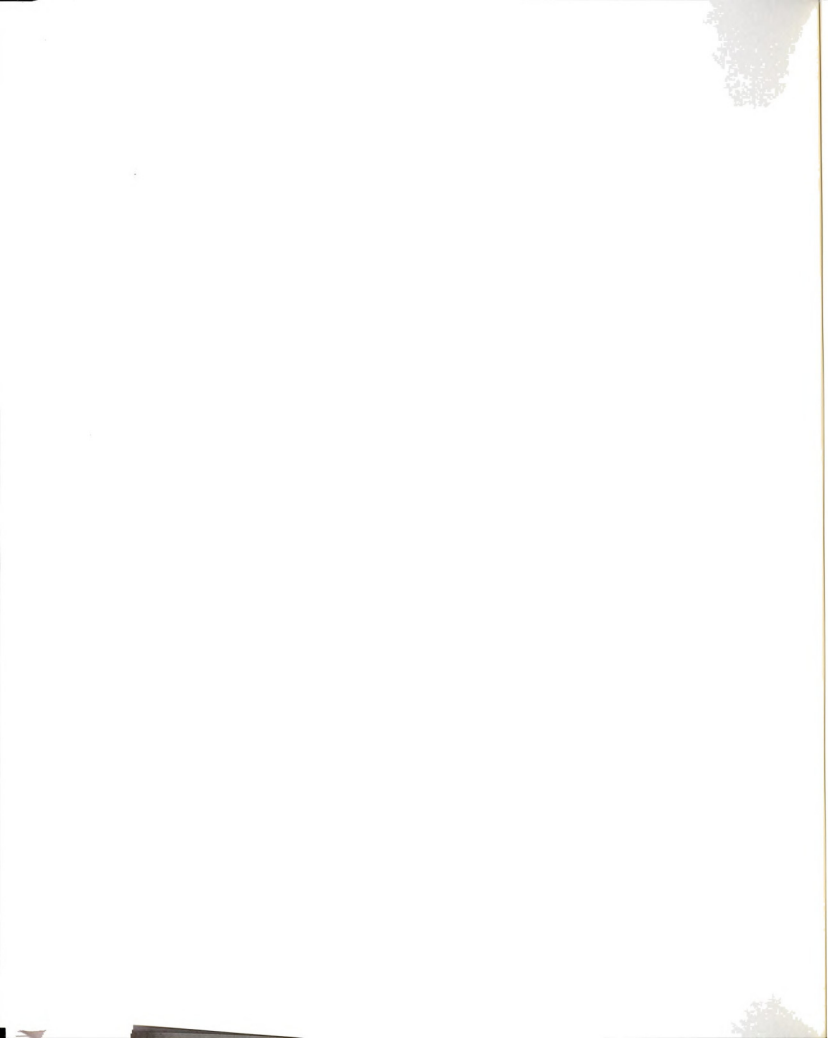


Figure 3.7. Example of dosage of air-entraining agent affected by slag replacement [138].



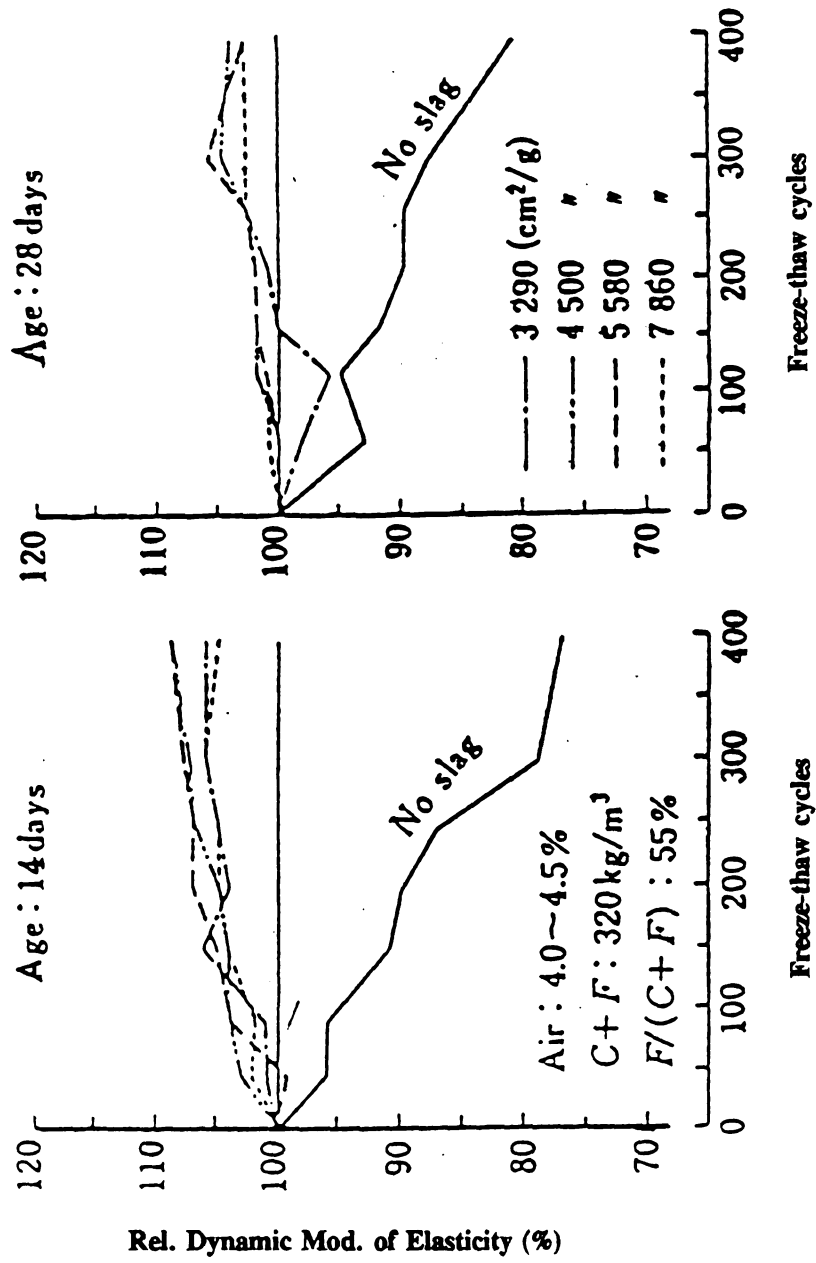
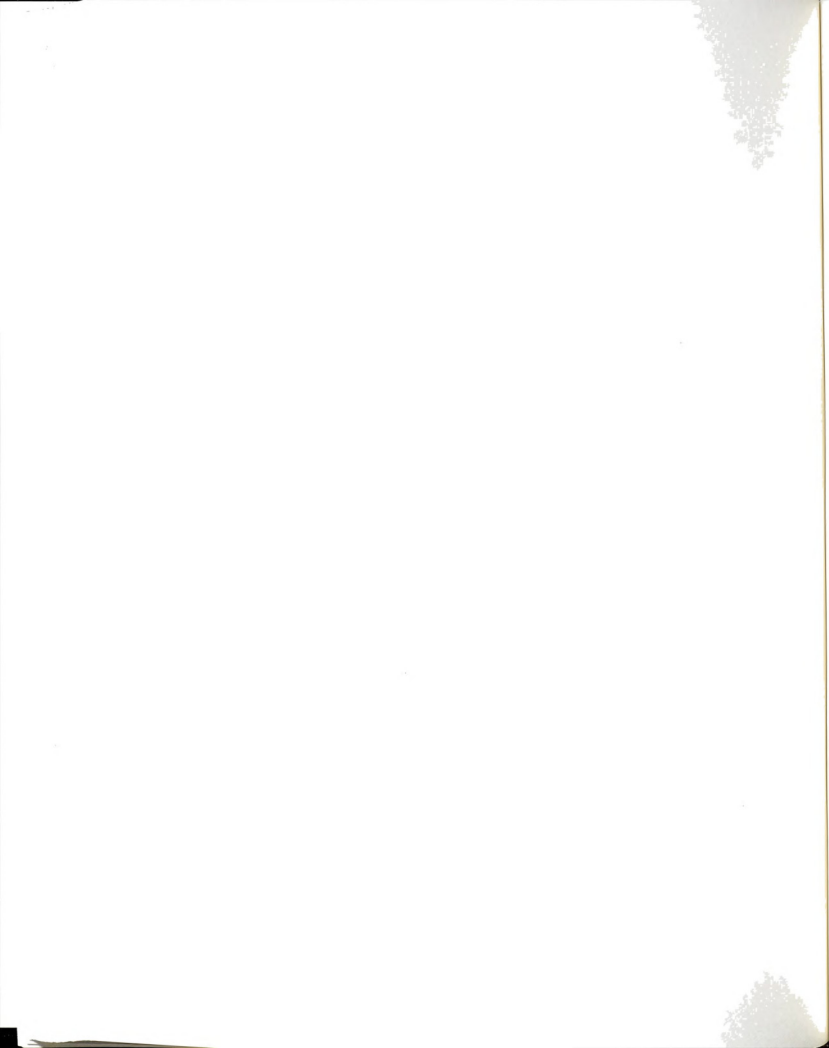


Figure 3.8. Freeze-thaw resistance of slag concrete [143].



has a specific gravity of 2.2, as compared to 3.1 for normal portland cement. It has a mean diameter in the range of 0.1 to 0.2 μm , which is approximately 100 times smaller than the average cement particle [145]. The extreme fineness and high silica content make it a highly pozzolanic material. It has an SiO_2 content in the range of 85-98%, a spherical particle shape with a number of primary agglomerates, and amorphous particles.

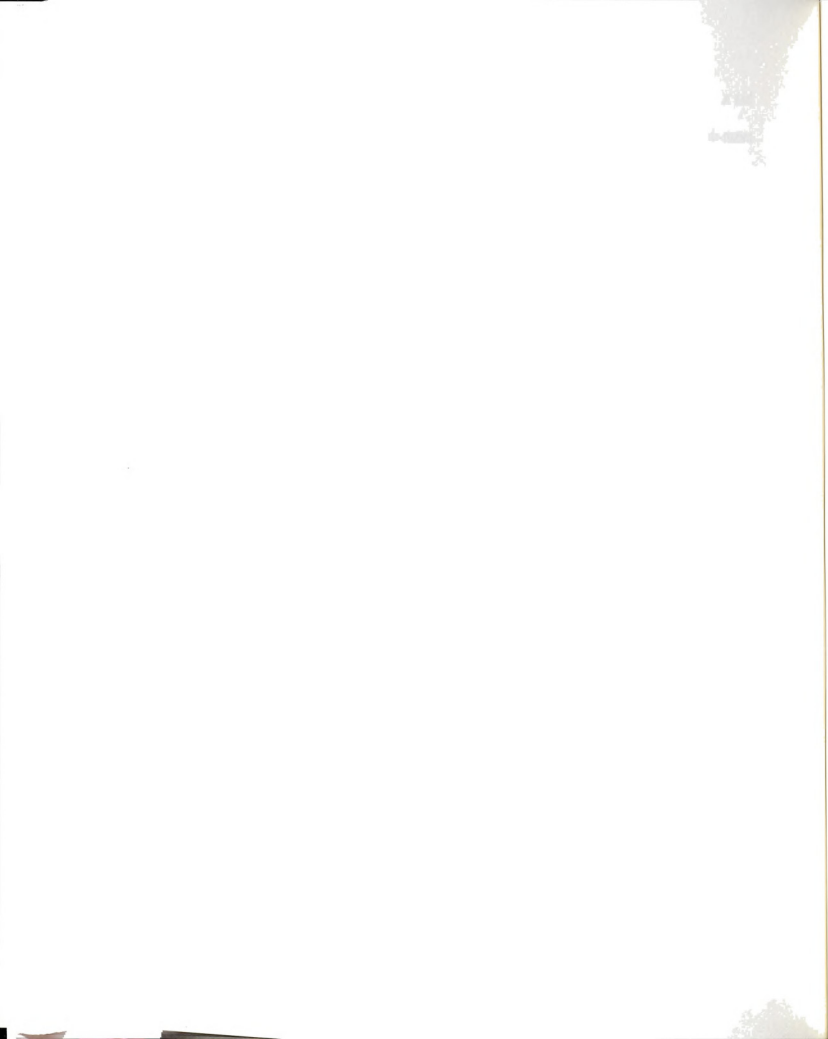
Although data from Russia and East European countries are not available, table 3.5 [20] shows the estimated production of CSF in 1984 from some major producers.

Table 3.5. Estimated production and use of CSF in 1984 [20].

Country	Total quantity produced: Mt.	Utilized in cement and concrete products: Mt.
Norway	140	40
United States	100	2
France	60	0
Australia	60	20
South Africa	43	0
Japan	25	0
West Germany	25	0
Canada	23	11
Sweden	14	5

Brazil, China and some other countries have silicon metal producing plants, but much of the fume is not filtered and not available to the concrete industry.

Most of the investigations use the term CSF from the production of silicon metal, or ferrosilicon alloy containing more than 75% silicon. The first tests of the silica fume in concrete were made in the early 1950s at the Norwegian Institute of Technology [20]. At approximately at the same time, CSF was added to a large number of additives used



for various purposes in a tunnel segment in the Oslo alum shale region. The first documented use of CSF in structural concrete was at the Fiskaa (Norway) smelting plant in 1971. The first use outside the Scandinavian countries, was near the end of the 1970s. In Canada the practical use of CSF began in ready mix plants in 1981. In the United States of America, its use was also reported in early 1980s. Recently CSF has received a tremendous amount of attention especially in the production of high strength concrete or for concrete with special durability problems.

Methods of Use

CSF is mainly used in two different ways: as a cement replacement (mainly for economic and environmental reasons) and as an additive to improve the properties of the concrete. CSF is currently available in uncompacted, pelletized/densified, and water slurry forms. The relative advantages/disadvantages of each of these forms are shown in table 3.4 [144]. General field experience and laboratory tests have shown very little difference in the properties of hardened concrete containing silica fume with different characteristics and or in different forms. This is in sharp contrast to experience with fly ashes [20].

Pozzolanic Reactivity and Filler Effects

Silica fume is a highly pozzolanic material and an effective filler. These properties have a combined effect on the performance of the concrete.

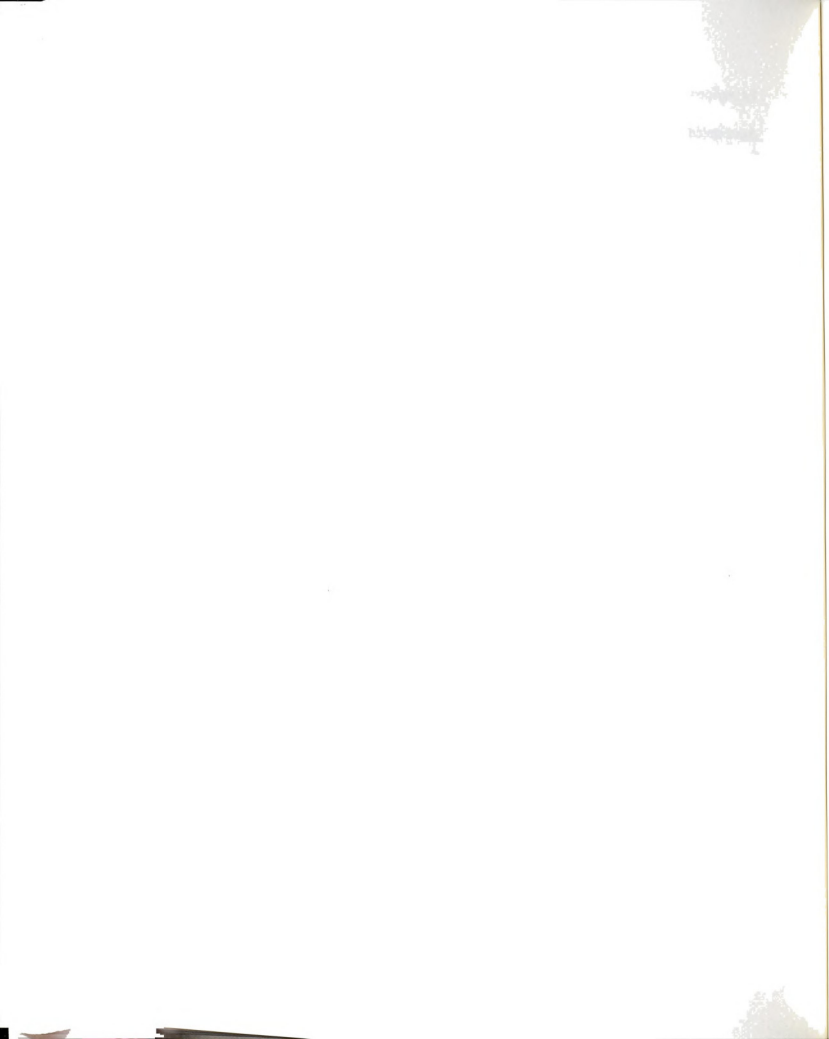
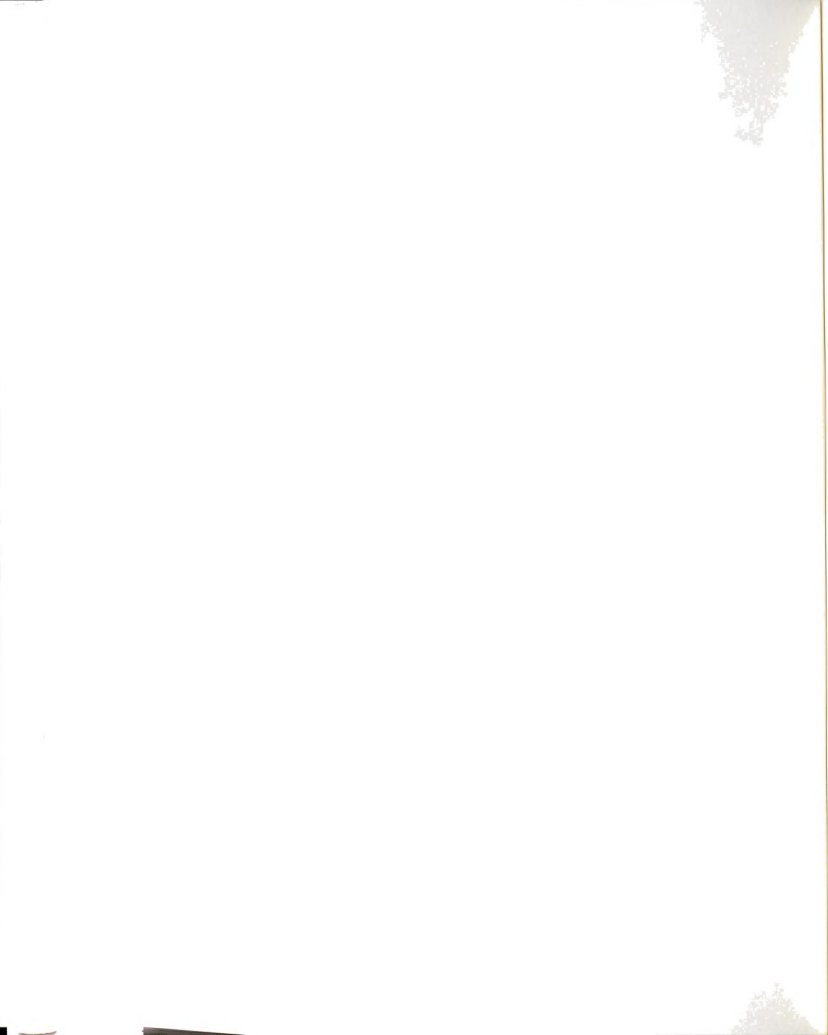


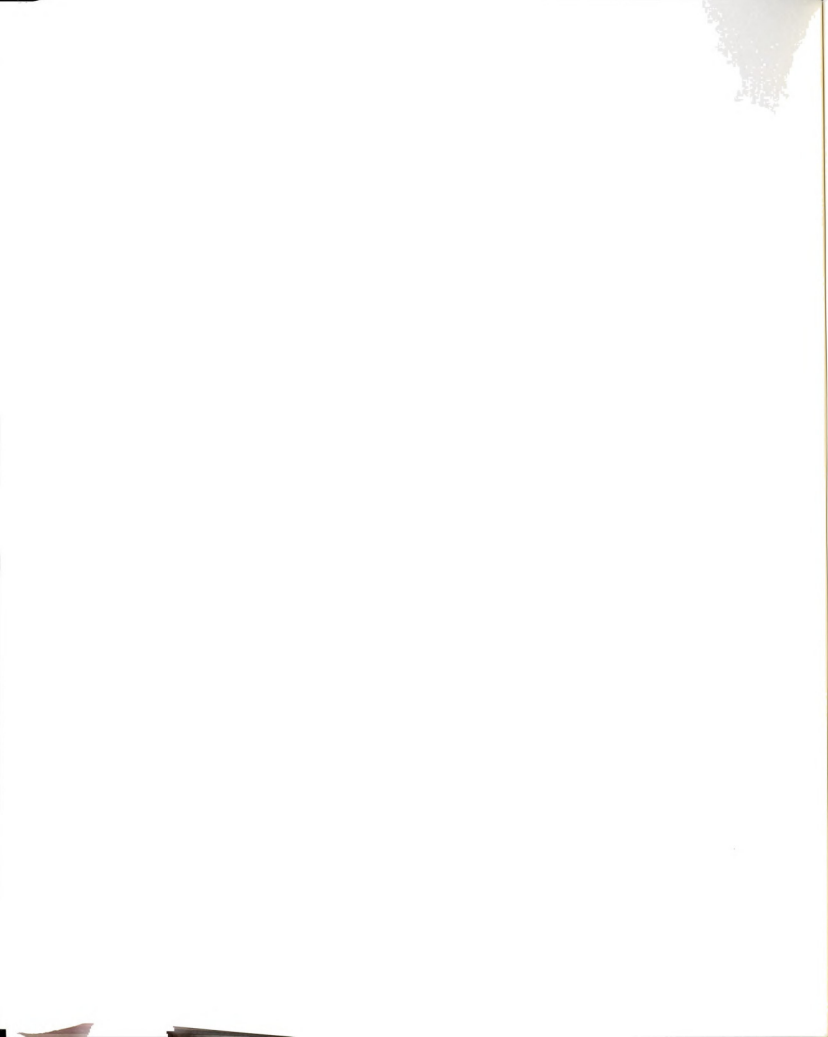
Table 3.4. Performance characteristics of different forms of silica fume [144].

Silica Fume Form	Positive Characteristics	Negative Characteristics
Uncompacted	-Highest pozzolanic activity, technical performance, and efficiency. -Temperature protection not required for transport, storage, or batching.	-Dusty and moisture sensitive -High transportation cost -Limited pneumatic transport length.
Pelletized/ densified	-lowest transportation cost -lowest storage and transport volume requirement. -Decreased dust	-Lowest pozzolanic reactivity performance and efficiency -Moisture sensitive
Water slurry	-No dust -Simplest transport and batching system	-Inaccuracy in silica dosage due to sedimentation -Difficult to control concrete water content -Storage and dispensing tanks must be constantly agitated to keep silica fume in suspension -Must control pH to prevent premature gel formation -Temperature control of transport, storage, and batching to prevent freezing



Its pozzolanic reactivity in cement paste is demonstrated by measuring the amount of calcium hydroxide at different times in the pastes with varying amount of CSF. The results of thermal gravimetric analysis (TGA) and X-ray diffraction methods generally indicate high pozzolanic reactivity [146,147,148,149,150]. However, some studies also indicate medium [151] and slow [152,153] reactivity. Figure 3.9 [148] shows the calcium hydroxide contents (as measured by TGA) of mature pastes with varying amounts of CSF. Telford [20] states that if this curve can be extrapolated, then calcium hydroxide can be eliminated, theoretically at a 24% replacement level. This theoretical replacement percentage varies in the literature, depending on the composition of the cement and the method used in determining the content of the calcium hydroxide.

It has been generally observed that the presence of CSF in cement pastes has an accelerating effect on the hydration process. Diamond [154] showed that, after two days at a 12% replacement level of CSF, the calcium hydroxide content in the mix was higher than the control, but later decreased. This may have been due to the calcium hydroxide being consumed faster by the pozzolanic reaction than it was produced by cement hydration. Wu and Young [154] studied the reaction of CSF with tricalcium silicate and calcium hydroxide and found an accelerating effect of CSF on the hydration of C_3S . Halse et al. [156] concluded from similar work that C_3S hydration was "enhanced" rather than accelerated. Cheng-yi and Feldman [149] found that CSF and ground quartz, when used as additives in varying amounts, accelerated the cement hydration in the first 14 days, but later on, a 30% CSF replacement eliminated the calcium hydroxide content. Grutzeck et al. [157,158] found the formation of silica-gel on the surface of silica fume mixes shortly after mixing the silica fume in a calcium



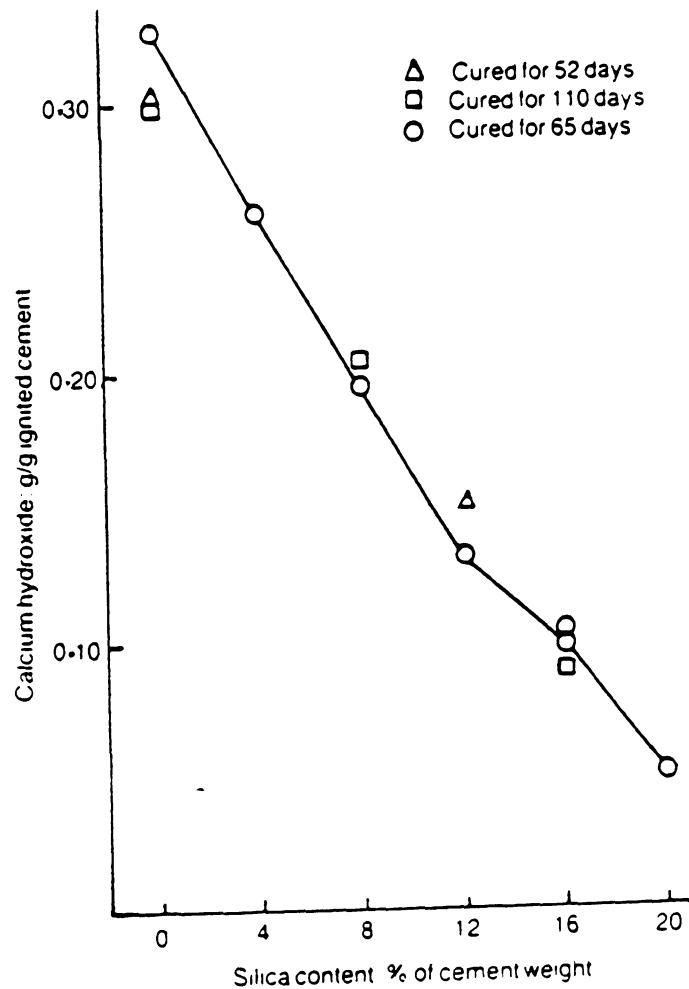
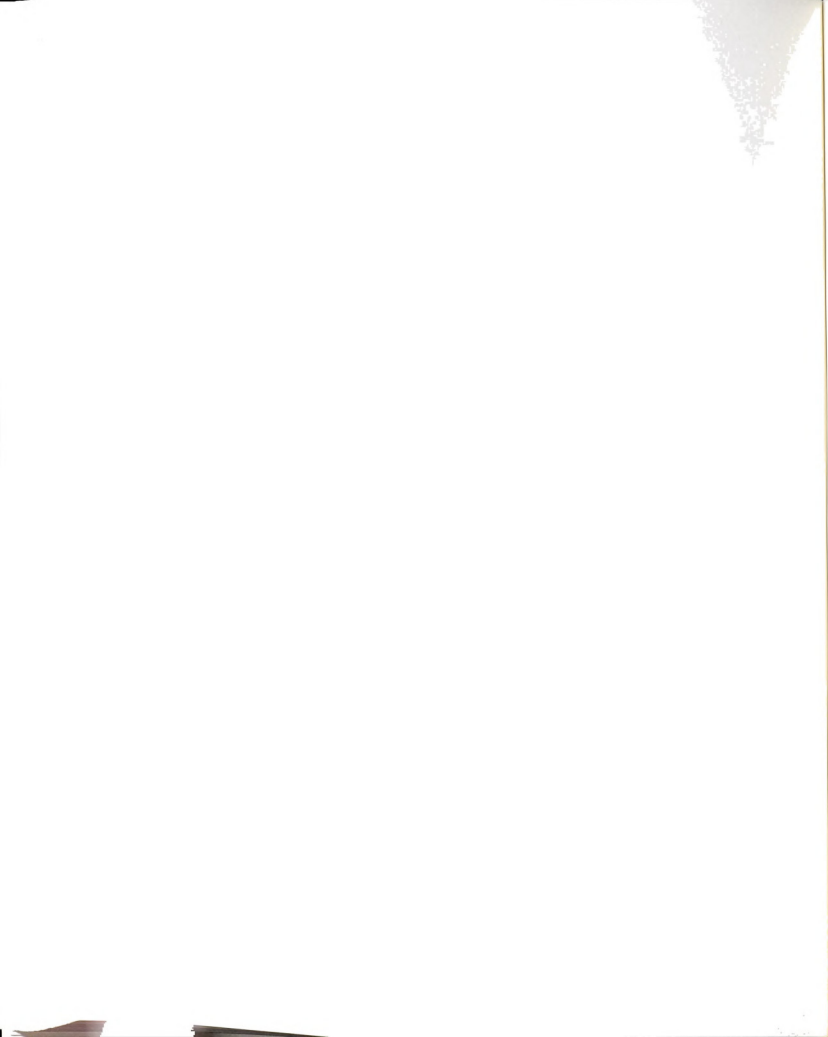


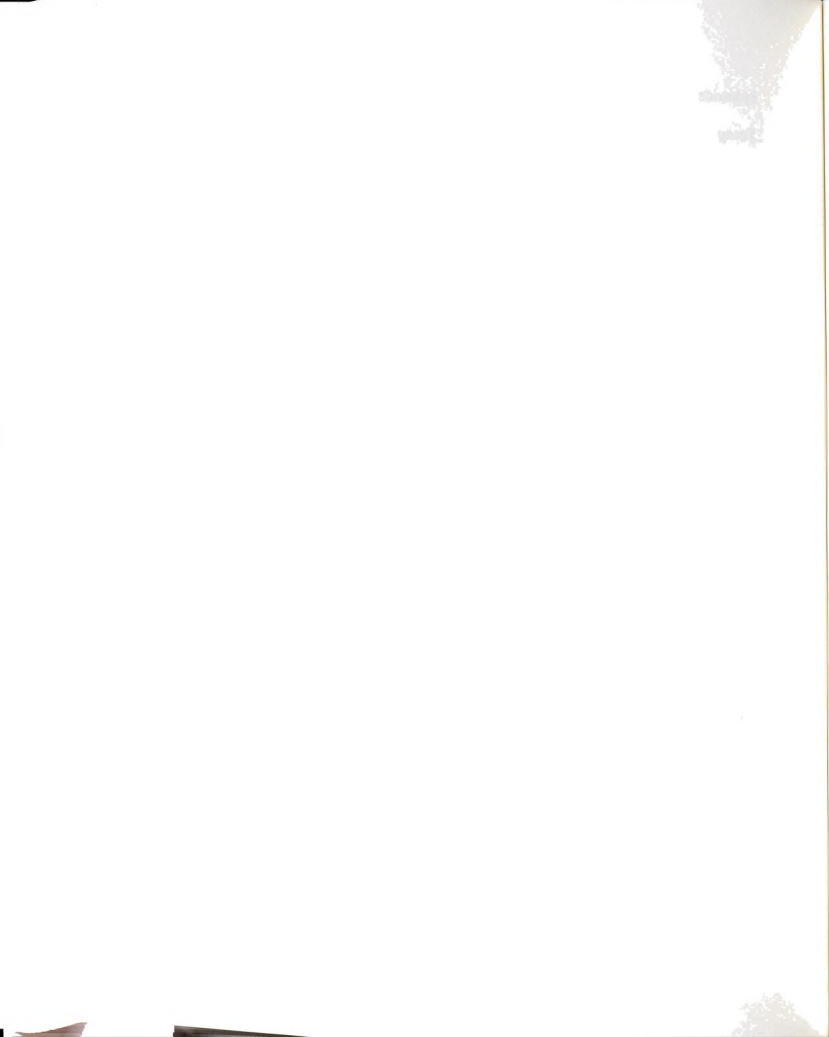
Figure 3.9. Calcium hydroxide contents (measured by thermal gravimetric analysis, TGA) of mature pastes made with white portland cement. The W/C is constant (0.60) and various amounts of CSF added [148].



hydroxide solution. The gel combined with calcium hydroxide to form C-S-H. Wu and Young [155] stated that three forms of C-S-H are formed in C_3S -CSF systems: (1) C-S-H formed from direct hydration of C_3S ; (2) C-S-H formed from the reaction of calcium hydroxide and silica fume; and (3) C-S-H formed from the reaction of C-S-H and CSF (with low C/S and high degree of polymerization). The latter is present in mixes containing more CSF than is required to consume all the calcium hydroxide.

Pore Structure

Concretes containing CSF have shown a more dense microstructure than plain portland cement concrete. Regourd [159] says that CSF concrete appears "very dense and amorphous". Diamond [160] found that, in contrast to PCC, the C-S-H gel particles in CSF concrete cannot be seen as individual particles but as a massive dense structure, whereas calcium hydroxide appears as a small local crystal. It has also been observed that the dense paste structure is essentially related to the boundary of aggregate in dense CSF (higher dosage) concrete. In this way, the normal porous structure of 40 to 50 μm , rich in calcium hydroxide around the aggregate as in normal concrete, is eliminated. For normal dosages of CSF, the changes in microstructure are less pronounced. Various researchers [148,149,154,161] recorded differences, however, in the amount of bound water in C-S-H and the amount contained in the calcium hydroxide. Thus, the relationship is not yet clear. However, it has been observed, by calorimetry and the development of non-evaporable water content or calcium hydroxide over time, that CSF accelerates the hydration reaction.



Mehta [78] and Manmohan and Mehta [162,163] have shown a relationship between pore structure, permeability, and the durability of concrete. Sellevold and Nilson [164] and Feldman [165] studied the pore structure of cement-silica fume using water adsorption, mercury penetration, and freeze calorimetry and found that increasing the dosage of CSF while holding water-cement ratio constant lead to the refinement of pore structure while the total porosity, measured by water, remained unchanged. This means that less pore space consisted of capillary pores where water could freeze and mercury could penetrate. They concluded from their work that silica fume was about three times more efficient than cement paste in reducing capillary porosity. They also used an inert filler of the same fineness and did not observe the same degree of pore refinement. They determined that much of the pore refinement observed in the CSF concrete was caused by the pozzolanic activity of the CSF. Their results for mercury penetration are shown in figure 3.10 [148]. Feldman [165] also observed that a relatively discontinuous system of fine pores exists in the hydrated cement paste made with CSF. Tr tteberg [166] concluded that CSF was very efficient in subdividing the pores.

Permeability and Porosity

Mehta [78] assumes that concrete permeability decreases rapidly with increasing dosages of CSF because the condensed silica fume is highly pozzolanic when compared to fly ash or slag. He refers to the results of Gj rv [167] and Markestad [168] on the water permeability of concrete in which the cement was varied from 100 to 500 kg/m³. They showed that a lean concrete mixture incorporating 100 kg/m³ cement and 10%

CSF IN CONCRETE

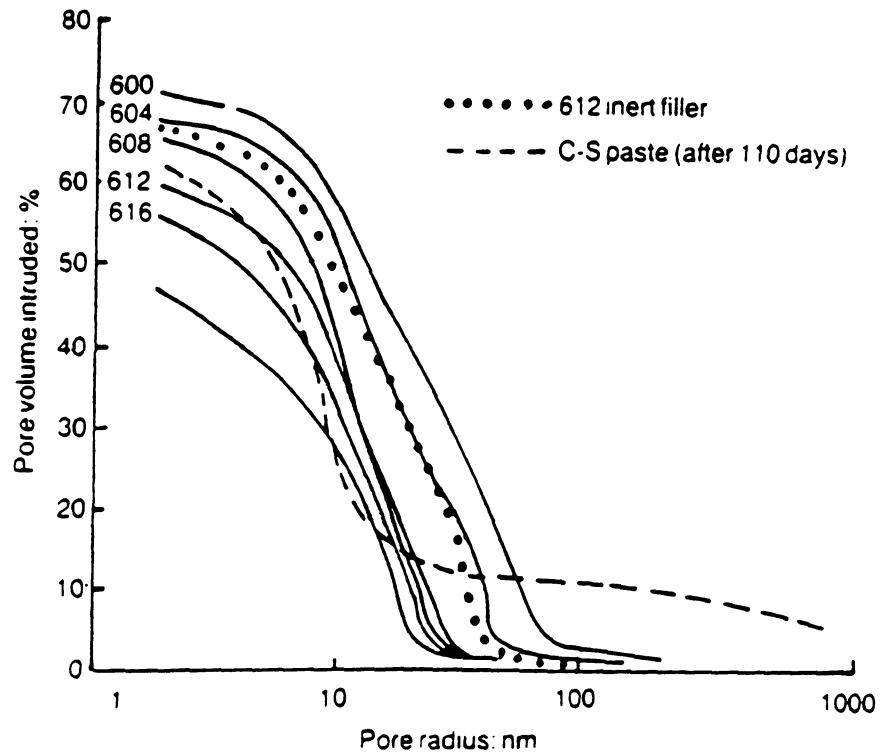
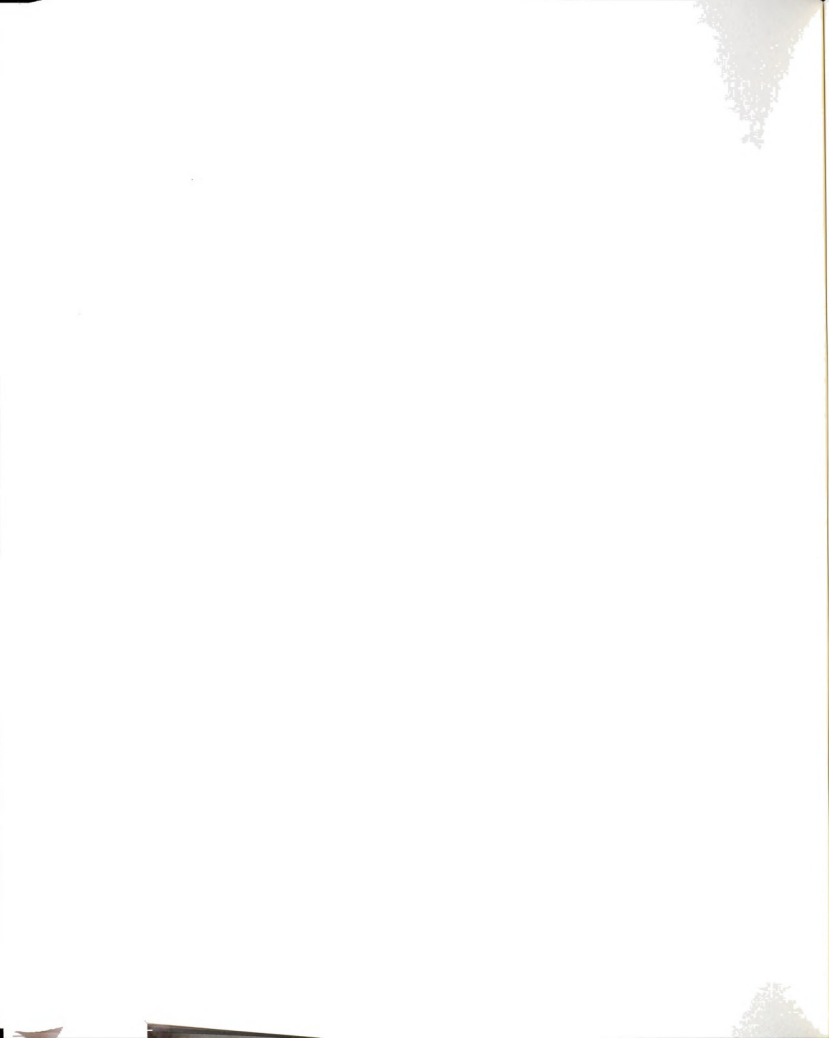


Figure 3.10. Mercury intrusion in mature (65-day-old) white cement pastes (W/C=0.60) [148].

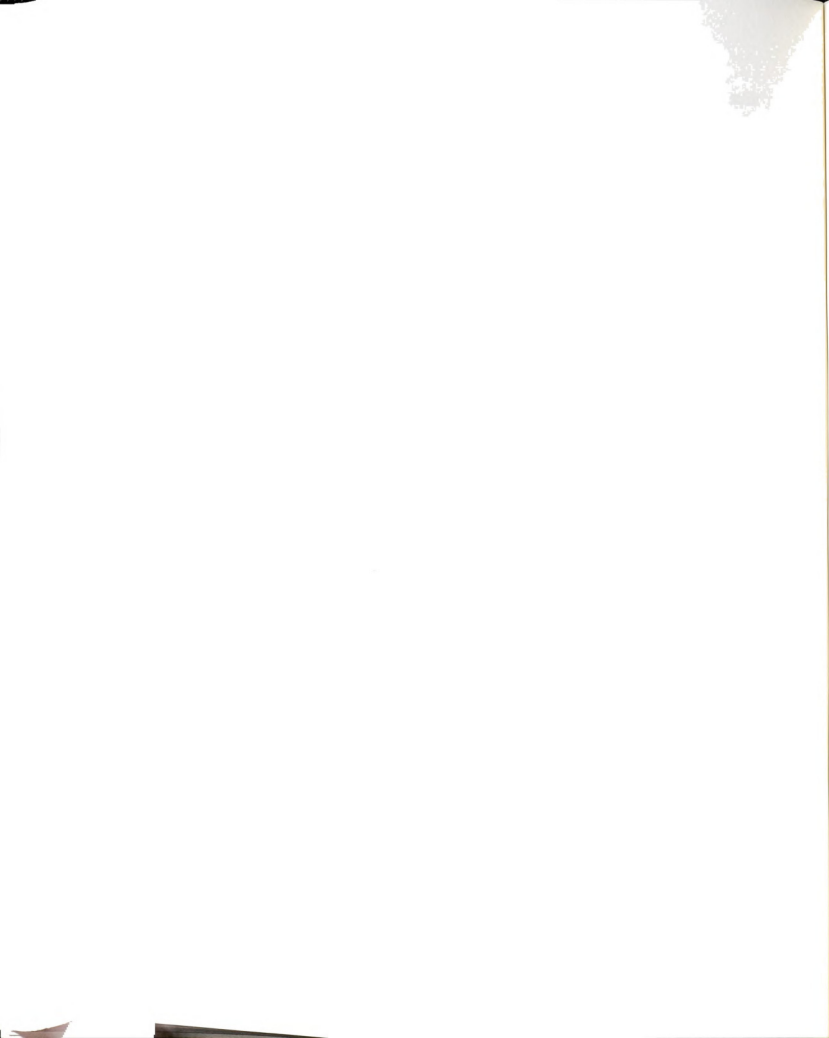
Note: The last two digits of the identification numbers indicate the percentage of CSF added. The inert filler is a fine precipitated calcium carbonate. The C-S paste is a calcium hydroxide-CSF mix with C/S = 1.0.



silica fume had its permeability decreased to about 4×10^{-10} m/s, compared to 1.6×10^{-7} m/s without silica fume. The permeability of concrete with 20% CSF and 100 kg/m³ cement was similar to that of concrete without silica fume and 250 kg/m³ cement. However, at higher cement contents, the effectiveness of CSF in reducing permeability diminished.

Christensen [169], using a method developed by The Technological Institute in Denmark in which the capillary porosity of concrete is estimated by microscopic examination of thin sections of samples from the laboratory and field impregnated with fluorescent epoxy and concluded that CSF is three times as efficient as concrete in reducing capillary porosity. Johansson studied the water permeability of mixes made without water reducers using 0, 10, and 20% silica fume replacement of cement. He found higher strengths for CSF mixes and one-half of the water penetration in 10% silica fume, as compared to plain concrete mix. Twenty percent silica fume concrete showed permeability than 10% CSF concrete, but the effect was not nearly pronounced. Sandvik [170], tested mixes with 0, 5, 10, and 20% replacement of cement by CSF (by weight) for hydraulic conductivity. The mix with 5% CSF produced a reduction in permeability coefficient from 3×10^{-11} to 6×10^{-14} m/s, whereas at higher replacement levels the coefficient was below 10^{-14} m/s. The results are shown in figure 3.11.

Telford [20] concludes from a review of his own work and the work of many other researchers that the combined effect of two factors, the very high pozzolanic reactivity and the filler effect, are responsible for the refinement of pore structure of concrete containing CSF. This refinement of pore structure leads to reduced permeability, which is considered to be the main factor responsible for the influence of silica fume on the mechanical and durability properties of the concrete. Comparing



CSF IN CONCRETE

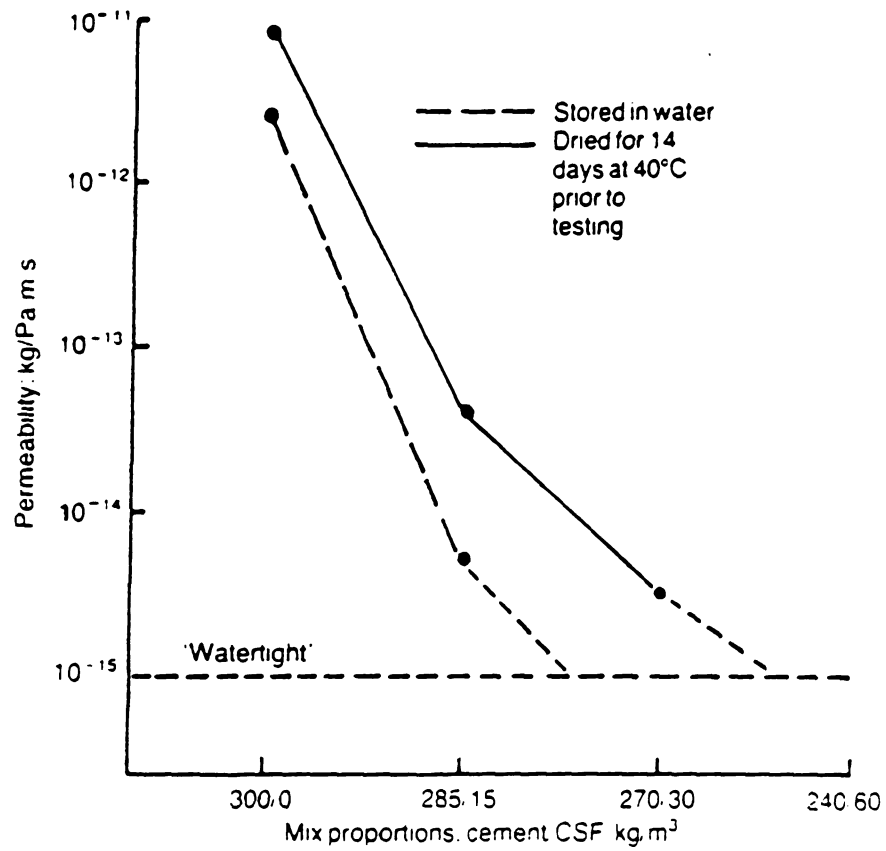
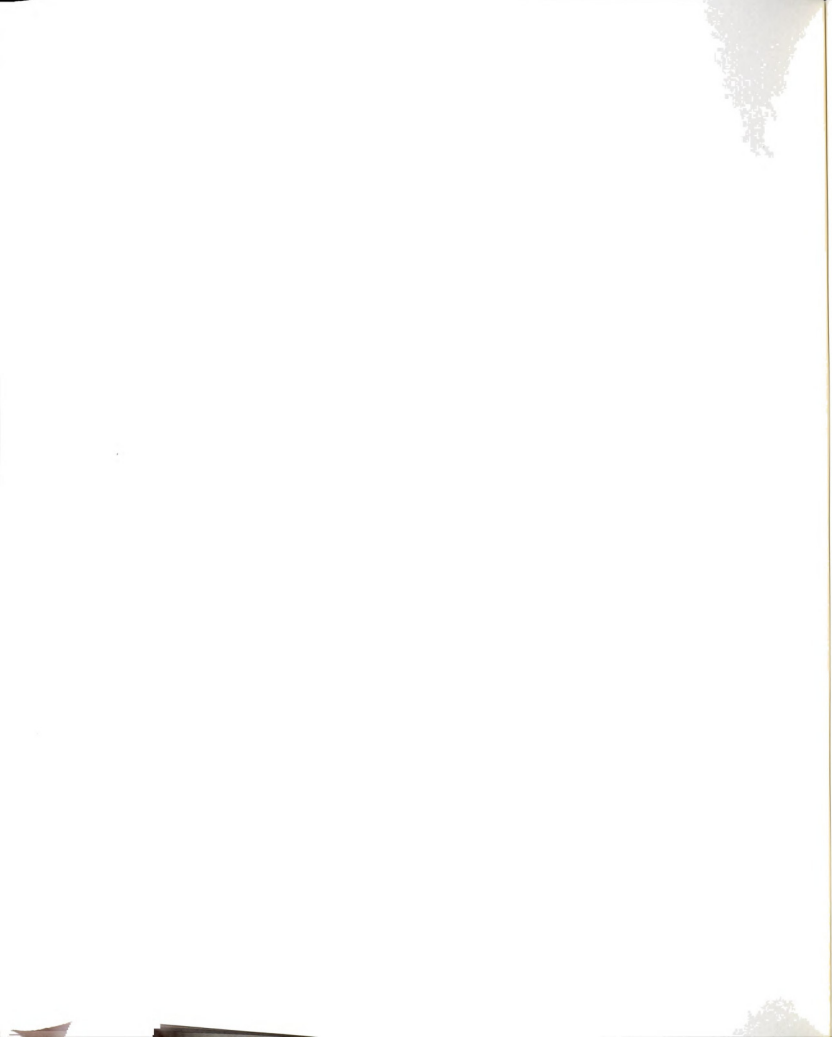


Figure 3.11. Hydraulic conductivity (permeability) of different concrete compositions given different storage condition [170].

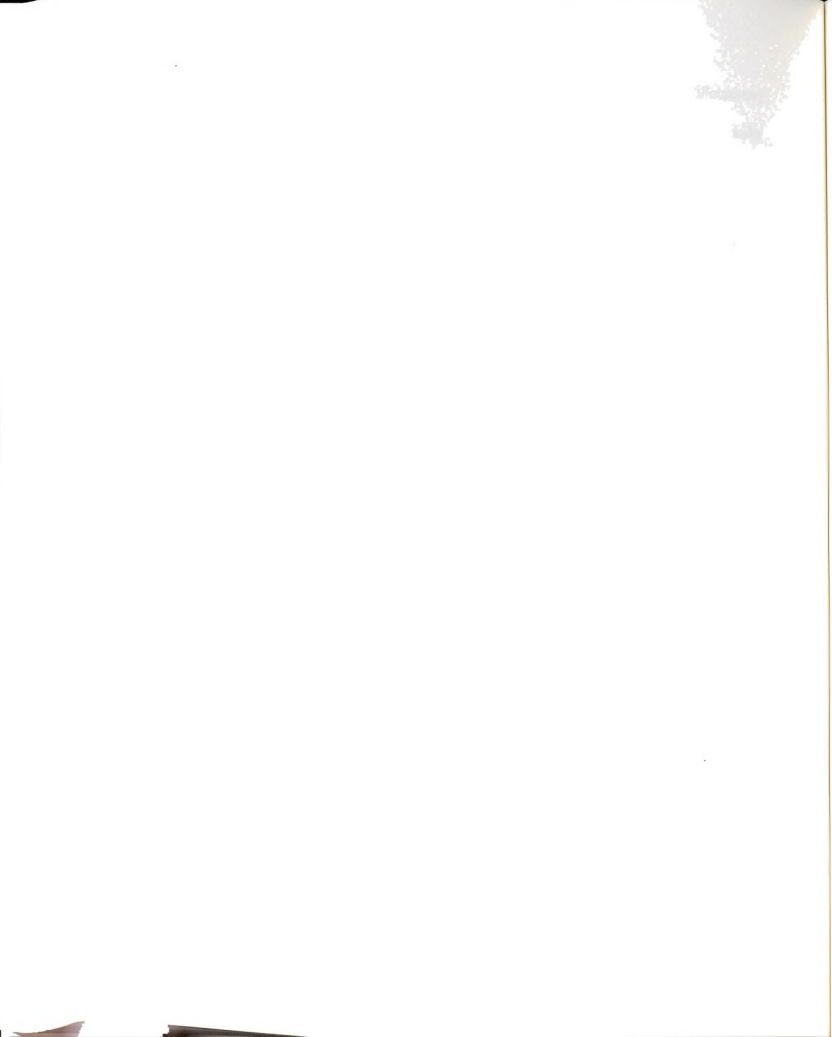


permeability with compressive strength, Telford opines that available data indicate that silica fume reduces the permeability more than it improves the strength, i.e., the efficiency factor for permeability is greater than that of the compressive strength. This is more evident at lower dosages of CSF and lesser strength levels. He also concludes from the comparison of cement paste and concrete that it is the aggregate-paste interface in particular that produces the improved results for concrete with CSF.

Air Content and Frost Resistance

The frost resistance of concrete made with silica fume has become the focus of many investigators due to its promising performance. The foci of these studies include the study void system, ice formation, pore structure, effect of admixtures, and so forth. Telford [20] refers to the work of Okkenhaug and Gjorv [171] and Okkenhaug [172], who studied the influence of CSF on the air void system, air content, and stability of the air void system as well as requirements for mixing time and aggregate grading. They determined that the desired total air content can be obtained in concrete with and without CSF by adjusting the dosage of the air entraining agent. Higher dosages are needed in CSF concrete, as compared to plain concrete without water reducers, but this difference is decreased in concrete with water-reducers. Air pore characteristics in CSF were found to be more favorable and the air content more stable with respect to vibration of the concrete, especially in mixes with water reducers.

Carette and Malhotra [173] measured the air void characteristics of hardened CSF concrete with superplasticizers. In contrast to Okkenhaug and Gjorv [171] who used 8%



CSF, the results did not show any consistent improvement. While a dose of 5% CSF improved the spacing factor and specific surface, but the higher dosages led to less favorable results than the reference mix. Virtanen [174] confirmed higher dosages of the air entraining agent for CSF concrete for a given air content, also pointed out that these dosages were less than for concrete with similar amounts of slag and fly ash.

In another experiment on high quality concrete, Virtanen [175] observed that, for a given dosage of an AEA, CSF concrete (16%) resulted in lower air contents in the fresh mix. Lehtonen [176,177] confirmed that higher dosages of AEA were required to produce equal amounts of air for concretes with 5, 10 and 15% CSF than the control for a $W/(C+S)=0.45$. He also confirmed a stable air content in CSF concrete with respect to vibration. This contrasted with previous work by Aitcin and Vezina [178] and Rasmussen [179], who reported somewhat greater loss of air for concrete containing CSF during handling and placement. Christensen and Jensen [180] found from their work that while 28% of the concrete specimens did not fulfil the target air requirement (3.5%), 10% filled the requirement for specific surface, and all tests gave satisfactory a spacing factor. They concluded that the requirement of an air pore system in hardened concrete should be in terms of the most directly measured values: air content relative to paste volume and the specific surface area of the pore system. They criticized the mathematically calculated values of the spacing factor, which are based on assumptions which, in their opinion, are usually not justified.

Fagerland [181] established that a given concrete possesses a "critical degree of saturation" (CDS) above which it is susceptible to rapid deterioration under freeze-thaw conditions and below which deterioration rates are very low. Lehtonen [177] showed

that in concretes with $W/(C+S)$ of 0.45 and 0 and 10% CSF content, the critical degree was not very different (83%) in spite of variations in air content.

The water suction behavior was observed to be quite different; the reference concrete quickly reached a plateau, whereas the CSF concrete showed much more gradual water absorption. In Swedish standards CDS is determined by a capillary suction experiment, which allows the prediction of service life equivalent to the time needed to reach the critical degree of saturation. "Finnish National Standards" [182] provide a criterion for a pore protection factor which is defined as the ratio between the unfilled pore space after capillary suction and the total pore space available to water, determined by pressure saturation of 150 atmospheres. A pore protection factor of at least 0.25 is suggested for concrete exposed to severe conditions.

Sellevold et al. and Preece et al. have shown that it is possible to produce CSF concrete which is frost-resistant without air entrainment, provided the water-cement is low and CSF content is high enough [20]. Concrete with a water-cement ratio of approximately 0.30 and CSF of 10% or more by weight was expected to meet this requirement. The initial study on silica fume concrete (10 to 30% replacement) was conducted without admixtures that required high cement content (730 kg/m^3). Frost resistance tests were conducted by freezing the concrete in air and thawing it in sea water with weight loss as a function of frost cycles taken as the measure of effectiveness. Concrete with CSF performed significantly better than the control, which is in agreement with later research work.

Cheng-Yi and Feldman [183] conducted tests on nonair-entrained concretes according to ASTM C 666 procedure B [52] on mortars with $W/(C+S)$ of 0.45 and 0.60

containing CSF 0, 10 , and 30%. A 10% replacement level lead to improved frost resistance, whereas mixes with 30% CSF showed poor frost resistance in spite of greater strength. The good results of the CSF concrete were thought to be due to the increase in the pore volume in the range of 0.35 to 20 microns, which they believed to act as air pores because of their ink-bottle shape. Cheng-Yi and Feldman believed that the possible reason for the low frost resistance of the strongest mix was due to a combination of low permeability and a higher CSF dosage than required for complete pozzolanic reaction.

Caratte and Malhotra used 0 and 30% CSF content in superplasticized and air-entrained concrete with $W/(C+S)=0.40$. They also observed decreased frost resistance with high dosages of CSF. The air void characteristics did not explain the apparently anomalous results. They also found identical strengths for 5 to 20% CSF at 28 days for no obvious explanation. This was contrary to previous work, which showed that the increased content of CSF should provide greater strengths.

The above discussion clearly indicates the improved performance of concrete with CSF. A replacement of approximately 5% to 15% is generally reported to bring an improvement in strength and permeability, but higher amounts adversely affect both permeability and frost resistance. A possibility of producing frost-resistant concrete without air entrainment at low water-cement ratio (0.30) has also been reported. The improvement in pore structure, impermeability, compressive strength, and a stable air void system provide a promise for producing frost-resistant concrete at marginal air content with typical water-cementitious ratios, which is the aim of this research work.

3.4 Summary

The admixtures investigated in this chapter are air entraining admixtures, water-reducing admixtures, fly ashes, slag, and silica fume. All of these admixtures have a direct or indirect bearing on the development of concrete air void and water pore systems. Their effects may or may not be favorable for the production of frost-resistant concrete at different replacement levels.

The type and the quantity of the AEA being used in a particular environment has specific effects on the development of a stable air void system. It has also been indicated that increases in air content adversely affect some properties of concrete, and reductions in compressive strength from 2-10% have been reported. Some researchers are of the view that this substantial loss of mechanical strength is unnecessary and can be avoided without loss of freeze-thaw durability.

The effect of water reducers/superplasticizers with respect to the freeze-thaw durability of portland cement concrete is still a controversial issue. Differences of opinion are basically about the interaction of superplasticizers with AEA and its failure to produce the air void system considered essential for frost resistance.

Two types of fly ashes, class F (low calcium, high carbon) and C (high calcium, low carbon), and slag are available as waste by-products, and are commonly used in concrete. The physical and chemical characteristics of these pozzolans affect the workability, strength development, and permeability of concrete differently, especially with respect to frost resistance. This becomes more complex in the presence of water-reducing admixtures, and spacing factors observed are sometimes higher than the

recommended values (0.008 in. or 0.20 mm) while still producing frost-resistant concrete. This problem needs to be resolved.

Good frost resistance appears to be possible by increasing the volume of small pores, thus avoiding the adverse strength loss effects. This has also been shown that the concretes which have a considerable percentage of pores in the range of 0.3 to 2 microns, are believed to improve frost resistance characteristics despite higher values of the spacing factor, in the range of 0.008 to 0.017 in. (0.2 to 0.43 mm). Thus using the properties of pozzolans, the pore water system can possibly be favorably altered.

The use of silica fume is gaining increased popularity due to its pozzolanic and filler properties. The literature has indicated improved performance of concrete with CSF. A replacement of approximately 5% to 15% is generally reported to bring an improvement in strength and permeability, but higher amounts may adversely affect permeability and frost resistance. The possibility of producing frost-resistant concrete without air entrainment at low water-cement ratios (0.30) has also been reported.

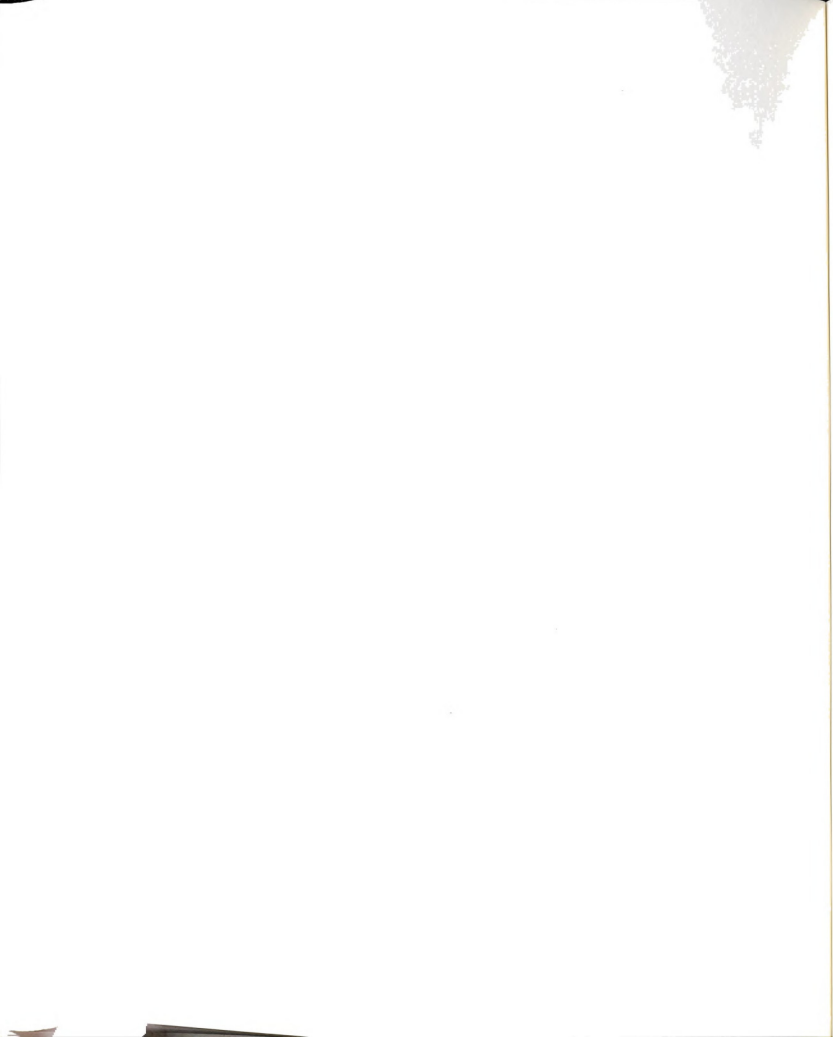
The improvement in pore structure, impermeability, compressive strength, and a stable air void system that often accompany CSF concrete provide a promise for producing frost resistant concrete at marginal air content with typical water-cementitious ratios, and curing periods, which is the aim of this research work.

CHAPTER IV

EXPERIMENTAL PROGRAM

4.1 Need for Proposed Studies

Since the development and use of different kinds of chemical and mineral admixtures, extensive research work has been directed towards the preparation of frost-resistant concrete according to the specifications initially recommended for portland cement concrete. It has been shown from an extensive literature review that mix designs with chemical admixtures, particularly when HRWRs are used, often fail to meet the recommended air void system requirements which are expected to produce frost resistance in ordinary portland cement concrete. Moreover, it has also been observed that the particle size distribution, chemical and physical characteristics of portland cement, and its widely-used replacement with mineral products play a vital role in the development of water pore structure, which in turn affects the frost resistance of PCC. A



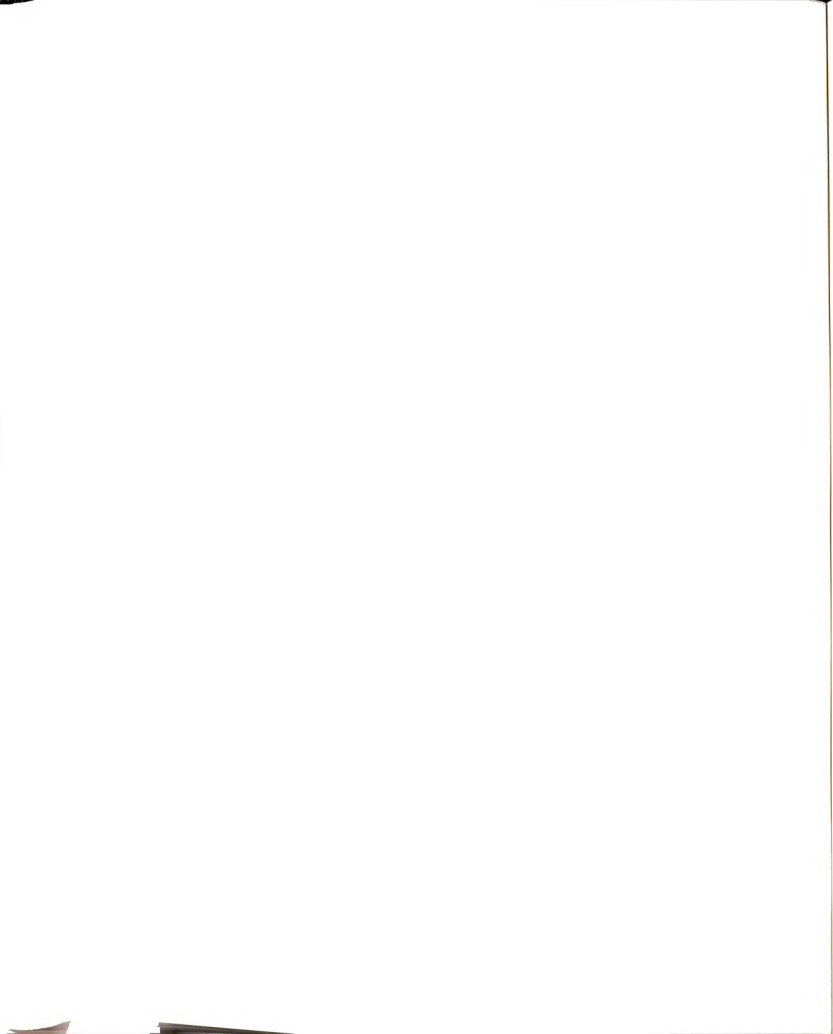
properly developed air void system in the hardened concrete is considered a key to the production of frost-resistant concrete. This system is altered by the use of various kinds of admixtures because of their chemical and physical properties. Previous work in this area has indicated the possibility of producing a frost-resistant concrete without air-entrainment, using silica fume in partial replacement of cement but this was for very low water-cement ratios and high-strength concretes only.

While the use of various kinds of admixtures are increasing in the production of normal strength concretes in freeze-thaw environments, there are inconsistencies that result in the failure of such structures. Enormous amounts of budget, time, and effort are being consumed, which concerns many users.

In this context, the research here has been directed towards a systematic laboratory study of concretes prepared with different kinds of mineral admixtures at different replacement levels in the presence of chemical admixtures at marginal air content for freeze-thaw environments. Further, it is essential to study and characterize the effects of these widely-used admixtures on air void system parameters that can be used as indicators of a frost-resistant concrete, and test the validity of existing criteria under these specific conditions.

4.2 Research Variables

Keeping in mind the above research needs, a comprehensive laboratory research program was designed to study the effects of commonly-used chemical and mineral admixtures on the frost resistance of concrete and the resulting air void and water pore

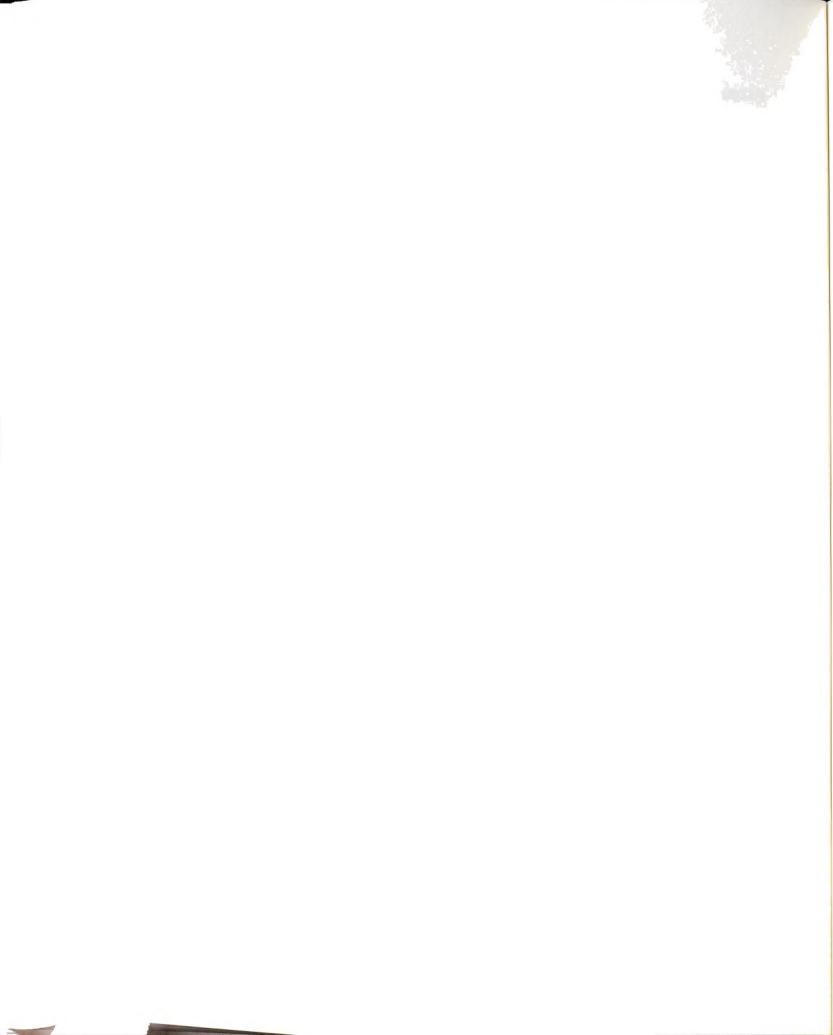


systems at marginal air contents.

This project was undertaken in three phases. In Phase I, three levels of air content and three levels of water-cement ratio were tested in all combinations (shown in figure 4.1) except for cell A1, which could be expected to produce satisfactory results because of its higher air content and low water-cement ratio. At least nine replicates were cast for each cell to measure the variability of test results and determine the number of replicates required for subsequent tests. Companion specimens were also cast for each cell to determine the compressive strength (as per ASTM C 39-86 [184]), air void parameters (as per ASTM C 457-90 [53]), and water pore system parameters. Based on the results of Phase I, future tests were planned for Phase II of the study.

Since many types of chemical and mineral admixtures are available in today's market, it was not possible to test all of these admixtures here because of time and economic constraints. It was, therefore, decided to select the variables that were representative of the admixtures and the conditions most commonly used and encountered in the production of improved PCC. Furthermore, these variables were only tested at levels that represent the current range of practice.

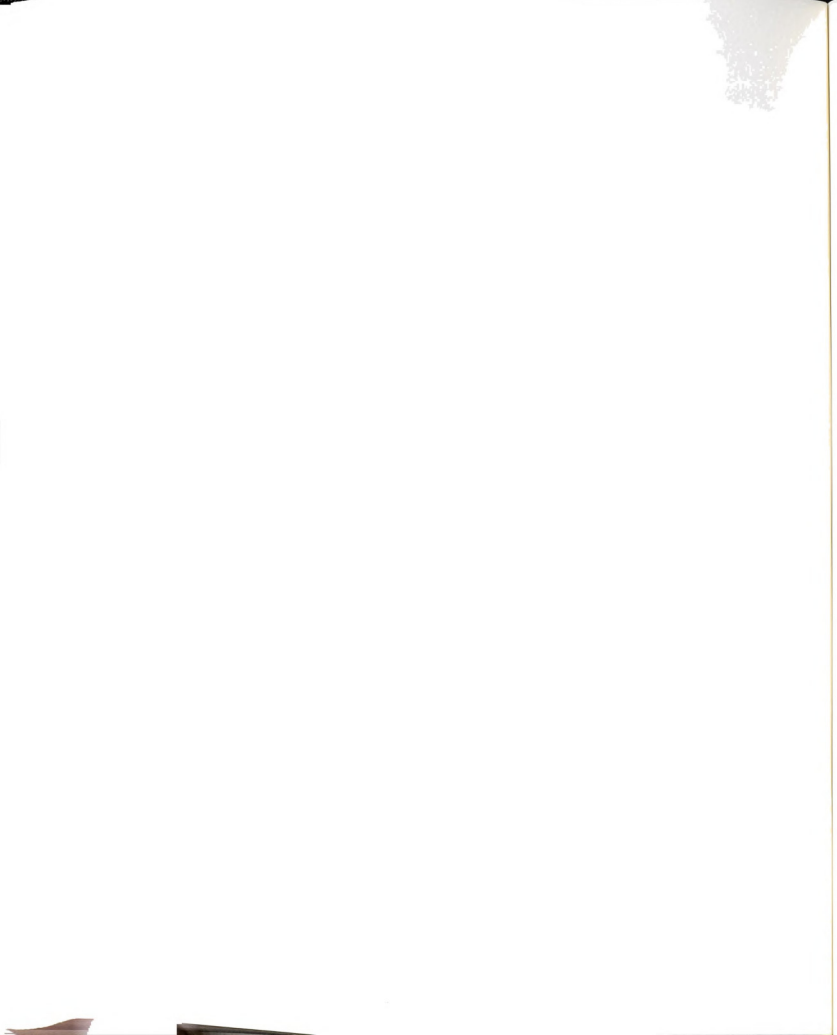
Two types of AEA, two types of WR/superplasticizers, and four kinds of pozzolans (class F and C fly ash, GGBF slag, and CSF) were selected for tests in Phase II. Curing periods of 28 and 56 days and $W/(C+P)$ of 0.40 and 0.45 were selected to be tested as nonmaterial factors. The silica fume was used in slurry form (suspended in superplasticizer and water). The fly ashes were tested at 15% and 30%, silica fume at 8% and 15%, and GGBF slag at 40% replacement levels by weight of cement for water-cement ratios of 0.40 and 0.45, both with and without water-reducer. The control mixes



		W/C		
		0.40	0.45	0.52
AC	7.5	A1	A2	A3
	5.0	A4	A5	A6
	2.5	A7	A8	A9

Figure 4.1: Experimental design Matrix A.

Note: (1) Within cell alphabet indicates matrix number and the figure shows cell number
(2) W/C - water-cement ratio
AC - target air content (percent)

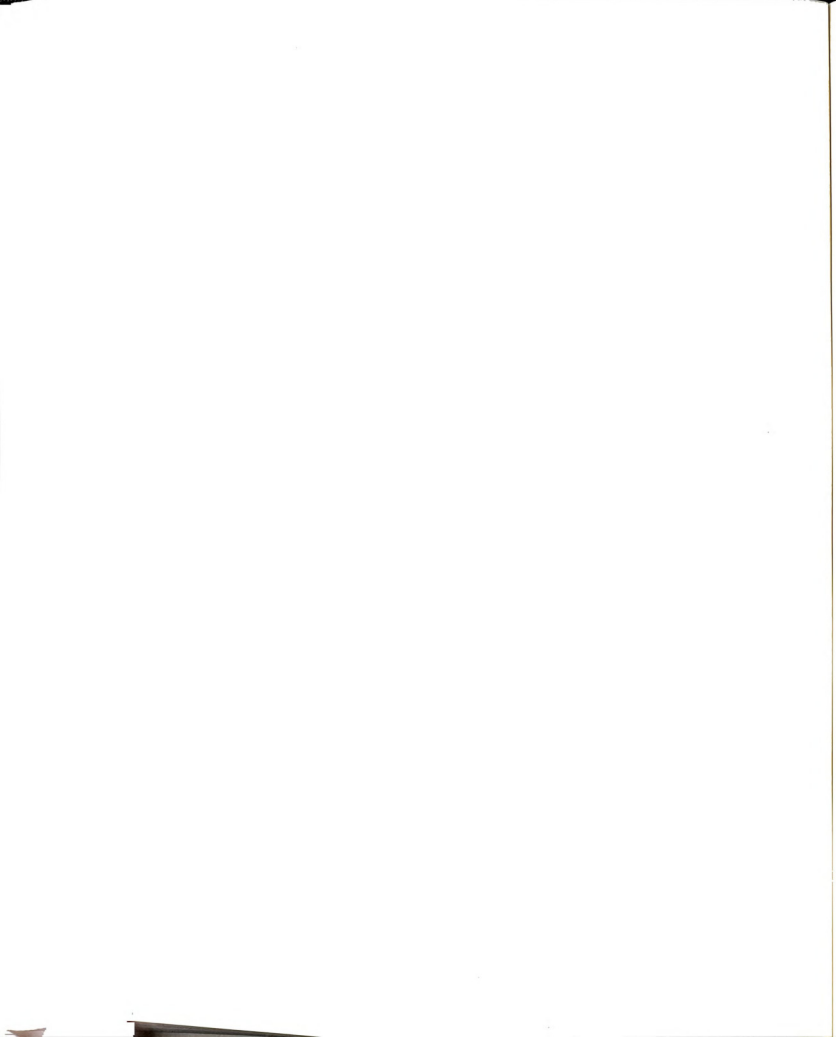


without any mineral admixtures were used as the third level of pozzolan dosage (0%) for comparisons. The target air content for all Phase II mix designs was kept at a marginal level (2.5%) so that the effects of the test variables on durability would be discernable.

The test matrices that were designed and used for Phase II are presented in figures 4.2 through 4.5. A total of six beams were cast for each cell: five were used for the freeze-thaw tests, and the sixth, selected at random, was used for microscopic analysis to determine the air void parameters. The results of these tests are summarized in Appendix B.

Phase III was comprised of a detailed analyses of all of the test results. The results of these analyses are summarized in Chapter VI.

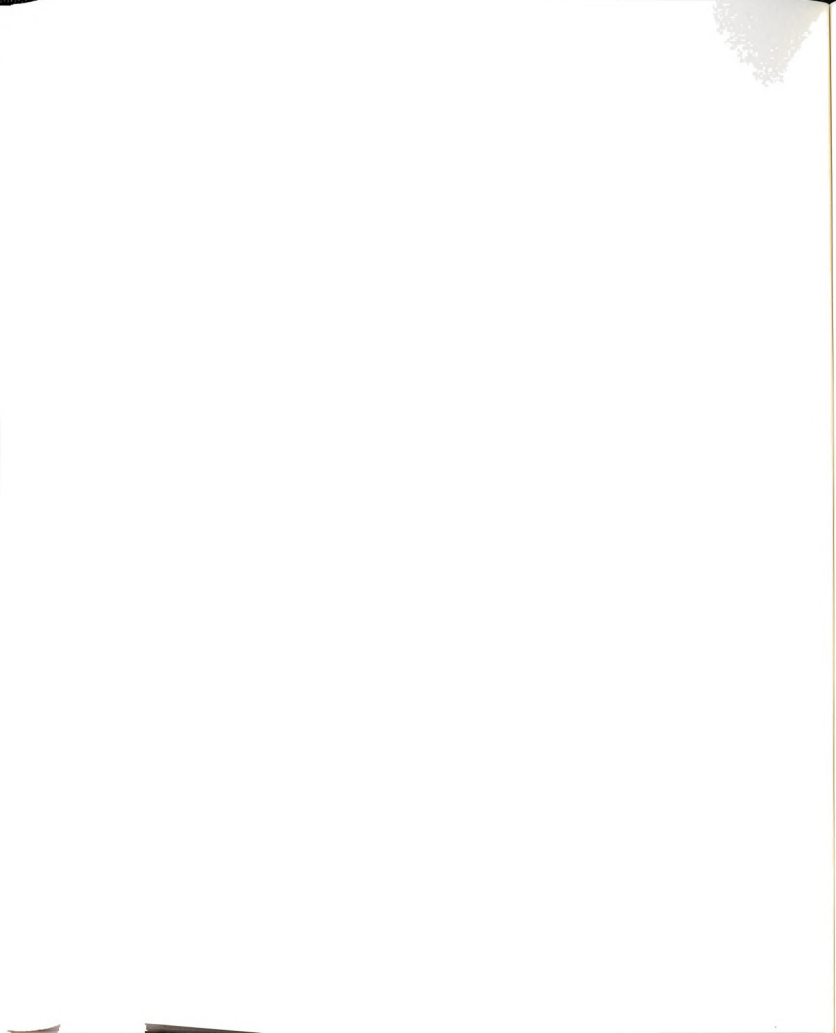
The details of materials used, and procedures for specimen preparation and testing are be discussed in chapter 5.



				AEA (AC=2.5%)			
				DARAVAIR		MICROAIR	
				W/(C+P)			
				0.40	0.45	0.40	0.45
P O Z Z O L A N T Y P E	NONE	W R / H R W R	1	B1	B2	B3	B4
	CLASS F FA		1	B5	B6	B7	B8
			2	B9	B10	B11	B12
	CLASS C FA		1	B13	B14	B15	B16
			2	B17	B18	B19	B20
	CSF		2	B21	B22	B23	B24

Figure 4.2: Experimental design Matrix B.

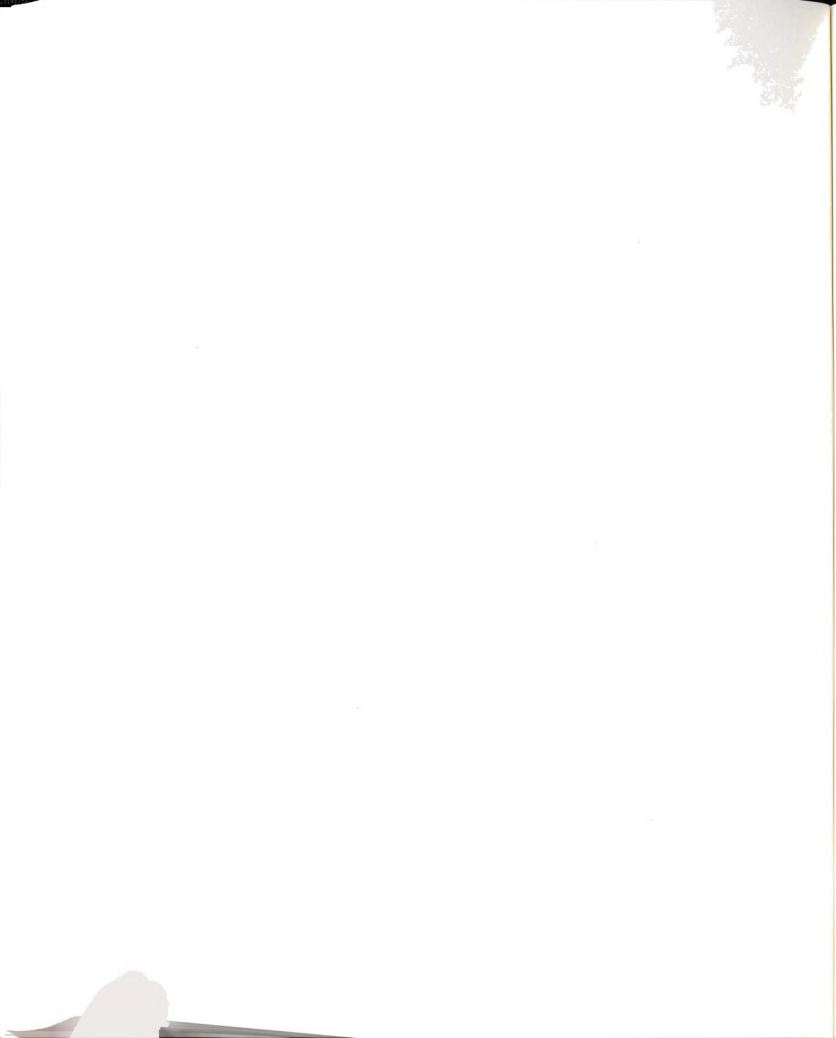
- Note:** (1) Pozzolans 15% replacement (by weight) of cement.
 (2) Within cell alphabet indicates matrix number and the figure shows cell number
 (3) W/C+P - water-cementitious ratio
 AEA - air entraining admixture
 WR - water-reducer...1
 HRWR - high-range water-reducer...2
 FA - fly ash
 CSF - condensed silica fume



		W/(C+P)	
		0.40	0.45
G G B S slag	NONE	C1	C2
	WR	C3	C4

Figure 4.3. Experimental design Matrix C.

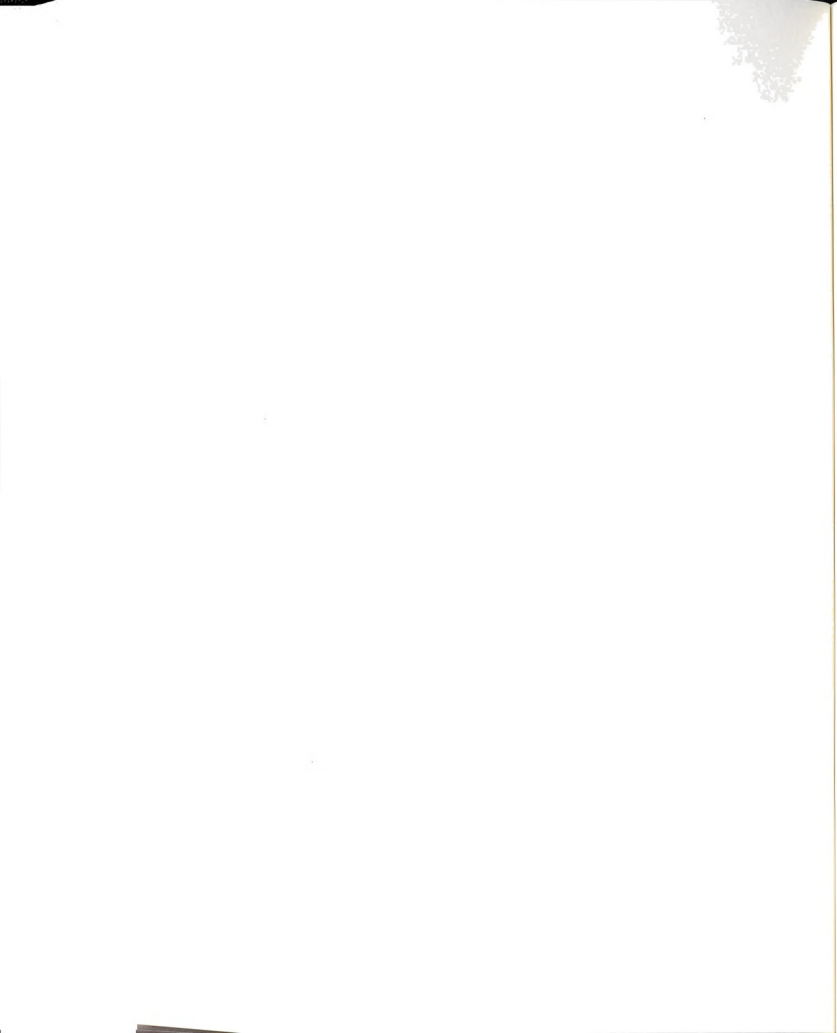
- Note:** (1) GGBF slag 40% replacement (by weight) of cement.
 (2) Within cell alphabet indicates matrix number and the figure shows cell number
 (3) W/C+P - water-cementitious ratio
 WR - water-reducer



				W/(C+P)			
				0.40		0.45	
				CURE TIME (DAYS)			
				28	56	28	56
F L Y A S H T Y P E	NONE	FA AMOUNT	NONE	D1	D2	D3	D4
	CLASS F FA		15%	D5	D6	D7	D8
			30%	D9	D10	D11	D12
	CLASS C FA		15%	D13	D14	D15	D16
			30%	D17	D18	D19	D20

Figure 4.4: Experimental design Matrix D.

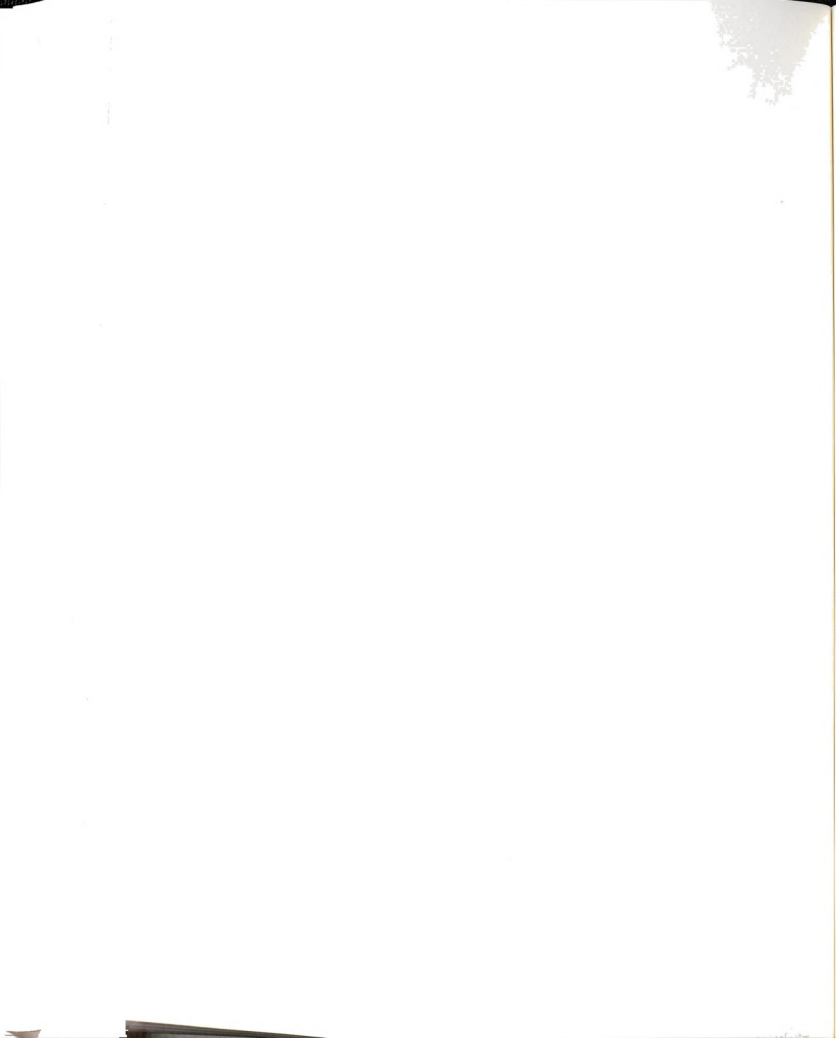
- Note:** (1) Fly ash percent replacement (by weight) of cement.
 (2) Within cell alphabet indicates matrix number and the figure shows cell number
 (3) W/C+P - water-cementitious ratio
 FA - fly ash



		W/(C+P)			
		0.40		0.45	
		CURE TIME (DAYS)			
		28	56	28	56
C S F	NONE	E1	E2	E3	E4
	8%	E5	E6	E7	E8
	15%	E9	E10	E11	E12

Figure 4.5: Experimental design Matrix E.

- Note:** (1) Silica Fume percent replacement (by weight) of cement.
 (2) Within cell alphabet indicates matrix number
 and the figure shows cell number
 (3) W/C+P - water-cementitious ratio
 CSF - condensed silica fume



CHAPTER V

TEST MATERIALS AND PROCEDURES

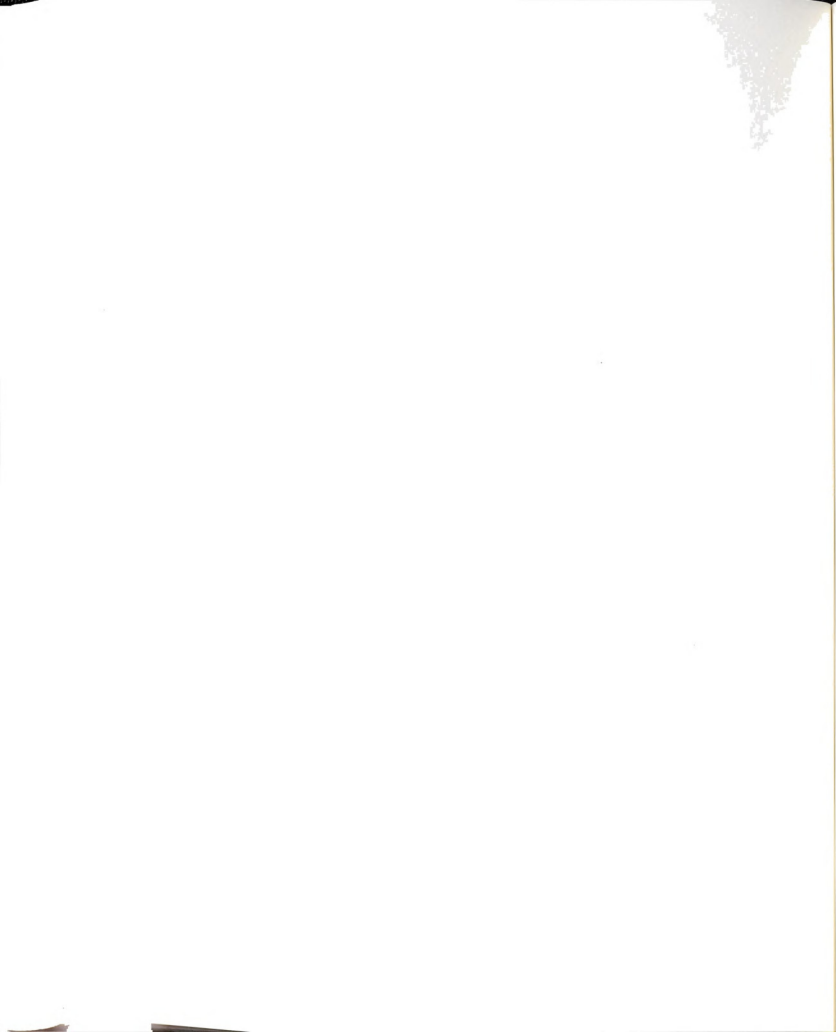
5.1 Introduction

The material presented in this chapter summarizes the specific procedures adopted concerning the casting, curing, preparation and testing of samples in this experimental program. The characteristics of the various materials used are also discussed.

5.2 Preparation of Test Mixes

5.2.1 Materials Used

As mentioned earlier, a high quality aggregate was used to restrict the durability study to the paste fraction of the concrete. Dolomite crushed limestone, which had a tested durability factor of 92 (ASTM C 666 procedure B) and a nominal top size of 1.25



in., was used. Other characteristics of the aggregate are shown in table A.1 (appendix A). The fine aggregate was glacial sand (brought from Washington) having a fineness modulus of 2.7. The bulk specific gravity (SSD) was 2.64, and the absorption capacity was 2.1%. Type I portland cement produced by St. Mary's Peerless Cement in Detroit, Michigan was used for all the mix designs.

The water reducer was Plastocrete provided by Sika Corporation; the high-range water-reducer was provided by Elkem Materials, Inc., and is the same type used in the production of their slurry form silica fume. The two types of air entraining admixtures used in this program were Daravair, a WR Grace vinsol resin (AEA1), and Microair, from Master Builders (AEA2). The fly ash (FA) used in this work was Class C (Cl C) from Laramie River, Wyoming and Class F (Cl F) from Centralia, Washington. The physical and the chemical properties of the fly ashes are shown in table A.2 and A.3 (appendix A). GGBF slag with water-reducer and silica fume in slurry form (mixed with superplasticizer and water) were used.

5.2.2 Mix Proportioning

Mix designs were developed using the absolute volume method [47]. After setting the water-cement or cementitious ratio and the amount of pozzolan replacement level to be studied, an air content at 2.5% and slump of 1-3 in. were targeted. The amount of the coarse aggregate was kept constant, and the amounts of fine aggregate and cement paste were adjusted to attain the desired workability. AEA dosage was varied to produce the desired target AC ($\pm 0.5\%$). Many trials were sometimes needed to develop the final

mix designs.

5.2.3 Casting of test specimens

The batch quantity of water was controlled by oven drying the fine aggregate before it was used for mixing, and the quantity of water was adjusted according to the absorption capacity and quantity of the sand. The coarse aggregate was brought to saturated, surface-dry condition by floor drying before batching. The water-reducing and air entraining admixtures were added separately to the mixing water (which was measured in two halves) so that these were thoroughly dispersed.

A four and one-half cubic-foot capacity drum mixer was "battered" with a small batch of test concrete prior to its first use each day. Whenever possible, materials were introduced while the mixer was running. Materials were added in the following sequence: (1) all of the coarse aggregate and all of the fine aggregate; (2) half of the water (mixed with WR/HRWR, when used); (3) cement and pozzolans if used; and (4) the remaining half of the water with the air entraining agent. After charging the mixer, materials were mixed for three minutes, followed by three minutes of rest and, finally, two minutes of mixing, in accordance with ASTM C 192 [185].

The entire mix was then emptied into a damp wheelbarrow for testing (air content and slump) and casting. The test specimens were prepared and cured according to ASTM C 192-90a [185] and ASTM C 490-89 [186]. Trial batches were made until the target air content of 2.5% was achieved within an allowable limit of $\pm 1/2\%$ (as measured by the pressure method, according to ASTM C 231-91 [187]) and a design slump of one to

three in. was achieved, as determined according to ASTM C 143-90a [188]. Six 3"x4"x16" beams , three 4"x8" cylinders, and one 6"x12" cylinder were cast from the final mix design for each cell, in accordance with ASTM C 192 [185].

The specimens were demolded 24 hours after casting, and the beams were placed in a lime water bath; the cylinders were kept in 100% humidity at 73°F for the desired curing period.

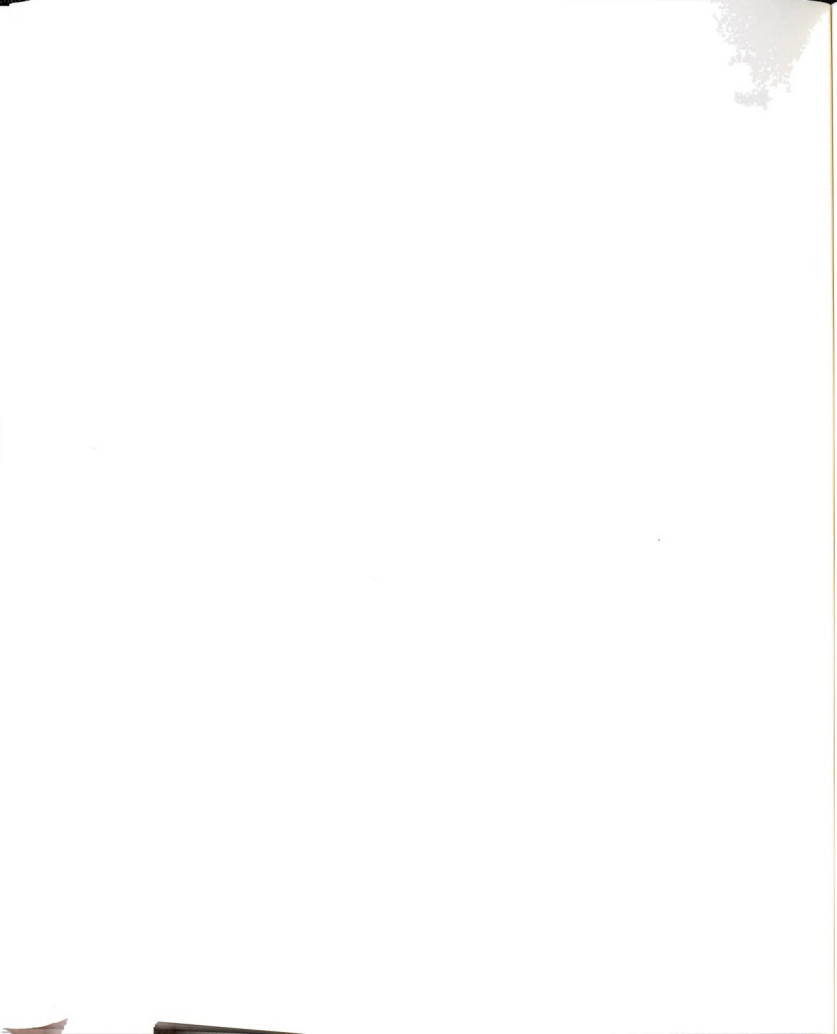
5.3 Test Procedures

5.3.1 Rapid Freezing and Thawing Test

Portland cement concrete in temperate regions undergoes periodic cycles of freezing and thawing. In the laboratory, these conditions are created by varying the temperature and moisture under controlled conditions using automatic equipment capable of producing continuous and reproducible cycles.

The freeze-thaw machine used for these tests was capable of testing eighty specimens at a time, and featured programmable temperature control. Figure 5.1 is a sample of the actual temperature record for a week's time. In this figure, the scale reading of 20 represents an actual reading of 0°F, and the higher limit of 40°F is shown as scale reading of 60. These chart settings were selected for easy and clearer readings.

After curing, the beams were removed from the lime water and placed in a constant temperature bath at 40°F for at least for one hour before conducting the initial durability tests. When the samples had attained a uniform temperature of 40°F, they



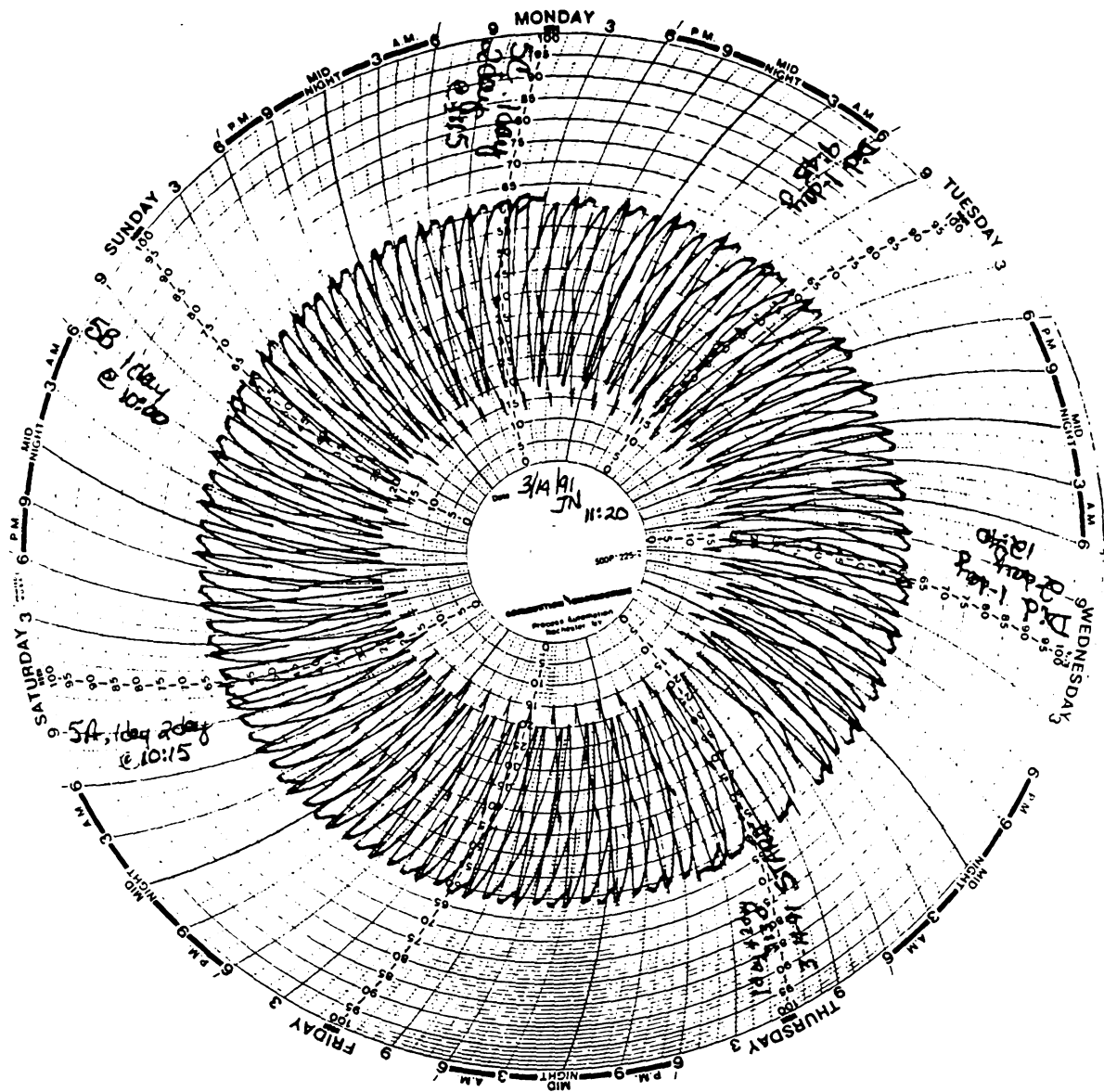
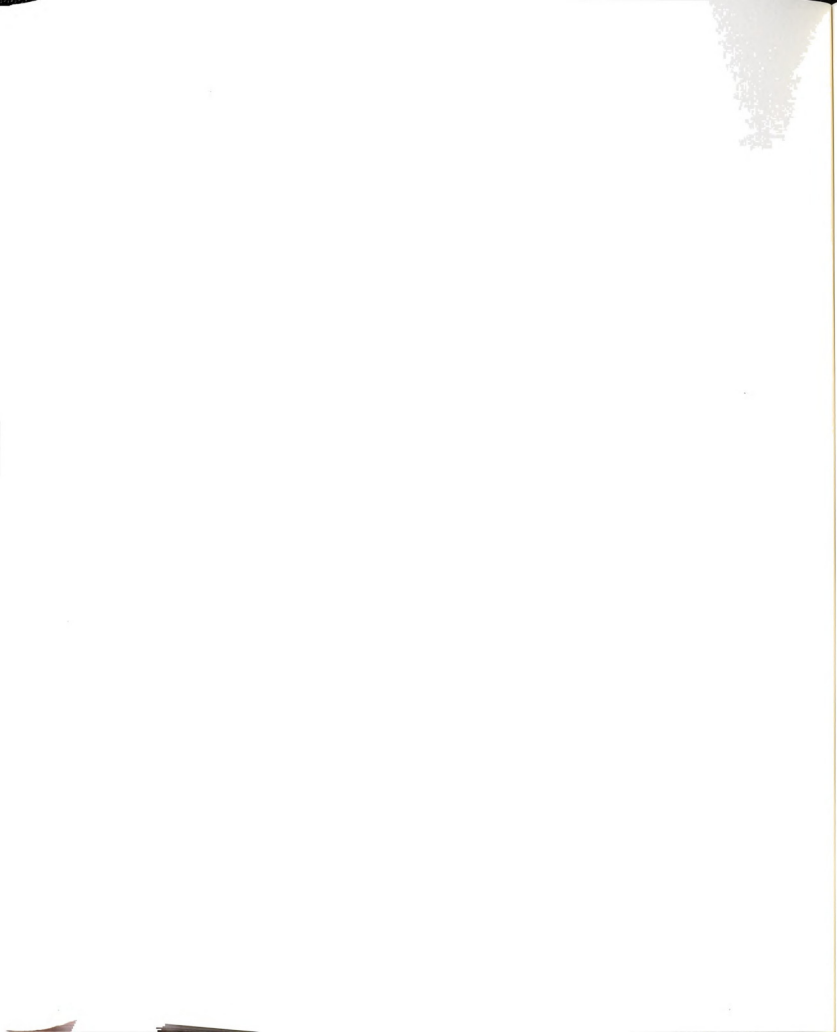


Figure 5.1. Sample record sheet, showing actual temperature profile for one week duration of freeze-thaw cycles.



were tested for resonant frequency according to ASTM C 215-85 [189]. Beam lengths were measured using a comparator, as per ASTM C 490-89 [186], capable of measuring lengths to the nearest 0.0001 in. The weight was measured with scales accurate to within one gram (the specification requires accuracy within 4.5 grams). The samples were then placed in the freeze-thaw machine during a thaw cycle.

Standard tests of concrete resistance to rapid cycles of freezing and thawing were conducted according to ASTM C 666-90 [52] procedure B, with some slight modifications. In our version of this test, the specimens were wrapped in specially designed cloth wraps. The purpose of the wraps was to keep the specimens moist during freezing, as in ASTM C 666 standard procedure A (freezing and thawing in water), and at the same time avoid the potential for specimen damage that has been observed with the use of normal procedure A containers. The use of these wraps offered the added advantage of a comparatively better visual assessment of scaling because one could see the scaled material in the wrap each time the specimen was taken out of the freeze-thaw machine for measurements/tests. This also reduced the cleaning and maintenance effort of the freeze-thaw machine by preventing much of the scaled material from sinking to the bottom of the machine, which could not be avoided in the case of procedure B; thus, the use of these wraps may prolong the life of the expensive test equipment. The selected procedure does involve wrapping and unwrapping each specimen, which, of course, consumes more time and effort in the testing of the specimens.

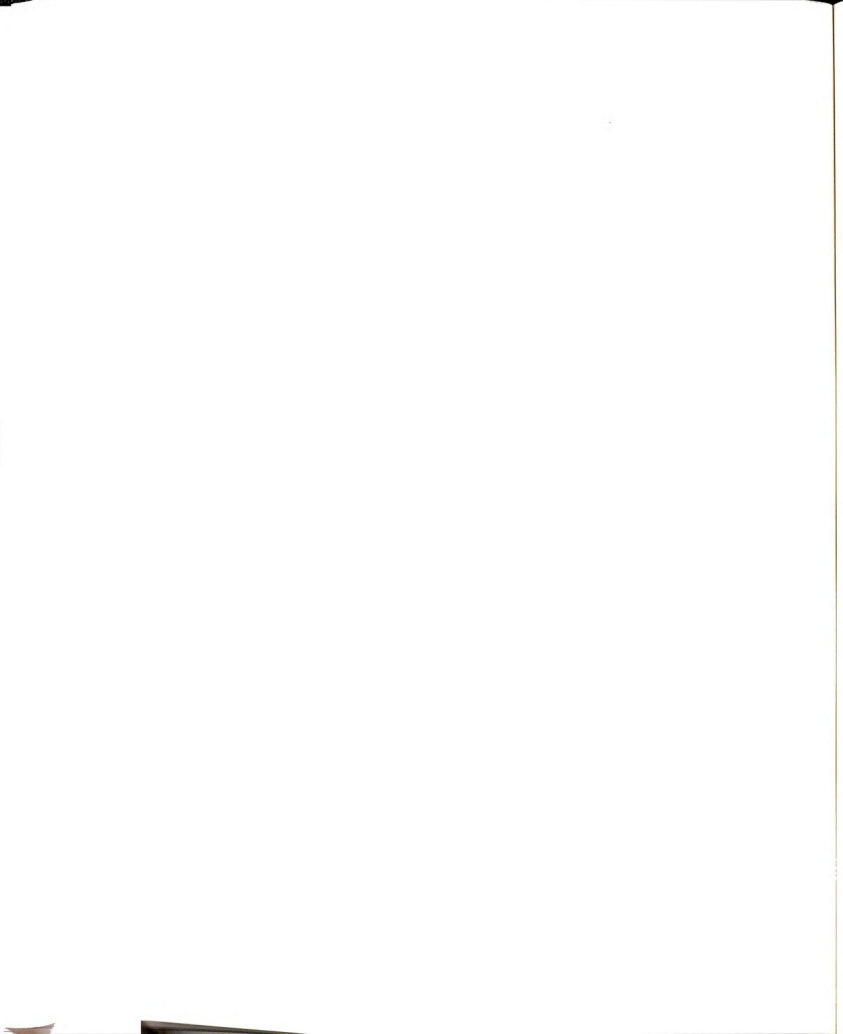
The freezing and thawing cycle consisted of alternately lowering the temperature of the specimens from 40 to 0°F (4.4 to -17.8°C) and raising it from 0 to 40°F (-17.8 to 4.4°C). At the end of the cooling period the temperature at the center of the

specimens is required to remain $0 \pm 3^{\circ}\text{F}$ ($-17.8 \pm 1.7^{\circ}\text{C}$), and at the end of the heating period the temperature shall be $40 \pm 3^{\circ}\text{F}$ ($4.4 \pm 1.7^{\circ}\text{C}$). The temperature of the heat-exchanging medium (water and air) is kept uniform within 6°F (3.3°C) throughout the specimen cabinet when measured at any given time on the surface of any specimen except during the transition between freezing and thawing or vice versa. The supports on which the specimens rest are such that they are not in contact with the full area of the supported side or end, and they do not subject this area to conditions substantially different from those imposed on the remainder of the specimen.

The specimens were tested for resonant frequency (for determining RDM), and change in length and weight every 30 cycles or less unless failure appeared imminent, in which case they were tested at more frequent intervals. Tests were discontinued when a specimen either survived 300 cycles or the RDM reached 60% of the initial modulus value. Any changes in the visual condition of the specimens were recorded at each testing.

5.3.2 Dynamic Modulus Testing

A James Instruments E-meter was used to determine the fundamental transverse frequency of each freeze-thaw test specimen. This apparatus consists of the frequency control cabinet, a test bench, the frequency driver or vibrator, and a pick-up device. The equipment produces a highly stable, variable frequency oscillation covering frequency bands of 10 Hz to 100 kHz in four switch ranges, with approximately 10% overlap at the end of each range. A power amplifier (0-14 volt peak to peak) capable of delivering



up to 8.3 watts into a 3 ohm vibration generator is also used. Output voltage is shown on a miniature indicator. A frequency meter is provided with a 6-digit LED display and switch-selected gate times of 1 or 10 second. The meter can be switched to monitor either the output driving frequency from the oscillator, or the received input frequency from the vibration detector.

For the determination of fundamental frequency, a specimen is placed on the support in such a manner that it may vibrate without significant restriction in a free-free transverse mode. The specimen is positioned in a way that the driving force is normal to the surface and is applied at a point distant from the nodal points, midway between the ends or near the end of the specimen for transverse oscillations. The pick-up unit is then placed against the surface of the specimen so that it will be actuated in the direction of vibration. To avoid distortion, the vibrating force is maintained as low as possible for good response at resonance.

5.3.3 Dilation Testing

This is an important indicator of frost resistance and is used in British Standards. With repeated cycles of freezing and thawing, the concrete develops microcracks through which the water enters and causes further deterioration. The dilation is considered to be an indicator of concrete deterioration and a 0.1% of increase in original length is often used as a failure criteria.

The comparator used for determining change in length of the specimen was capable of measurements accurate to within 0.0001 in. A reference bar was used to

calibrate the comparator prior to each use and whenever it was felt necessary. The sample was carefully placed in the comparator and slowly rotated; the maximum reading was recorded. The comparator anvils were cleaned before taking each measurement.

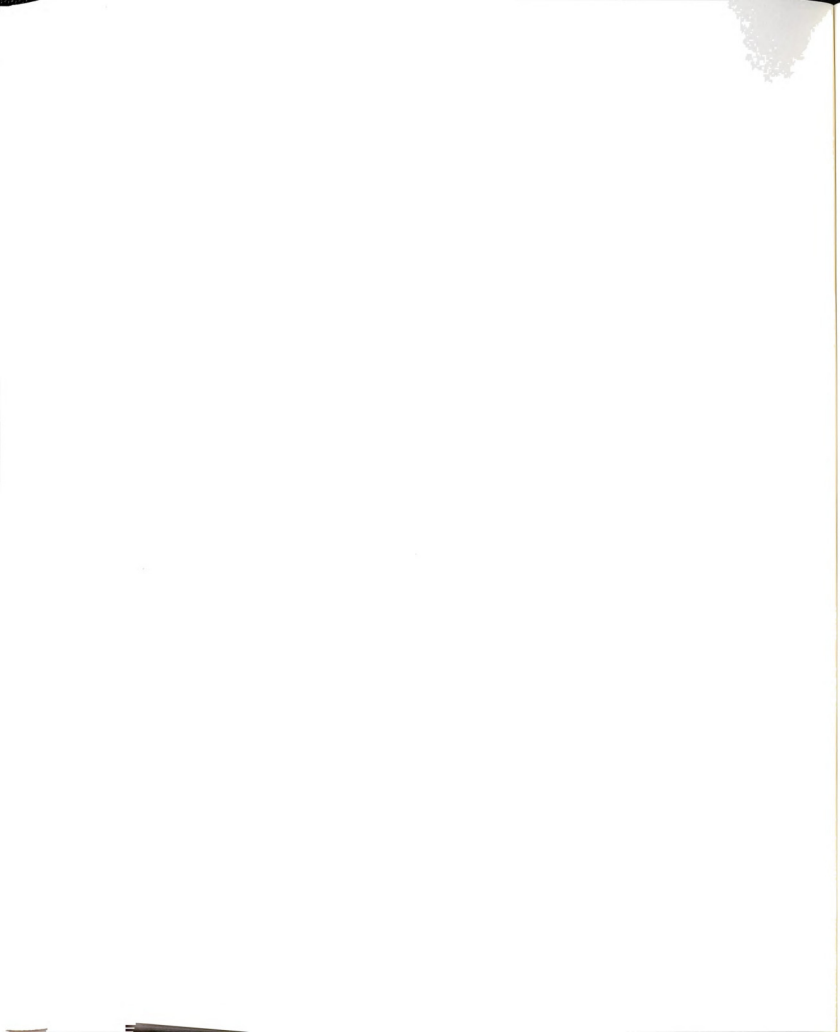
The same target specimen temperature (40°F) was used throughout the testing, since changes in specimen temperature at the time of length measurement can affect the length of the specimen significantly.

5.3.4 Weight Change Measurements

Change in weight has also been used as a measure of concrete frost resistance. The development of microcracks allows additional water to enter the concrete, which, with repeated cycles of freezing and thawing, causes further deterioration. The ingress of this water is observed by recording the change in weight of the specimen during the tests. The increase in weight of the specimens during testing indicates the deterioration. But this increase in weight can be offset by loss of mass due to scaling, which needs to be observed and interpreted accordingly.

5.3.5 Microscopic Examination

The air content, specific surface, spacing factor, and other air void parameters were determined by using data obtained by microscopic examination (linear traverse, as per ASTM C 457-90 [53]). Specimens of 3"x4" and approximately three-quarters of an inch in thickness were sliced from the center of one of the six beams cast after the



specified curing period. These were then washed and scrubbed with a brush using a fine, high-velocity spray of water after the sawing operation to remove the grit and loose particles of concrete. After a visual inspection, the comparatively smooth side was then prepared for microscopic analysis using the following procedure:

- (1) Use abrasive paper of 75 μm and/or 35 μm for 8 minutes;
- (2) Wash specimen carefully with water;
- (3) Use abrasive paper of 14.5 μm for 8 minutes;
- (4) Again wash specimen with water;
- (5) Apply "cutex" on the surface of the specimen smoothly with a fine brush or cotton swab and let it dry in the air for 5 minutes;
- (6) Repeat the application of cutex for 5 times in similar manner so that it saturates in the surface;
- (7) Use abrasive paper of 12.5 μm for ten minutes; and
- (8) Wash the specimen with water.

The prepared specimens were then examined under the microscope and air void measurements were made using ASTM C 457-90 [53] procedures.

The linear traverse apparatus consists mainly of: a device to provide a platform with leveling arrangement on which the specimen can be mounted; a stereoscopic microscope and support; a microscope lamp; and a computerized apparatus for recording and analyzing the measurements. A prepared sample of concrete is placed on the stage of the linear traverse device, and is leveled so that the surface may be traversed and microscopically examined with a minimum of refocusing. After adjusting the light and

magnification, the specimen is traversed for a specific length, depending on the top size of the aggregate. Measurements are collected and recorded using the computer data acquisition system. The skill, experience and continuity of the performance of the test by the same operator are important factors that contribute to the accuracy of the results. A program is then run on the computer to analyze the test data.

5.3.6 Strength Testing

After the specified period of curing, 4"x8" cylinders were subjected to a compression test as per ASTM C 39-89 [184]. An average of three cylinders were tested for each cell.

5.3.7 Permeability and Freezable Moisture Testing

Permeability and freezable moisture testing was carried out on specimens sliced from the 6"x12" cylinders and the remaining portions of the beams used for air void characteristics. These were shipped to the University of Washington in a sealed container of lime water for permeability and freezable moisture testing. Three-inch thick samples were cut for permeability testing with a diamond saw using water as a coolant. The details of sample preparation and testing are given in reference [190].

The coefficient of permeability calculations were made by employing a falling head analysis, as described in section 5.4.6.

The samples for the freezable moisture testing were cut from the 6"x12" cylinders

and portions of the 3"x4"x16" beams. These specimens were dried to various moisture contents in cabinets with varying relative humidities. They were weighed and then oven dried and re-weighed. The adjusted equilibrium moisture content for an individual mix was based on weighted average of the samples [190] using the following equation:

$$w\%_{adj} = S \times w\%_{SSD}$$

where:

S = average degree of saturation; and

$w\%_{SSD}$ = percent of saturated surface-dry moisture content.

The equilibrium moisture content and the corresponding equilibrium relative humidity then used for determining the amount of freezable moisture in the sample, as described in section 5.4.7.

5.4 Calculations

The following calculations were made in accordance with ASTM specifications for the determination of various numerical values:

5.4.1 Relative Dynamic Modulus of Elasticity (RDM)

The numerical value of RDM was calculated as follows:

$$RDM = (n_1^2/n^2) \times 100$$

where

100
100
100

RDM = relative dynamic of elasticity, after C cycles of freezing and thawing, (percent),

C = number of cycles at time of testing,

n = fundamental transverse frequency at 0 cycles of freezing and thawing, and

n_1 = fundamental transverse frequency after C cycles of freezing and thawing.

5.4.2 Durability Factor (DF)

The durability factor (DF) is calculated as follows:

$$DF = PN/M$$

where:

DF = durability factor of test specimen;

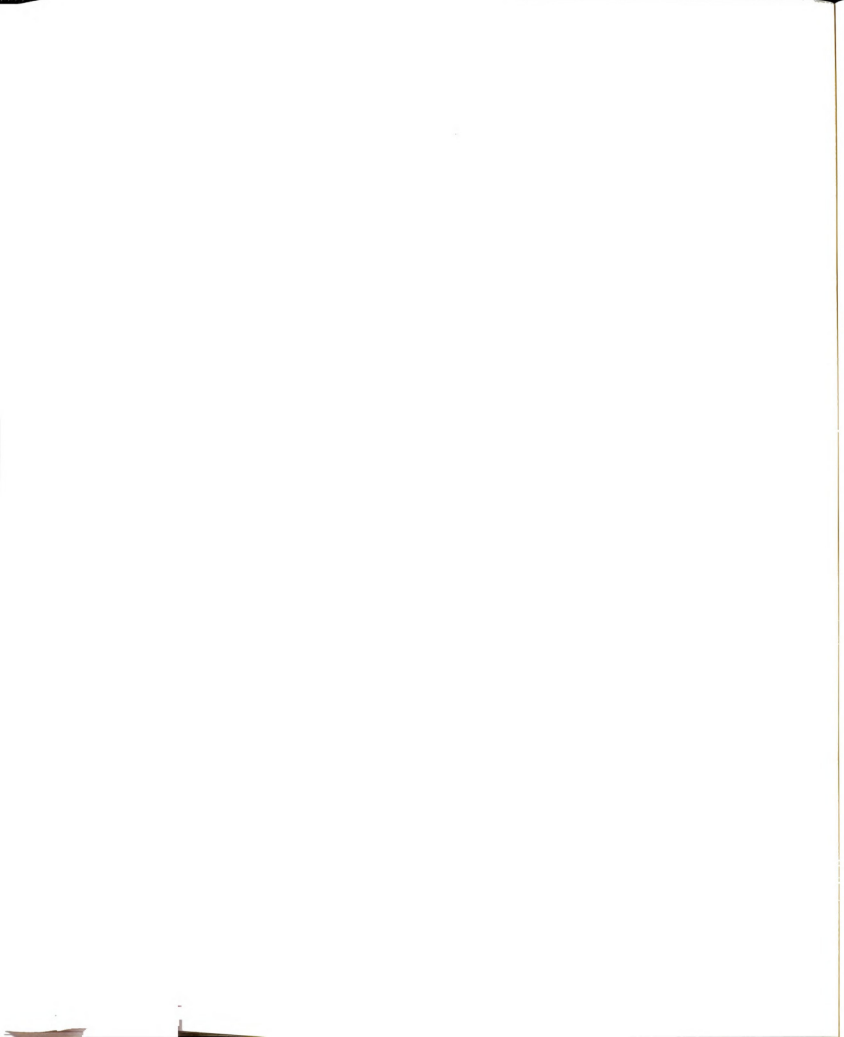
P = RDM at N cycles, percent;

N = number of cycles at which P reaches the specified minimum value for discontinuing the test or the specified number of cycles at which the exposure is to be terminated, whichever is less; and

M = specified number of cycles at which the exposure is to be terminated.

The scale for durability factor varies from 0-100. The 100 represents the best possible frost resistance performance and zero represents the worst possible performance.

In the literature, there is no subjective rating of the durability factor, (e.g., (1) DF values above 90 are referred to as good or excellent, (2) above 60, considered durable, etc.) and the criteria for acceptance varies between user to user. For this work, the following arbitrary subjective rating scale was used:



Excellent-----	Greater than 80
Good -----	60 to 80
Marginal -----	40 to 60
Bad -----	20 to 40
Poor -----	Less than 20

5.4.3 Change in Length (Dilation)

Change in length is calculated as follows:

$$L_c = [(l_2 - l_1)/L_g] \times 100$$

where:

L_c = length change of test specimen after C cycles of freezing and thawing, (percent);

l_1 = length comparator reading after 0 cycles;

l_2 = length comparator reading after C cycles; and

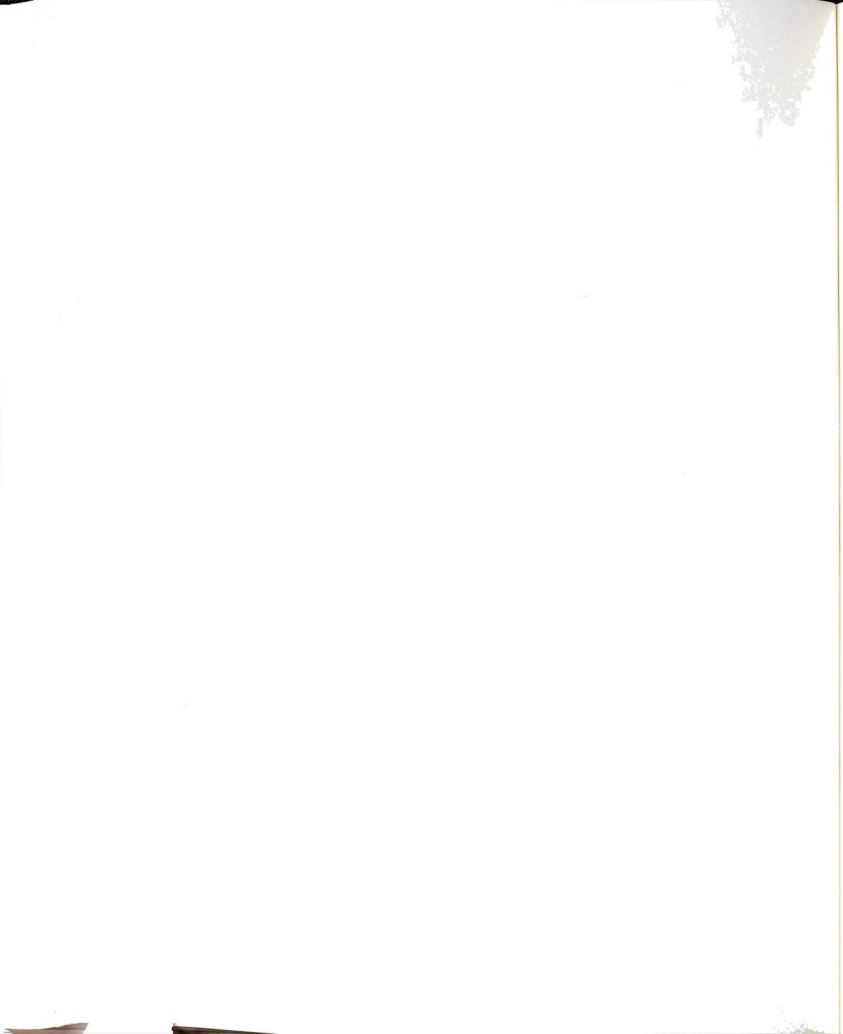
L_g = the effective gage length between the innermost ends of the gage studs.

5.4.4 Mass Change

The change in weight due to the repeated cycles of freezing and thawing is calculated as follows:

$$W = [(W_1 - W_2)/W_1] \times 100$$

where:



W = weight change of specimen at C cycles of freezing and thawing, (percent);

W_1 = weight of the specimen at the beginning of the test, (lbs); and

W_2 = weight of the specimen after C cycles (lbs).

5.4.5 Air Void Parameters

The Powers spacing factor was calculated in accordance with the procedure given in paragraph 14 of ASTM C 457-90 [53]. The Philleo factors (PH90 and PH99) were calculated using the Hydrair program developed by the University of Washington. This program is based on the equations developed by Philleo [62] and uses lognormal distribution. Attiogbe mean spacing was calculated using the equation developed by Attiogbe [66].

5.4.6 Coefficient of Permeability

The following equation was used to compute the coefficient of permeability of concrete:

$$k = \left[\frac{aL}{A'(t_f - t^o)} \right] \{ \ln(h_o/h_f) \}$$

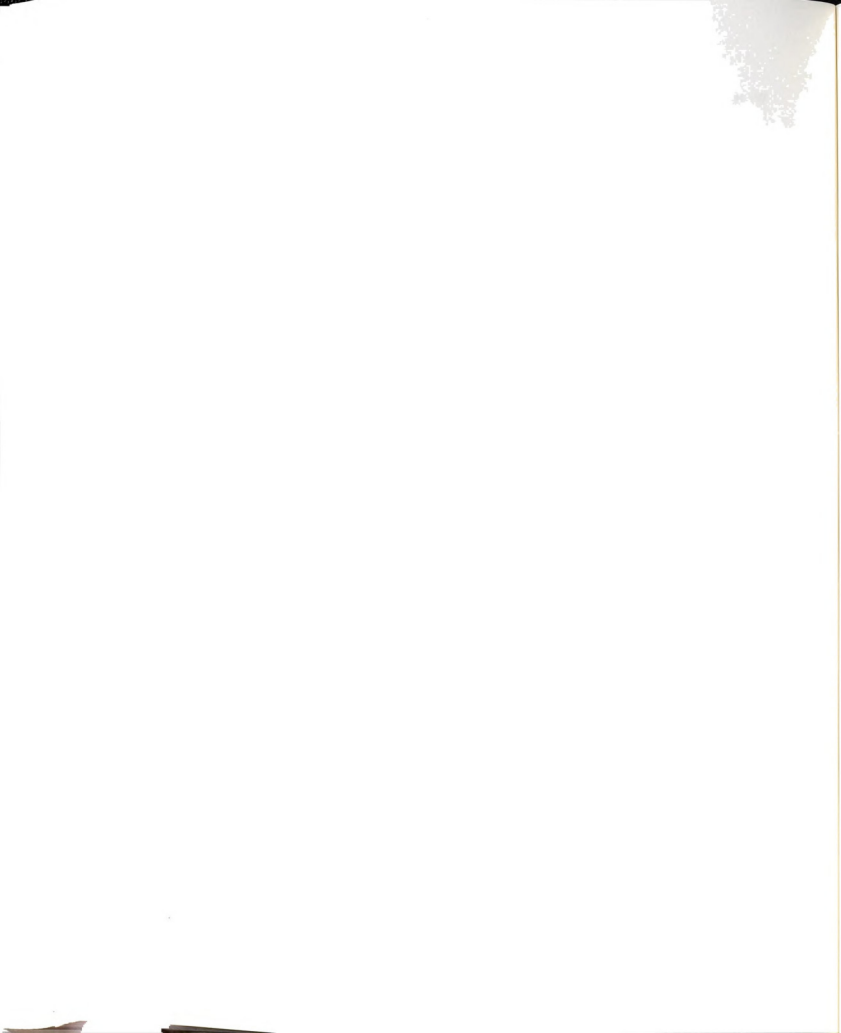
where:

k = coefficient of permeability;

a = cross-sectional area of the pipet;

L = sample thickness;

A' = effective cross-sectional area of sample;



$(t_f - t_0)$ = time between readings;

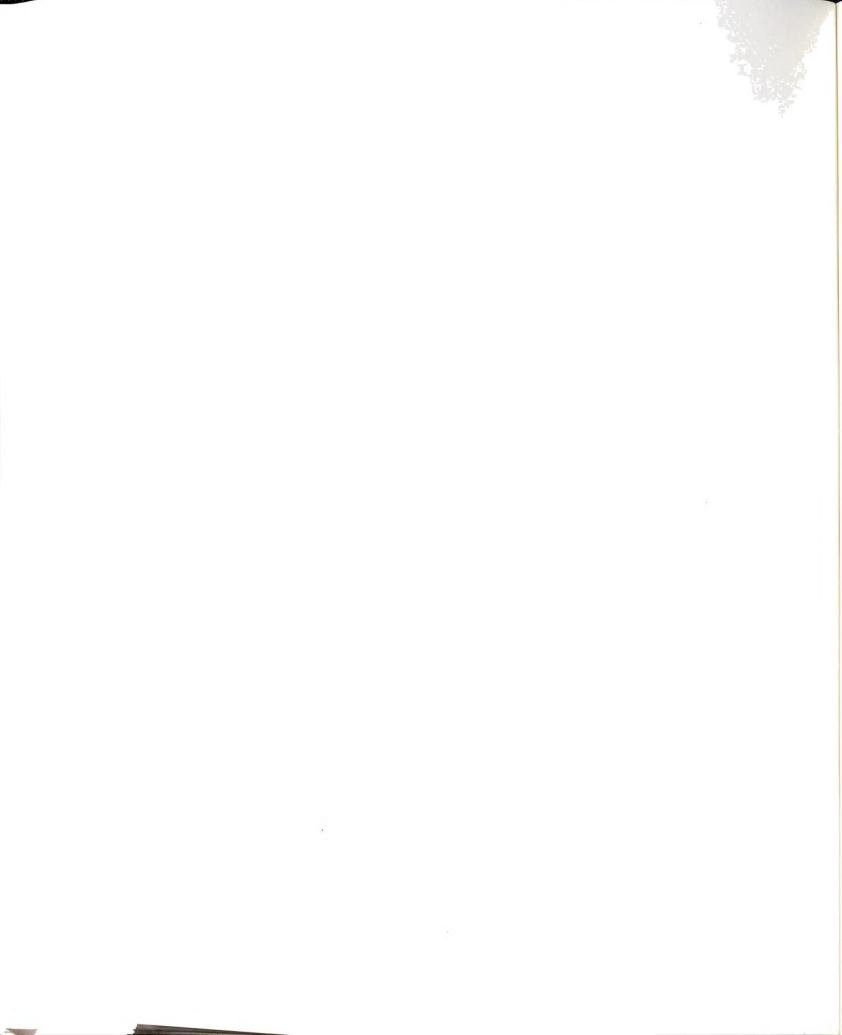
h_0 = water level at time t_0 ; and

h_f = water level at time t_f .

5.4.7 Freezable Moisture Calculations

Powers [194] referred to freezable moisture as the difference between the moisture content at a given degree of saturation and the equilibrium moisture content at a specific relative humidity corresponding to the concrete freezing point. The maximum amount of freezable moisture is found by considering a sample as initially saturated. Each of the individual mixes tested showed that the amount of the moisture removed from concrete varied linearly between 97% to 53% relative humidity, and the extrapolated value to 100% was used for calculations (figure 5.2). The upper portion of the curve is important because the amount of moisture that will freeze in concrete pores at -17°C (0°F) can be found from the amount of moisture that is removed from concrete at 85% relative humidity [194], figure 5.3.

It may be noted that all the mixes in this study contained the same volume of coarse aggregate and had slumps between one and three inches. The paste content was varied, depending on $W/C+P$ used, which accounts for the similar total porosity of all mixes [190]. Thus it was assumed that the total porosity of varying $W/C+P$ mixes remained relatively constant, while the pore size distribution changed with changes in water-cementitious ratio and paste mix design. It was also shown in this study that the amount of freezable moisture in a sample was dependent on the slope of the relative



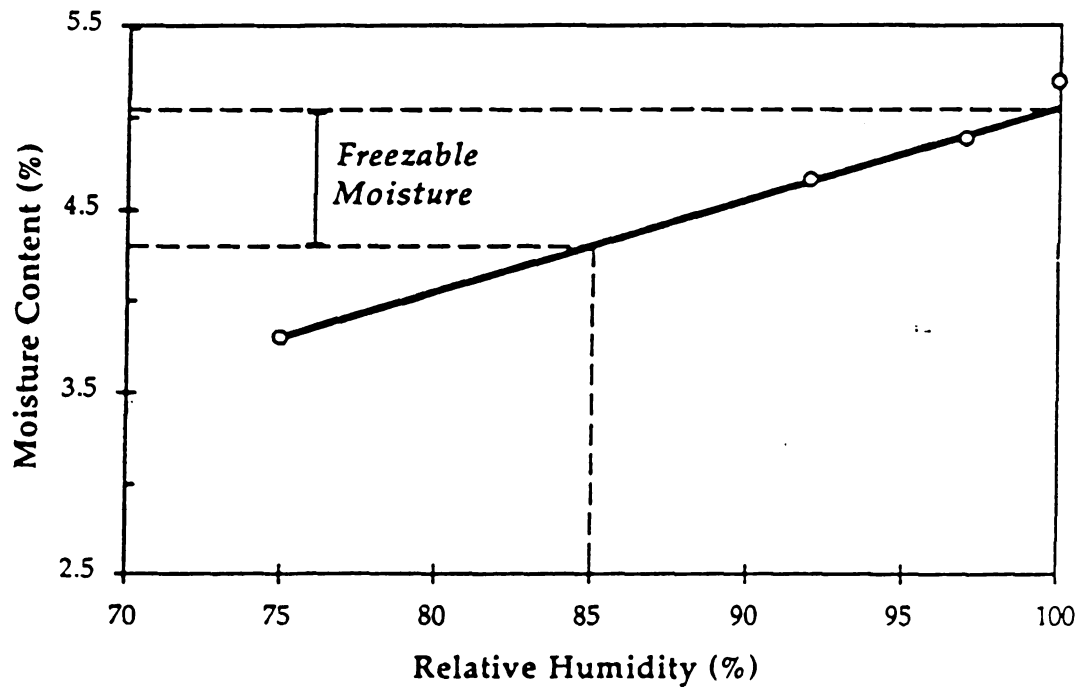


Figure 5.2. Freezable moisture determination [190].



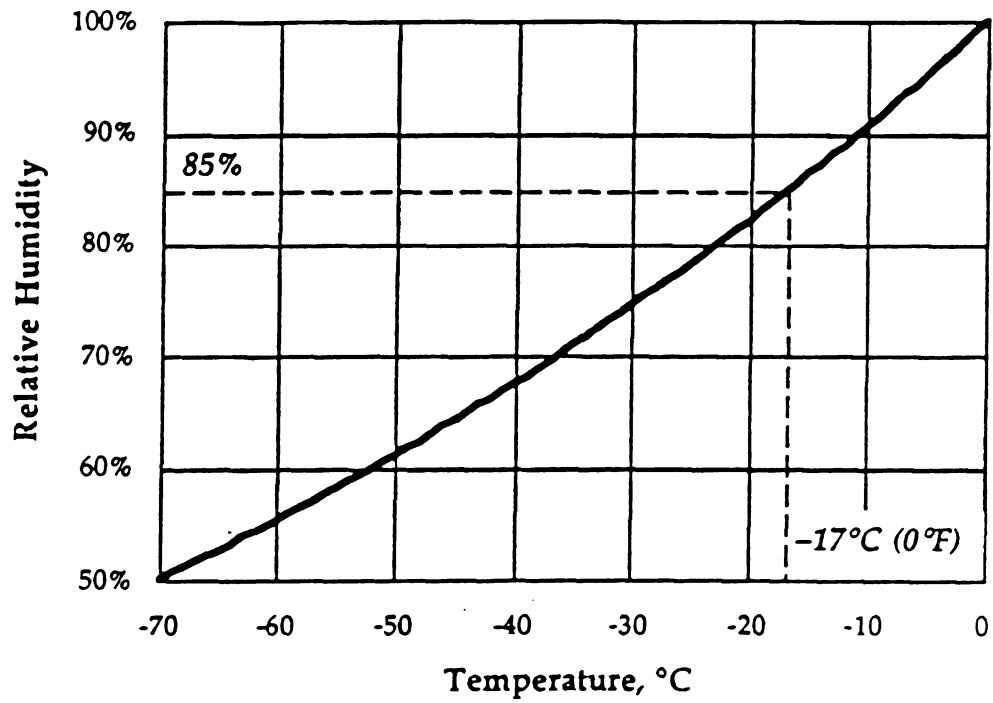


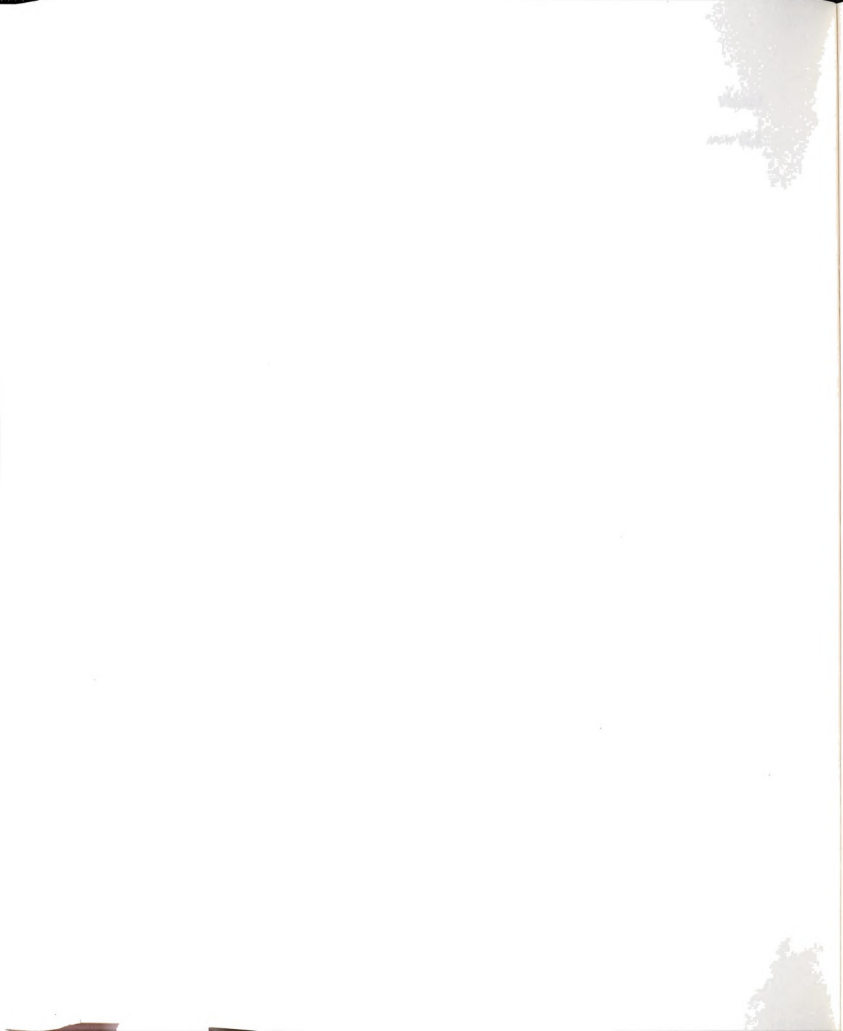
Figure 5.3. Relationship between relative humidity and freezing point [192].



humidity versus moisture content curve rather than total porosity. A steep slope (figure 5.2) would mean that less energy is required to remove moisture; whereas in the case of a shallower slope, the reverse would be true. Since more energy is required to remove moisture from smaller pores than from larger pores, the slope of this line indicates effective pore size distribution. This indicates that the shallower the slope, the finer the effective pore system, and the steeper the slope, the coarser the effective pore system. The slope of this line could then be used to determine the amount of freezable moisture in concrete at -17°C (0°F).

5.5 Summary

This chapter was devoted to: the discussion on the various materials used; sample preparation techniques with selected mix designs; and test procedures adopted to determine air void and water pore systems and performance characteristics. The discussion and analyses of the results are presented in the next chapter.





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**FROST RESISTANCE OF PORTLAND CEMENT CONCRETE PREPARED
WITH CHEMICAL AND MINERAL ADMIXTURES AT
MARGINAL AIR CONTENT**

By

Shamshad Ahmad Khan

Volume II

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Civil and Environmental Engineering

1992

CHAPTER VI

RESULTS AND DISCUSSION

6.1 Preliminary Studies

6.1.1 Mix Designs, General Properties and Performance

Phase I of this research work consisted of conducting the preliminary testing. Beams and cylinders were cast for Matrix A (figure 4.1). The only cell not cast was A1 (alphabet indicates Matrix and the number indicates cell number) because of the obvious expected response (good performance) due to low W/C and high air content. This testing was done to evaluate repeatability, to study the response of control cells (cast without the use of pozzolans or WR/HRWR) for Phase II testing, and to standardize procedures for future testing. Standard test materials, (i.e., Daravair air entraining admixture, a selected type I cement, and selected coarse and fine aggregates) were used. Trial batches were cast until the requisite air and slump were obtained for each test cell. The final mix

proportions and concrete characteristics are shown in table 6.1. Note that air entraining admixture demand increases with higher air requirement as well as with decrease in water-cement ratio (see table 6.1).

The Phase I samples endured between 42 and 300 freeze-thaw test cycles, after which the test was discontinued per ASTM C 666-90 [52] specifications. The freeze-thaw durability test results are summarized in table 6.2. The performance histories of the two control cells, A7 and A8 (target FAC 2.5% and, W/C 0.40 and 0.45, respectively), showing the drop in relative dynamic modulus and change in length and weight with increasing numbers of freeze-thaw cycles are given in figures 6.1 and 6.2, respectively.

6.1.2 Sample Size Selection

The sample size was calculated using the following statistical equation:

$$n = \{(Z_{\alpha/2}^2 * \sigma^2) / d^2\}$$

where:

n is sample size;

$Z_{\alpha/2} = 1.96$ ($\alpha/2 = 0.025$, corresponding to 95% reliability); and

precision limit, $d = \pm 10$.

A sample size of five beams was selected for Phase II testing based upon the results of Matrix A (table 6.1). This provides a 95% confidence level for a durability factor precision of ± 10 , except for the range of DF 45 to 55, where the required sample size would be six. A sixth beam was cast to provide specimens for linear traverse testing.

Table 6.1. Mix proportions and concrete properties for design Matrix A.

Cell #	C-str (KPa)	CA-SSD (#/cyd)	FA-SSD (#/cyd)	H-water (#/cyd)	Cement (#/cyd)	AEAI (ml/cyd)	FAC (%)	Paste-Content (%)	k x10 ⁻¹² (m/s)
A2	35287	1888	1258	226	502	167.4	7.0	29.9	2.9
A3	25812	1966	1263	215	414	83.7	7.5	28.1	1.6
A4	42660	1849	1246	249	623	156.6	4.5	31.0	18.0
A5	41882	1879	1252	249	554	116.1	5.0	30.3	-
A6	34624	2030	1279	218	420	62.1	5.4	26.3	15.0
A7	41889	1899	1266	253	633	40.5	2.5	29.5	4.3
A8	38864	1894	1352	251	559	27.0	2.2	27.7	-
A9	35423	2064	1293	238	462	4.0	2.4	25.2	12.0

Table 6.2. Freeze-thaw test results for Matrix A.

Cell #	# Cycles Endured	Std.Dev. (s)	L-Chg (%)	Wt-Chg (%)	RDM (%)	DF	Std. Dev. (s)	Actual/Recomm Range (D2S)	Remarks
A2	300	0	0.0297	0.146	92.4	92	3.26	11/4.5	11 Beams
A3	300	0	0.0424	0.274	87.3	87	2.94	9/10.2	12 Beams
A4	297	12.66	0.0822	0.305	73.8	68	8.42	20/23.2	11 Beams
A5	300	0	0.0542	0.212	79.0	79	5.17	12/19.7	5 Beams
A6	300	0	0.0284	0.461	88.2	88	4.79	15/10.2	9 Beams
A7	133	21.56	0.0871	0.131	60.0	26	4.22	13/12.2	9 Beams
A8	143	27.26	0.0888	-0.103	60.0	28	6.83	19/13.3	5 Beams
A9	42	17.77	0.1269	0.255	60.0	8	3.40	10/4.7	10 Beams

Note : + sign indicates increase in length/weight compared to initial reading
 - sign indicates decrease in length/weight compared to initial reading

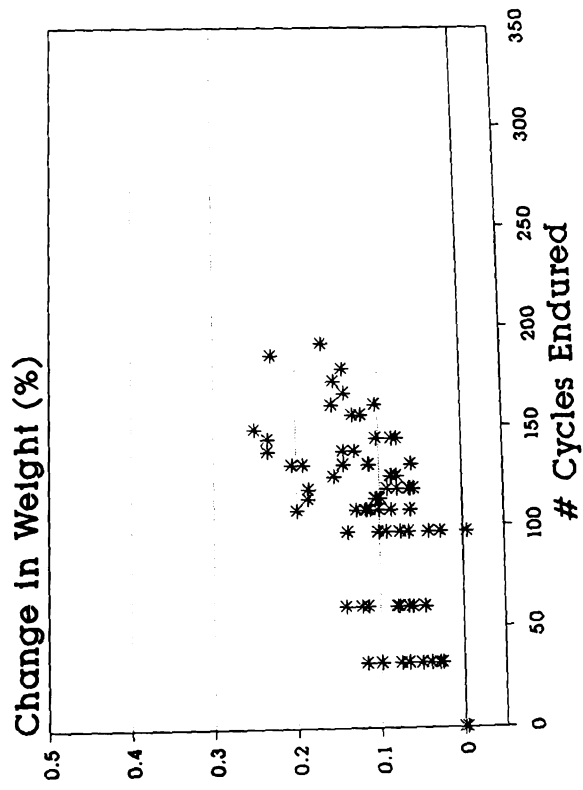
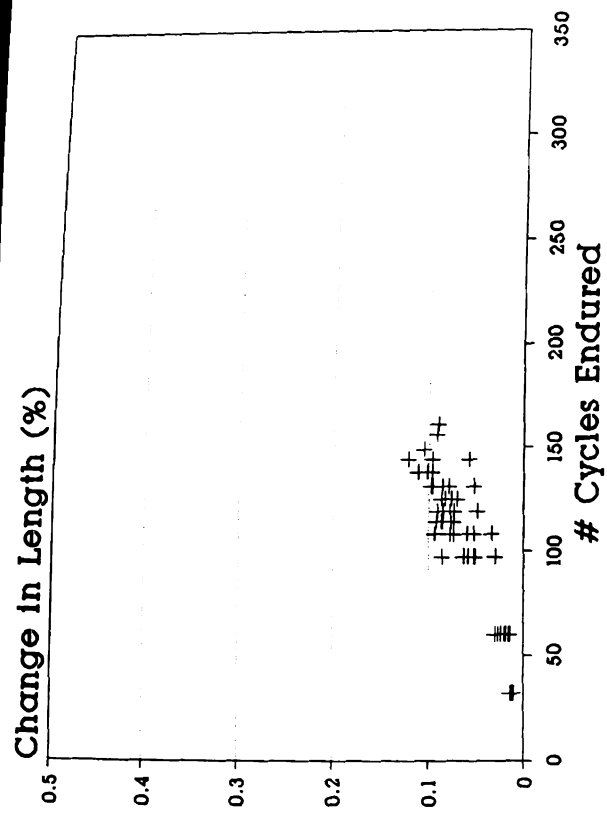
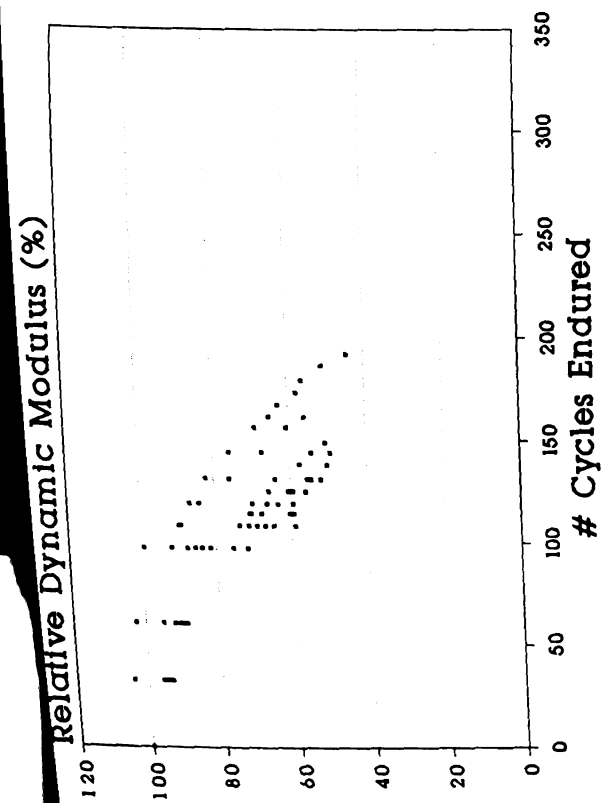


Figure 6.1. RDM, change in length, and weight versus no. of freeze-thaw cycles endured for PCC with W/C=0.40 and AC=2.5%.



100 Relative Dynamic Modulus (%)

0.5 Change in Length (%)

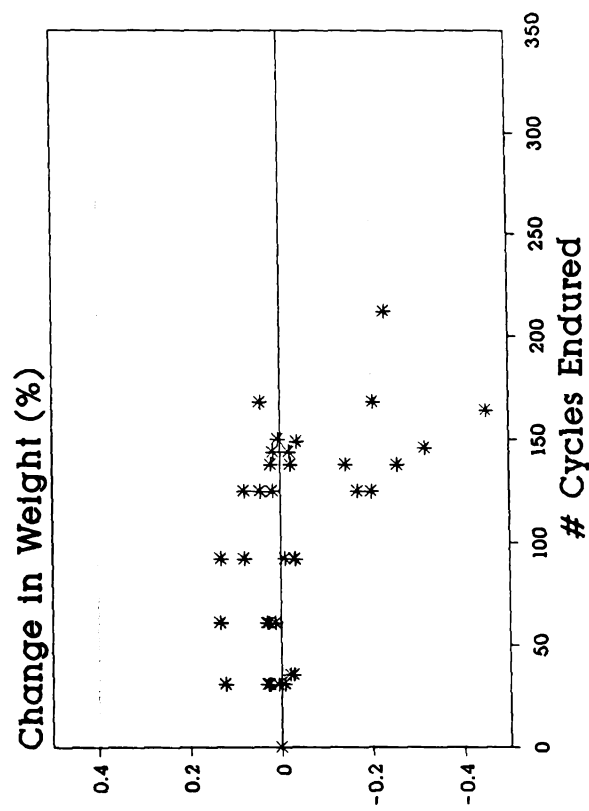
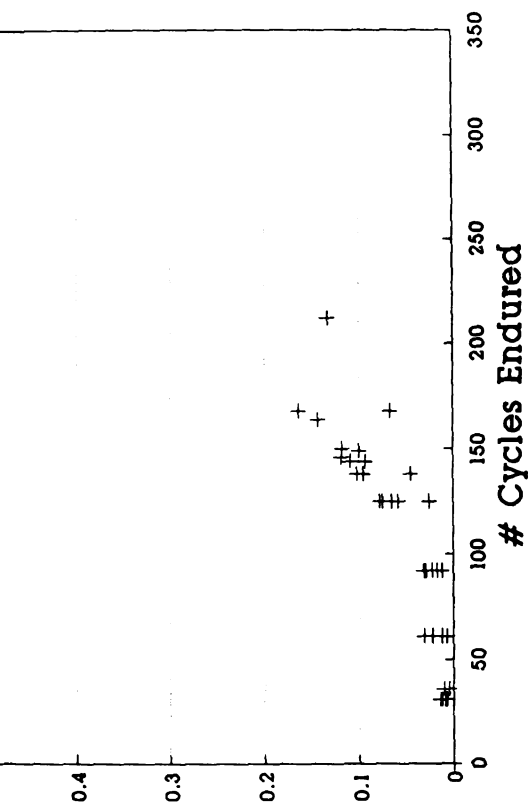


Figure 6.2. RDM, change in length, and weight versus no. of freeze-thaw cycles endured for PCC with $W/C=0.45$ and $AC=2.5\%$.

6.1.3 Air Void System Measurements

Standard hardened air void parameters, as determined by ASTM C 457-90 [53], are shown in table 6.3. The linear traverse specimens were selected and prepared as follows to ensure the use of unbiased samples. An unbiased freeze-thaw beam was selected at random. Two slices, each approximately 0.50 in. thick, were cut near middle of the beam. One side of one slice was randomly selected for preparation unless a visible defect was observed. Finally, the starting point and the line of traverse were also selected at random.

As can be seen from the results, the hardened air contents were consistently observed to be less than the FAC values presented in table 6.1, with the difference between the two increasing as the AC increased. This may be because the vibration of the mixes caused some of the larger size bubbles to be lost, with greater losses for the higher air content mixes. This observation was in agreement with the findings of previous research [70].

A plot of the hardened air content and the Powers spacing factor for all the cells of Matrix A is shown in figure 6.3. It can be seen that the AC decreases as the spacing factor increases, which shows the consistency of the observed results with theory.

6.1.4 Effect of W/C and AC on Frost Resistance

The results of this study showed that the effects of W/C and AC on frost resistance are interrelated, as shown in tables 6.1 and 6.2. Consider first the changes

Table 6.3. Air Void Characteristics for Matrix A.

Cell #	ACI (mm)	VPMM (mm)	SS mm ² /mm ³	P/A	HTA (%)	SF (mm)
A2	0.166	0.231	24.1	6.78	3.84	0.221
A3	0.161	0.300	24.9	5.40	4.83	0.193
A4	0.146	0.274	27.4	7.52	3.99	0.203
A5	0.185	0.294	23.3	11.92	3.18	0.294
A6	0.195	0.224	20.5	7.95	4.37	0.279
A7	0.201	0.090	19.9	13.20	1.81	0.361
A8	0.192	0.093	20.9	12.19	1.78	0.331
A9	0.240	0.076	16.6	20.67	1.83	0.523

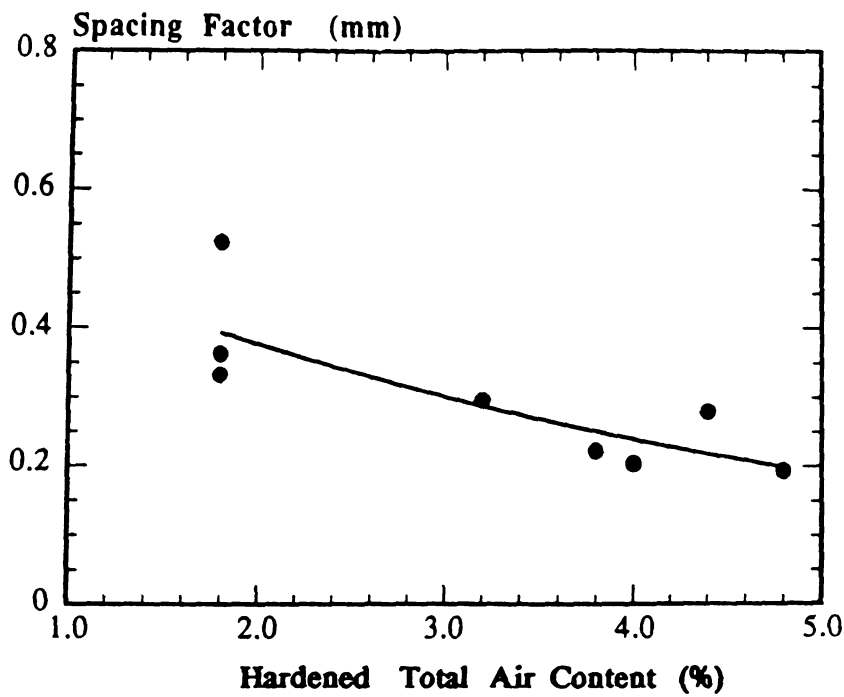


Figure 6.3. Matrix A specimens HTA versus SF.

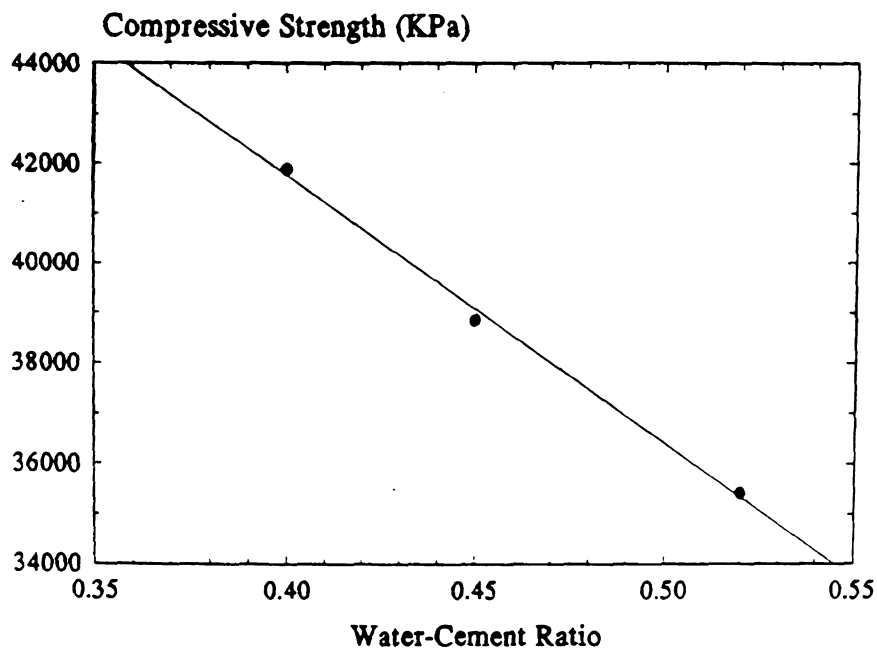


Figure 6.4. W/C versus C-str with AC = 2.5%.

observed at a specific target air content, 2.5% (test cells A7, A8, and A9, corresponding to W/C of 0.40, 0.45 and 0.52, respectively). The measured FAC of the three mixes were 2.5, 2.2 and 2.4 percent, respectively, and the measured HAC of the mixes were 1.81, 1.78, and 1.83%, respectively (see table 6.3). However, the number of air voids per mm (VPMM) of traverse were 0.090, 0.093, and 0.076, respectively, and spacing factors of 0.361, 0.331, and 0.523 mm, respectively, were observed. Thus, the dispersion of the air bubbles is greater (and the bubbles are larger, as indicated by the general decrease in the specific surface) when W/C increases above a critical level. The result of these changes in the air void system was a loss of durability of about 70% when W/C was increased from 0.40 to 0.52 (durability factor decreased from 26 to 8). The observed trends are in agreement with the literature.

The second point of interest at this marginal air content is the effect of compressive strength on the frost resistance of concrete. Again comparing cells A7, A8, and A9, a reduction in compressive strength can be seen as W/C increases, as shown in figure 6.4. Note that the decrease in compressive strength is very small (2.4%) when W/C increases from 0.40 to 0.45, and durability remains about constant (an increase of about 7%). However, the reduction in compressive strength when W/C is increased from 0.40 to 0.52 is 15.5%, and the resulting loss of durability is about 70%, which is highly significant at the 99% confidence level (see table D.2). The reduction of compressive strength and durability with increasing W/C indicates the effect of the water pore system and is in agreement with the results of previous studies.

Thus, it appears that the effect of W/C on durability is quite significant at marginal air contents because increasing water-cement ratio reduces the strength of the

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concrete and adversely affects the air void and water pore systems.

Now consider the effects of W/C and AC on compressive strength and frost resistance using the results of tests on cells A4, A5, and A6 (varying W/C for target AC = 5.0%), which are presented in figures 6.5 and 6.6. The reduction in strength as W/C increases from 0.40 to 0.52 is 18.8% (compared to 15.5% for target AC = 2.5%), and the quality of the air void system is generally decreased (specific surface decreases and spacing factor increases), but the durability factor actually improves by 30% (from 68 to 88). The only apparent explanation for this phenomena is that the effect of total air content quantity overshadows the effects of reduced strength and decreased air void system quality (note that fresh air and hardened air contents generally increase with W/C for these specimens). It is also worth noting that the average durability of the specimens in all three of these cells was much higher than the durability of the specimens that were cast with a target of 2.5% air content.

The specimens cast with 7.5% target air content (cells A2 and A3) were most durable of all and exhibited trends similar to those cast with 5.0% target air content, except that the large decrease in strength associated with the higher air content and higher W/C of cell A3 produced a slight loss of durability factor, in spite of a better quality air void system (slightly smaller spacing factor, somewhat larger specific surface, etc.).

In summary, W/C has a large influence on the durability of concrete placed at marginal air contents (i.e., 2.5% or less), presumably due to reductions in concrete strength and air void system quality. This influence appears to decrease as larger quantities of entrained air are included in the concrete (at some point, the higher W/C

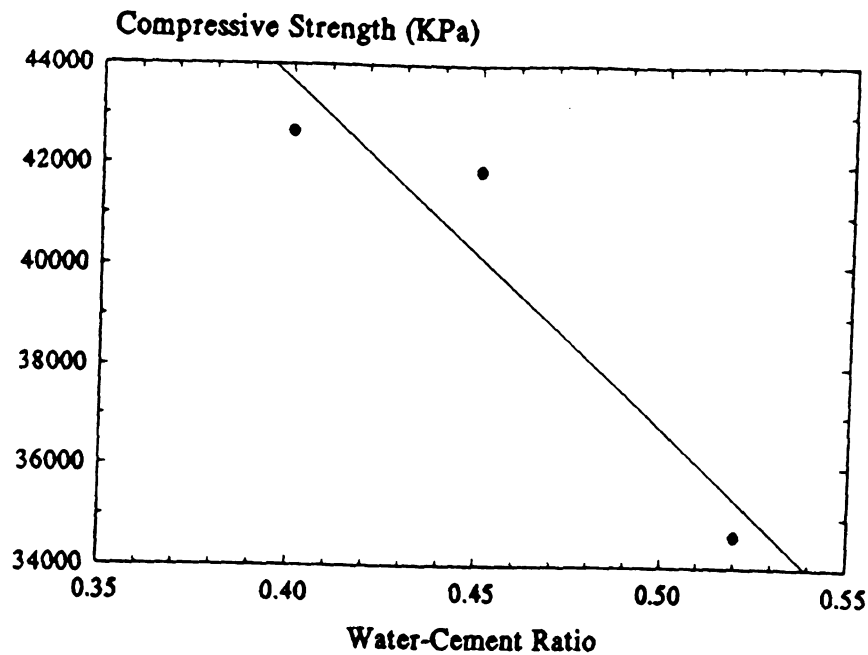


Figure 6.5. W/C versus C-str with AC = 5.0%.

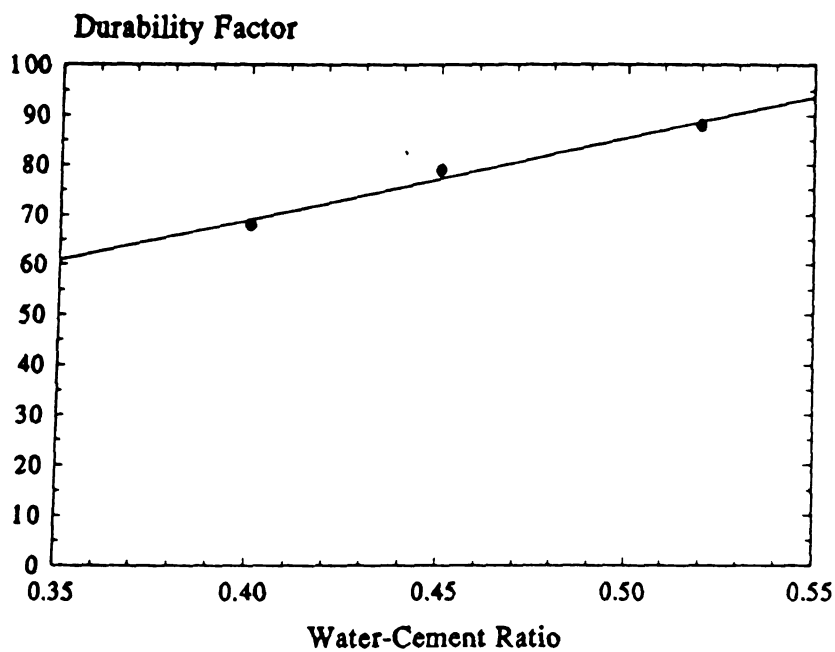


Figure 6.6. W/C versus DF with AC = 5.0%.

produces improved workability, which may actually aid in the production of a frost-resistant air void system). At high air contents (7% or more), increases in W/C no longer produce improvements in the air void system and only weaken the concrete, resulting in durability losses.

6.1.5 Permeability Testing

The results of permeability testing conducted on companion specimens at the University of Washington do not indicate a significant difference in the permeability coefficient of concrete, k , for $W/C=0.40$, $W/C=0.45$, and $W/C=0.52$ at marginal AC (figure 6.7) [190]. This figure shows the mean permeability at each W/C with ± 1 standard deviation. Traditionally, a decrease in W/C is expected to decrease the permeability, but the results did not support this point for the mix designs studied. A range of permeability of (within one standard deviation of the mean) $5.5\text{--}6.1 \times 10^{-12}$ m/s was observed for all three water-cement ratios. These results lead to the conclusion that concrete permeability is not well correlated with water-cement ratio.

A total of 109 samples were eventually tested, including the use of both chemical and mineral admixtures. These also showed that essentially no distinction could be made in concrete permeability for various W/C, W/C+P, water-reducing admixtures, and pozzolanic admixtures. Therefore, concrete permeability appears to be a poor predictor of concrete durability.

This could be because the water-cement ratios tested were too close to each other to make a distinction in permeability testing. The other possible cause was thought to be

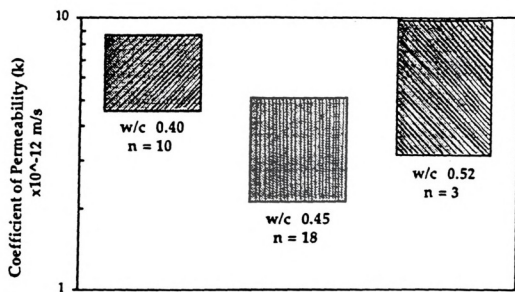


Figure 6.7. Effect of W/C on permeability [190].

in the primary assumption that the flow of water through concrete is laminar and uniform; however, it seems that the flow of water through concrete is controlled by a relatively few larger continuous channels that are minimally affected by reductions in W/C or changes in chemical and mineral admixtures. These channels may be the result of (1) aggregate interface problems that develop from poor bonding between paste and aggregate, (2) several large particles, which may occur close to each other, or (3) hydration-related microcracking in the cement paste itself, which forms almost continuous channels for moisture passage.

6.1.6 Freezable Moisture

Freezable moisture (FM) testing was conducted at the University of Washington on samples taken from the same specimens from which samples were cut for permeability testing. The results indicated a significant reduction in FM between W/C of 0.52 and 0.45, and 0.45 and 0.40 for mixes without pozzolans (see table 6.4). This was attributed to improvements in pore size distribution. These results are in overall agreement with the results of freeze-thaw durability testing for these mixes (table D.1). Freezable moisture is discussed further in the next section.

Table 6.4. Freezable moisture for non-pozzolanic Phase I mixes [190].

	W/C		
	0.40	0.45	0.52
FM	0.66 (n=4, s=0.07)	0.77 (n=5, s=0.07)	0.86 (n=3, s=0.01)
Freezable Moisture (%) (n = number of samples, s = Std. Dev.)			

6.1.7 Frost Resistance Performance

The picture becomes clearer when we compare the performance histories of the two cells A7 and A9 (see figures 6.1 and 6.8). RDM of 60% was reached in one case (W/C=0.40) in 133 freeze-thaw cycles (averaged over 9 beams), while in the other case (W/C=0.52) it was reached in only 42 freeze-thaw cycles (averaged over 9 beams). Although the performance of both cells is poor due to low air content (2.5% or less), it is certainly worse in the case with higher the W/C (i.e., 70 % decrease in durability factor from the cell with W/C of 0.40). The sample with higher W/C also shows a much higher rate of mass gain and increase in length (figures 6.1 and 6.8), and it reaches the critical test values much earlier than the samples with lower W/C. This indicates that higher water contents produce greater internal deterioration of concrete. However, mixes with higher air contents (5% and more) did show a significant improvement in frost resistance and almost all these beams did complete the 300 freeze-thaw cycles (table 6.2).

100
Relative Dynamic Modulus (%)

0.5
Change in Length (%)

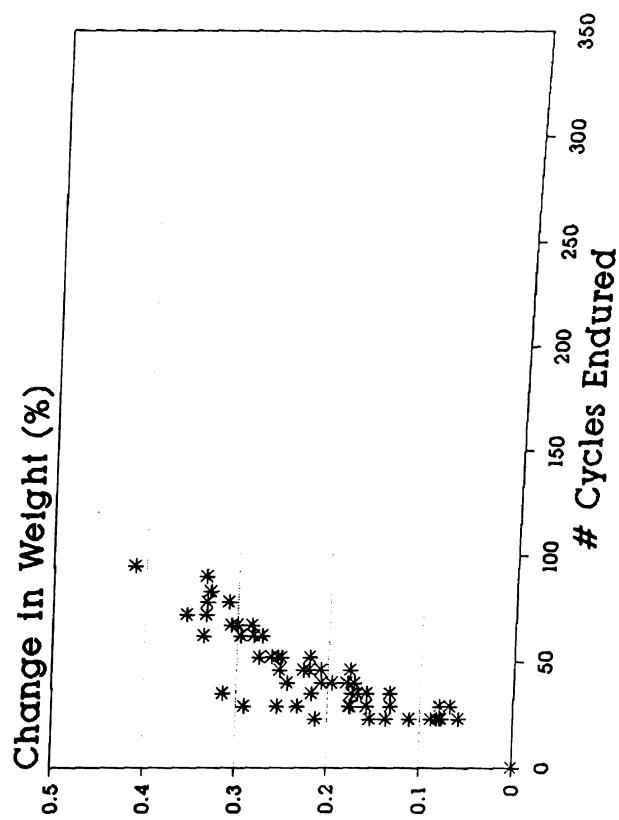
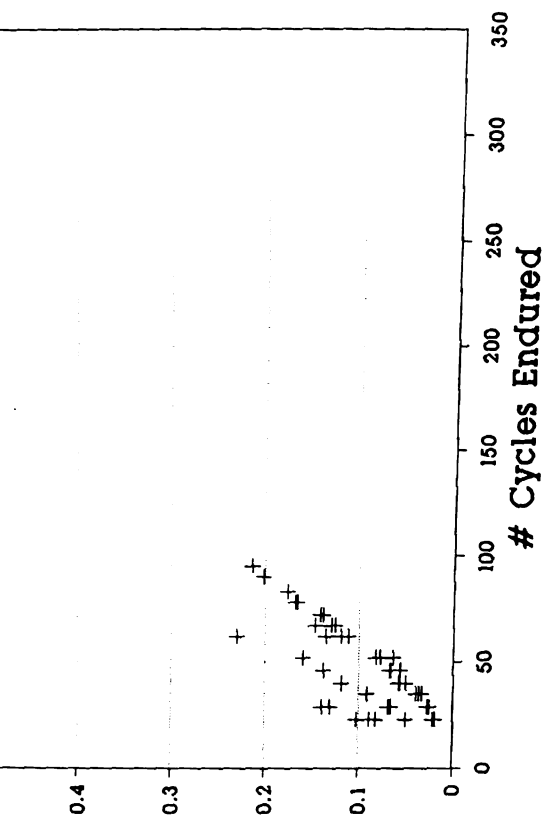


Figure 6.8. RDM, change in length, and weight versus no. of freeze-thaw cycles endured for PCC with $W/C=0.52$ and $AC=2.5\%$.

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6.1.8 Summary of Preliminary Study Conclusions

In summary, at marginal air content, the frost resistance appears to be strongly influenced by water-cement ratio. This is probably due to improvements in the air void and water pore systems at lower ratios. With an increase in air content (5% or more), water-cement ratio appears to be less influential as better air void systems are produced due to air entrainment. The increase in water-cement ratio results in a decrease in compressive strength, which becomes more evident at higher air contents (greater than 7%). This could be a significant factor where both compressive strength and frost resistance are desired.

Water permeability proved to be indistinguishable between the water-cement ratios tested, possibly due to the narrow range of W/C tested or violation of the assumption that flow within the hardened concrete is laminar and uniform. The freezable moisture varied strongly with the water-cement ratios, and appears to be a good indicator of frost-resistant concrete.

6.2 Effects of Air Entraining Agents

Two commonly used AEAs, Daravair and Microair (AEA1 and AEA2, respectively) were used in this study. Daravair is based on vinsol resins, which is perhaps the simplest of admixtures that have complex formations, whereas Microair is classified as a synthetic detergent and has the industrial source of petroleum distillates.

Except for the preliminary testing where AC was tested at three levels, the AC

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of the mixes was kept at a marginal level ($2.5\% \pm 0.5\%$) to determine the relative effectiveness of the various treatments. At higher AC, the effects of the different admixtures on the AVS and the water pore structure could be masked by the fact that all mixes generally perform well. Later on, the hardened AC measured by the linear traverse test was further separated into entrained air voids and total air voids using the Hydrair program (an air void analysis program developed at the University of Washington). An air void chord size of 1000 microns (1 mm) was selected as the maximum size for entrained air voids. The hardened total air content (HTA) observed remained between 1.3 and 3.8 percent, with a mean of 2.5474% and a standard deviation of 0.5515% (49 mixes). It was really very hard to attain the target AC in some of the mixes, irrespective of the type of the AEA used, especially when silica fume and HRWR were used (possibly due to interactions between the AEA and the HRWR in the silica fume slurry).

The two types of AEA were tested in combination with Cl F and C fly ashes, and silica fume, as shown in Matrix B, figure 4.2. The mix proportions and concrete characteristics for the mixes in Matrices B through E are shown in table B.1 (Appendix B); freeze-thaw test results and air void characteristics for these matrices are shown in tables B.2 (freeze-thaw test results), and B.3 and B.4 (air void characteristics). The statistical analyses are shown in tables D.3 through D.7 in Appendix D. All of the statistical tests are conducted at a 95% confidence level using the 't test', unless otherwise noted.

The non-pozzolanic concrete mixes made with WR cells (B1-B4) failed to show a significant difference in durability between the two types of air entrainers used. AEA1 produced significantly better frost resistance at the lower W/C (0.40), while AEA2 showed significantly better frost resistance with higher W/C (0.45). The freeze-thaw test

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performance histories for cells B1-B4 are shown in figures C.1 through C.4. All four cells showed loss in mass initially, but gained weight gradually as the RDM continued to decrease. The initial mass loss was due to slight scaling, while the subsequent gain in mass was probably due to the increased water content that accompanied the dilation of the capillary system under freezing and thawing. Thus, this weight gain due to increased moisture content was basically considered indicative of the destructive expansion of the concrete in the absence of the escape boundaries provided by an adequate quantity of entrained air voids.

It should be noted here that all precision and bias statements in this work are based on the '1S' and 'D2S' limits described in ASTM C 670-91a [192] and ASTM E 177-90a [193]. The durability factors computed in this work have been compared with table 3, ASTM C 666-90 [52], which takes into account '1S' and 'D2S' limits. The results obtained were generally within the accepted ranges, but did sometimes exceed the limits. The recommended and the actual durability factor ranges are shown in the Freeze-Thaw Durability (FTD) tables (tables 6.2 and B.2). Cases showing greater differences (though very few) were investigated, and the reasons for their variance are discussed as each mix appears in the discussion. Some of the possible reasons for the higher variance of our test results include:

- (1) The precision statements are probably based on properly air-entrained concrete (although the basis of the precision statements is not specifically mentioned), all of the work in this experiment was conducted at a marginal AC. It was seen in Matrix A (table 6.1) that most of the test results for the mixes with higher AC were within the specified limits, while mixes with marginal AC showed higher

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- (2) The recommended precision statements were probably based on the frost resistance of non-pozzolanic concrete, while this research included a large number of pozzolanic mixes. This indicates the need to establish new precision statements for pozzolanic concretes.
- (3) The established criteria are based on ASTM C 666-90 [52] standard procedure B. For our work, this procedure was modified slightly to address some shortcomings inherent in the standard procedure. These modifications may be another source of increased variance, although they are not believed to be.

The effects of the AEA on concretes prepared with water-reducer and a 15% replacement of cement with C1 F and C fly ashes are shown in figures C.5 through C.12 for cells B5-B8 and B13-B16. At this point, we will focus on the effects of the two AEAs and will not consider the effects of WR/HRWR or pozzolan type.

Table 6.5 shows the results of some of the tests for C1 F fly ash concrete made with WR. Strong interactions were observed between AEA, WR/HRWR, W/C, and type of pozzolan (see table D.3). AEA1 with WR produced significantly better frost resistance than AEA2 for C1 F fly ash concretes, especially at low W/C+P. An examination of the air void data in table 6.5 provides possible explanations for this performance.

The total hardened air content of the AEA2 mixes was 16% and 8% greater than the HTAs for vinsol resins (at W/C+P=0.40 and 0.45, respectively). However, the HEA in the paste was observed to be 30% and 10% lower for the AEA2 mixes for the same W/C+P. Consideration of other air void parameters presented in table 6.5 confirm the presence of a better entrained air void system with the use of the vinsol resin-based

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Table 6.5. Comparison of AEA for Cl F fly ash with WR.

		W/C+P	
		0.40	0.45
Type of AEA	1	B5 2.5/2.5/2.0 0.186/0.167 229/225 94/0.088/0.1140 42335	B6 2.8/2.4/2.0 0.245/0.224 187/185 89/0.206/0.0267 38846
	2	B7 2.6/2.9/1.4 0.272/0.192 179/170 36/0.128/0.0754 39488	B8 2.8/2.6/1.8 0.246/0.202 183/179 78/0.203/0.0610 32144

KEY

Cell #
 FAC%/HTA%/HEA %
 SFTA(mm)/SFEA(mm)
 AVTA/AVEA
 DF/Wt-Chg%/L-Chg%
 C-str(Kpa)

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AEA1. This could be due to a better chemical interaction of the vinsol resin-based AEA1 with the mix constituents and/or the production of a more stable air void system with AEA1.

It is important to point out that the range of DF obtained for B7 (five beams) was 50, which is significantly greater than the D2S limit (19.5). The five beams in this cell were cast in two batches. The first batch produced two beams with an average durability factor of 55 and a range of 10, which was well within the precision limit (40.2). The second batch produced three beams with much lower durability. Although both batches utilized the same mix design, the second batch may have lost more air during vibration or casting, producing a less frost-resistant air void system. This illustrates the sensitivity of the test results to apparently random factors.

The results of tests performed on C1 F fly ash concretes made with HRWR for the two types of AEA are shown in table 6.6. The freeze-thaw performance of these concretes are shown in figures C.13 through C.16. Strong interactions were observed between the AEA and W/C+P. AEA2 showed superior performance with W/C+P=0.40, whereas AEA1 produced better performance for W/C+P=0.45. The air void system measurements help to explain these performance measurements. At W/C+P=0.40, the HEA for both AEA mixes (B9 and B11) was 1.5%, but the number of entrained air bubbles produced by the AEA2 mix was much higher (190 vs. 110). At W/C+P=0.45, the AEA1 mix showed a greater number of entrained air bubbles (227 vs. 181) and had a higher HEA content in spite of a lower HTA content. Although the performance of both AEAs was variable, AEA1 generally showed much smaller differences between HTA and HEA (i.e., better air retainment) than AEA2. Figure 6.9 shows the comparison

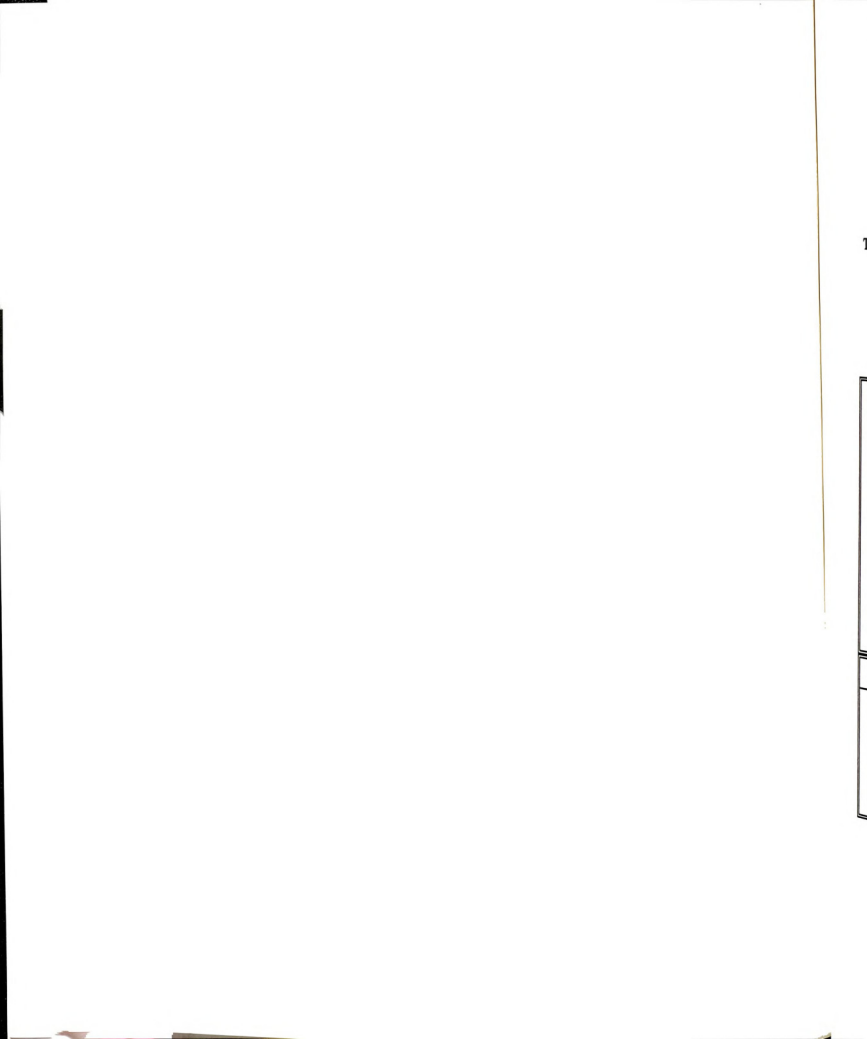


Table 6.6. Comparison of AEA for Cl F fly ash with HRWR.

		W/C+P	
		0.40	0.45
Type of AEA	1	B9 2.2/1.8/1.5 0.399/0.367 113/110 14/0.295/0.099 41549	B10 2.8/2.3/1.9 0.221/0.198 229/227 39/-0.02/0.0514 34123
	2	B11 2.8/3.0/1.5 0.297/0.213 199/190 43/0.188/0.0964 32862	B12 2.5/3.5/1.5 0.259/0.235 190/181 23/0.065/0.0634 41604

KEY
Cell # FAC%/HTA%/HEA% SFTA(mm)/SF EA(mm) AVTA/AVEA DF/Wt-Chg%/L-Chg% C-str(Kpa)

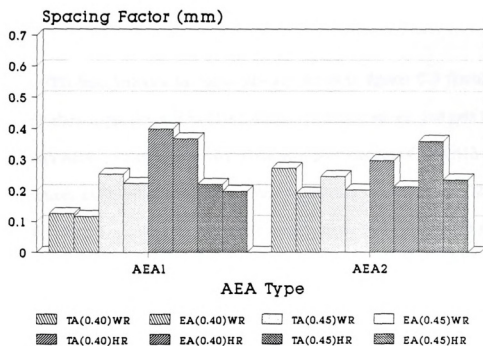


Figure 6.9. AEA versus SFTA, and SFEA for CI F FA with WR/HRWR.

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of AEA spacing factors (SFTA and SFEA) for WR/HRWR. This indicates the better entrained air dispersion obtained with AEA1 for both water-reducers in the presence of C1 F fly ashes.

The results of tests performed C1 C fly ash with WR and two AEA are shown in table 6.7. The frost resistance of concrete cast using AEA2 was significantly better than that of concrete cast using AEA1 for C1 C fly ash with WR. However, the air void dispersions obtained with either AEA were not as good as seen in concrete cast using C1 F fly ash.

The FTD tests histories for these cells are shown in figures C.9 through C.12. These clearly show a quicker drop in RDM, dilation to critical values, and gain in weight for mixes with AEA1, which is reflective of the poor performance of cells B13 and B14. All of the mixes exhibited variances that were marginally outside of the D2S ranges (except B16, which was within the acceptable range), possibly for the reasons explained earlier.

The test results for concretes cast using C1 C fly ash with HRWR are shown in table 6.8. These results show significantly better frost resistance performance for concrete cast using AEA2 with $W/C+P=0.40$ than for any other mix, but especially when compared to the similar cell using AEA1. The performance of concretes cast using the two AEAs was indistinguishable at $W/C+P=0.45$. It is interesting to note that the use of AEA2 produced generally improved durability in spite of producing higher spacing factors. This may be because the AEA2 concretes also had significantly higher strengths.

The FTD histories for B17-B20 are shown in figures C.17 through C.20. These show a greater amount of initial loss of mass due to scaling with AEA2 mixes as

Table 6.7. Comparison of AEA for Cl C fly ash with WR.

		W/C+P	
		0.40	0.45
Type of AEA	1	B13 2.0/2.2/1.6 0.222/0.190 140/135 29/0.230/0.0888 38201	B14 2.5/2.2/1.2 0.383/0.284 113/108 15/0.227/0.0717 37323
	2	B15 2.0/1.3/0.9 0.421/0.349 76/74 50/0.210/0.0766 38502	B16 2.0/2.5/1.4 0.336/0.254 148/144 70/0.218/0.0774 -

KEY
Cell # FAC%/HTA%/HEA % SFTA(mm)/SFEA(mm) AVTA/AVEA DF/Wt-Chg%/L-Chg % C-str(KPa)

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Table 6.8. Comparison of AEA for Cl C fly ash with HRWR.

		W/C+P	
		0.40	0.45
Type of AEA	1	B17 2.3/1.6/1.0 0.512/0.400 89/85 12/0.106/0.0927 25643	B18 2.9/3.7/2.2 0.430/0.338 163/155 35/0.275/0.0804 24925
	2	B19 3.0/3.4/1.5 0.598/0.404 118/1.7 56/0.077/0.0761 31069	B20 2.3/2.8/1.1 0.630/0.405 94/86 37/0.083/0.0842 42501

KEY
Cell #
FAC%/HTA%/HEA%
SFTA(mm)/SFEA(mm)
AVTA/AVEA
DF/Wt-Chg%/L-Chg%
C-str(KPa)

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compared to AEA1, in spite of comparatively better frost resistance performance.

Figure 6.10 shows a comparison of spacing factors (SFTA and SFEA) for both air entrainers with WR/HRWR. Although nearly all of the spacing factors generally exceed the recommended maximum of 0.20 mm, this figure clearly indicates the higher spacing factor values produced with AEA2 and the overall better air entrainment obtained with AEA1.

Table 6.9 shows the test results for some concretes cast using various AEA for silica fume mixes. The silica fume concrete produced excellent to good frost resistance at a marginal AC for both AEAs. The credit for this performance goes primarily to the type of the pozzolan that was used, and pozzolanic effects are discussed later in this chapter. At this point the discussion is focused on the effects of the AEAs.

Figures 6.11 and 6.12 show the effects of AEA on DF and spacing factor, respectively. The freeze-thaw test histories for these four cells are shown in figures C.21 through C.24. AEA1 produced significantly better performance (32% better) than AEA2 at $W/C+P=0.45$. An insignificant but similar trend was observed for $W/C+P=0.40$. Increasing $W/C+P$ reduced the quality of the AVS and the concrete strength for either AEA. However, the AEA2 concrete saw the biggest increase in spacing factors and a large decrease in the total air void count, which resulted in a large loss of durability. This again points out a relatively unstable AVS that may be produced with AEA2.

The AEA2 mixes showed greater loss of weight than the AEA1 mixes (as in case of C1 C fly ash with HRWR), which varied between 0.1 to 0.3%. This indicates the greater scaling that was observed with the AEA2 mixes, possibly because of the larger water pores that were observed. Another interesting thing observed was that dilation in

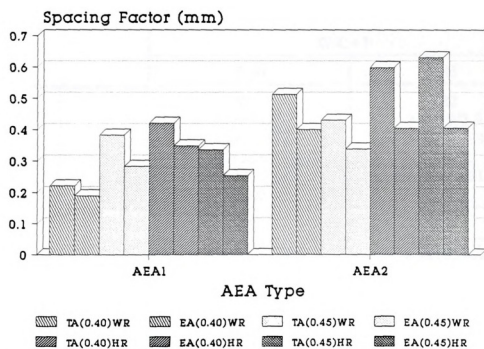


Figure 6.10. AEA versus SFTA, and SFEA for Cl C FA with WR/HRWR.

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Table 6.9. Comparison of AEA for CSF with HRWR.

		W/C+P	
		0.40	0.45
Type of AEA	1	B21 3.0/3.4/2.5 0.199/0.173 214/207 88/0.071/0.043 61303	B22 3.0/2.9/2.3 0.222/0.199 216/212 93/0.004/0.0184 52443
	2	B23 2.9/3.4/3.0 0.215/0.200 290/288 83/-0.114/0.0118 59456	B24 2.8/3.3/2.7 0.261/0.235 217/213 70/-0.169/0.0287 53092

KEY
Cell # FAC%/HTA%/HEA % SFTA(mm)/SFEA(mm) AVTA/AVEA DF/Wt-Chg %/L-Chg % C-str(KPa)

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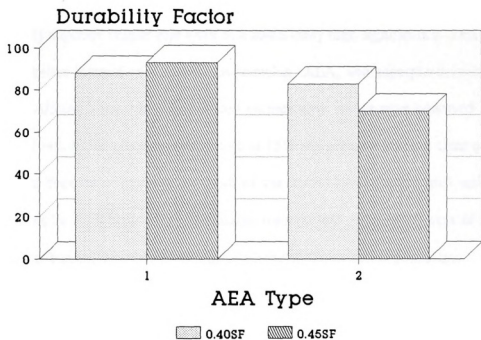


Figure 6.11. AEA versus DF for silica fume mixes.

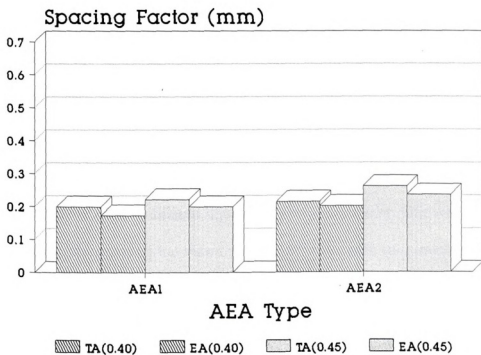


Figure 6.12. AEA versus SFTA, and SFEA for silica fume.

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no case reached the limit of 0.1%, which indicates the accumulation of less freezable water. Although the performance of AEA2 mixes was good, AEA1 mixes produced distinctly superior results that were of a statistically high significance. This was possibly due to better interaction between the pozzolan, AEA, and superplasticizers.

Although considerably reduced permeability values were observed with $W/C+P=0.40$ for silica fume concrete at 15% replacement level, a clear distinction did not exist because of the large variance in test results [190]. Better frost resistance at this point can be attributed to the pozzolanic reaction and the development of a better pore size distribution, which will be discussed under the effect of pozzolans.

It was difficult to attain the target AC with the silica fume mixes and very small quantities of AEA were used in most mixes. The FAC, as seen from the above table, was 3.0, 3.0, 2.9, and 2.8, whereas the HTA was 3.4, 2.9, 3.4, and 3.3 for cells B21-B24, respectively.

In summary, it appears that no significant difference exists between the effects of the two AEAs for non-pozzolanic concrete. The vinsol resin-based AEA generally produced a superior AVS in concretes cast with Cl F fly ash and WR. The synthetic AEA2 produced significantly better performance in concrete with Cl C fly ash and either WR or HRWR. Good frost resistance was observed in mixes cast with silica fume and either AEA, but AEA1 produced significantly better durability. This was attributed to the better AVS developed by the vinsol resin-based AEA with the pozzolan. Neither tested level of $W/C+P$ can be considered superior to the other in terms of producing frost-resistant concrete. This implies that neither type of air entraining admixture has rendered superior frost resistance to others in all applications, and this finding is also supported

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6.3 Effects of Water Reducing Admixtures

The effects of water-reducer/superplasticizer admixtures were studied on concretes made using a 15% replacement of cement (by weight) with C1 F or C fly ashes or silica fume. In the case of the fly ashes, both water reducing admixtures were used; for the silica fume, only HRWR was used, because the silica fume was delivered in slurry form with the HRWR already added. GGBF slag was tested with and without WR.

Much of the information presented here is represented from the previous section concerning AEA, but the discussion now focuses on the effects of WR/HRWR instead of AEA.

Table 6.10 show the results of concretes cast using AEA1, C1 F fly ash, and WR/HRWR. In this case, the frost resistance performance was significantly better with WR than HRWR. At $W/C+P=0.40$, the WR specimens clearly had superior AVS and performed well ($DF=94$). At $W/C+P=0.45$, the WR and HRWR cells have comparable AVS (the HRWR cell actually looks slightly better than the WR cell), and yet the WR cell had much greater durability ($DF=89$ vs. 39). The only major difference between the two cells was the greater strength and lower dilation of the WR cell, indicating more resistance to stress and a more favorable capillary system.

Looking at the FTD performance histories for B5, B6, B9, and B10 in figures C.5, C.6, C.13 and C.14, respectively, we notice that the WR cells showed very little drop in the relative dynamic modulus. None of the beams failed before 300 cycles ($s=0$,

Table 6.10. Comparison of WR/HRWR for Cl F fly ash with AEA1.

		W/C+P	
		0.40	0.45
Type of WR/HRWR	1	B5 2.5/2.5/2.0 0.186/0.167 229/225 94/0.088/0.0114 42335	B6 2.8/2.4/2.0 0.245/0.224 187/185 89/0.206/0.0267 38846
	2	B9 2.2/1.8/1.5 0.399/0.367 113/110 14/0.295/0.099 41549	B10 2.8/2.3/1.9 0.221/0.198 229/227 39/-0.02/0.0514 34123

KEY
Cell # FAC%/HTA%/HEA % SFTA(mm)/SF EA(mm) AVTA/AVEA DF/Wt-Chg %/L-Chg % C-str(KPa)

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for both cells). On the other hand, mixes with HRWR showed a quicker drop in RDM (73 and 203 cycles to failure for cells B9 and B10, respectively), which indicates failure in the internal structure of concrete at a lesser number of freeze-thaw cycles. Similarly, mixes with HRWR also showed greater dilation (about 8 times that of mixes with WR for $W/C+P=0.40$ and double that of mixes with $W/C+P=0.45$).

The test results for the Cl F fly ash concrete mixes cast using AEA2 are shown in table 6.11. The relatively low durability factor in cell B7 was discussed in the previous section. The use of a mean durability factor of 55 (corresponding to the average durability of one of the batches) may be justified and provides reasonable results.

Using $DF=55$ for cell B7, we again see better spacing factors and durabilities with the use of WR rather than HRWR. However, the performance of the either WR or HRWR was greatly improved when WR was used in combination with AEA1 (rather than AEA2) for Cl F fly ash.

Freeze-thaw histories for B7, B8, B11, and B12 are shown in figures C.7, C.8, C.15 and C.16. We see that the RDM of most of the WR beams did not reach 60% of the original dynamic modulus, whereas all the HRWR beams drop to 60% of original dynamic modulus before undergoing 300 cycles. In addition, the dilation of the HRWR beams exceeded the failure criteria much earlier than the mixes with WR. This indicates the development of a better water pore structure in the mixes with WR for Cl F fly ash.

Results for concrete cast using Cl C fly ash and AEA1 are shown in table 6.12. The frost resistance of Cl C fly ash concretes for the vinsol resin-based AEA and either of the water-reducing admixtures was relatively poor. However, the use of WR with Cl C fly ash and AEA1 generally produced slightly better air void systems (i.e., lower

Table 6.11. Comparison of WR/HRWR for Cl F fly ash with AEA2.

		W/C+P	
		0.40	0.45
Type of WR/HRWR	1	B7 2.6/2.9/1.4 0.272/0.192 179/170 36/0.128/0.0754 39488	B8 2.8/2.6/1.8 0.246/0.202 183/179 78/0.203/0.0610 32144
	2	B11 2.8/3.0/1.5 0.297/0.213 199/191 43/0.188/0.0964 32862	B12 2.5/3.5/1.5 0.259/0.235 190/181 23/0.065/0.0634 41604

KEY
Cell # FAC%/HTA%/HEA % SFTA(mm)/SFEA(mm) AVTA/AVEA DF/Wt-Chg %/L-Chg % C-str(KPa)

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Table 6.12. Comparison of WR/HRWR for Cl C fly ash with AEA1.

		W/C+P	
		0.40	0.45
Type of WR/HRWR	1	B13 2.0/2.2/1.6 0.222/0.190 140/135 29/0.230/0.0888 38201	B14 2.5/2.2/1.2 0.383/0.284 113/108 15/0.227/0.0717 37323
	2	B17 2.3/1.6/1.0 0.512/0.400 89/85 12/0.106/0.0927 25643	B18 2.9/3.7/2.2 0.430/0.338 163/155 35/0.275/0.0804 24925

KEY
Cell #
FAC%/HTA%/HEA %
SFTA(mm)/SFEA(mm)
AVTA/AVEA
DF/Wt-Chg%/L-Chg%
C-str(KPa)

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Performance was closely related to AVEA and AVTA, increasing with higher numbers of air voids. Performance also generally improved with decreasing spacing factor, except for cell B18, which had the best durability in spite of a higher spacing factor and lower compressive strengths. The reasons for the performance of B18 are not clear.

Frost resistance performance histories for cells B13, B14, B17 and B18 are shown in figures C.9, C10, C17, and C.18, respectively. All of these cells indicate a quick drop in RDM and a large amounts of dilation, indicating a great ingress of water. The poor results could possibly be attributed to the unfavorable interaction of AEA1 with WR, HRWR, and the type and quantity of pozzolan.

Table 6.13 shows the results of tests performed on Cl C fly ash concrete made with AEA2 and WR or HRWR. The WR/HRWR, Cl C fly ash concrete made with AEA2 exhibited much better performance than comparable mixes made with AEA1. The use of water-reducer generally produced lower spacing factors than did the use of HRWR, although this did not always guarantee better performance (see cell B15 and B19). The best overall indicators of performance were again AVTA and AVEA. It is worth noting that AVEA and AVTA did not always correlate directly with spacing factor. It is also worth noting that all of these mixes had spacing factors that greatly exceed recommended maximums for durability, and yet most of the specimens exhibited fairly good durability. This was especially true for the cells cast using HRWR.

The freeze-thaw performance histories of B15, B16, B19 and B20 are presented in figures C.11, C.12, C.19, and C.20. Greater gain in mass is observed for C.11 and

Table 6.13. Comparison of WR/HRWR for Cl C fly ash with AEA2.

		W/C+P	
		0.40	0.45
Type of WR/HRWR	1	B15 2.0/1.3/0.9 0.421/0.349 76/74 50/0.210/0.0766 38502	B16 2.0/2.5/1.4 0.336/0.254 148/144 70/0.218/0.0774 -
	2	B19 3.0/3.4/1.5 0.598/0.404 118/107 56/0.077/0.0761 31069	B20 2.3/2.8/1.1 0.630/0.405 94/86 37/0.083/0.0842 42501

KEY
Cell # FAC%/HTA%/HEA % SFTA(mm)/SFEA(mm) AVTA/AVEA DF/Wt-Chg %/L-Chg % C-str(KPa)

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C.12, while much smaller weight gains were observed for C.19 and C.20, which exhibited greater amounts of initial scaling. This indicates the greater evidence of scaling in mixes made with superplasticizer than for mixes made with WR. Most of the beams showed a similar drop in RDM up to about 150 cycles, but later showed greater variations. This may indicate the development and rapid deterioration of durability cracking.

The test results for concrete mixes made with GGBF slag, AEA1 and WR are shown in table 6.14. Granulated ground blast furnace slag was used at a 40% replacement level for cement, both with and without WR. These mixes showed significant differences in frost resistance performance for both water-cementitious ratios (although these were in the range of bad to poor for all mixes), as shown in table D.4. Durability factor correlated fairly well with AVTA and AVEA, but not very well with spacing factor (note that the highest spacing factor had the best durability). The use of WR did generally reduce spacing factors and dilation; however it also seemed to have little effect (or a slightly negative effect) on durability for these cells. Mixes without WR showed a reduction from total AC to entrained AC of 43.8% and 51.4% for $W/C+P=0.40$ and 0.45 , respectively. Mixes with WR showed a reduction of 33.3% and 23.5% for the same $W/C+P$ values. This means that WR did produce some improvement in the stability of the AVS. The comparatively better frost resistance performance of cell C2 can be attributed to higher total AC and not to the performance of WR.

The freeze-thaw performance histories for these cells are presented in figures C.25 through C.28. A significantly quick drop in relative dynamic values, and high gain in weight and length is evident without exception for all GGBF slag beams.

Tab

[illegible]

Table 6.14. Comparison of mixes with and without WR for GGBF slag and AEA1.

		W/C+P	
		0.40	0.45
GGBF slag	None	C1 2.2/1.6/0.9 0.344/0.245 122/119 19/0.247/0.0843 53312	C2 2.8/3.7/1.8 0.385/0.268 178/169 30/0.039/0.0871 43301
	WR	C3 2.4/2.1/1.4 0.249/0.205 155/150 15/0.185/0.0702 43742	C4 2.4/1.7/1.3 0.323/0.287 129/126 13/0.258/0.0738 43073

KEY
Cell # FAC%/HTA%/HEA % SFTA(mm)/SFEA(mm) AVTA/AVEA DF/Wt-Chg%/L-Chg % C-str(KPa)

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When compared to Cl F fly ash with WR and AEA1, Cl C fly ash with WR and AEA2, or silica fume, GGBF slag failed to produce frost-resistant concrete at a 40% replacement of cement and marginal AC, in spite of generally increased strengths. The effects of interactions of GGBF slag and chemical admixtures may bear further study to help explain the observed performance.

From the above discussion, the following overall conclusions can be made:

- (1) The use of WR generally produced lower spacing factors than the use of HRWR for most mix designs. WR also produced lower spacing factors in GGBF slag mixes than in mixes without WR.
- (2) The use of AEA1 (a vinsol resin-based product) generally produced lower spacing factors than the use of AEA2 (a synthetic, petroleum-based product) for most mix designs.
- (3) AVTA and AVEA were generally better predictors of concrete durability than spacing factor or air content.
- (4) Vinsol resin-based air entrainer showed comparatively much better air retainment property with both of the fly ashes than the AEA2.
- (5) Cl F fly ash concrete mixes made with AEA1 exhibited greater strengths than when made with AEA2; the reverse was true for Cl C fly ash. The increased strength was probably an important contributing factor for their better performance at marginal air content.

Water-reducing and pozzolanic admixtures are reported to reduce the permeability of concrete, but testing on the companion specimens did not support this [190].

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Permeability test results for $W/C+P=0.40$ and 0.45 are shown in figures 6.13 and 6.14, respectively. These figures present a range of permeability values ($4.9-6.1 \times 10^{-12}$ m/s, and $3.9-5.1 \times 10^{-12}$ m/s, respectively), that fall within one standard deviation of the mean. A summary of the permeability test results for 109 samples are shown in table 6.15.

Table 6.15. Permeability test results [190].

Pozzolan	Water-cementitious ratio		
	0.40	0.45	0.52
None	5.5 (n=28, s=2.1)	4.8 (n=38, s=1.8)	6.6 (n=3, s=3.5)
Fly Ash	6.3 (n=12, s=2.0)	5.5 (n=17, s=2.2)	
Silica Fume	2.8 (n=4, s=2.1)	4.7 (n=7, s=1.8)	
Permeability $\times 10^{-12}$ m/s, (n = number of samples, s = Std. Dev.)			

Table 6.4 shows the results of the freezable moisture testing for mixes with and without WR/HRWR. It was concluded that a trend of lower freezable moisture did exist between samples with and without WR/HRWR. However, due to the small sample size and large variance of the test results, the results can not be considered statistically significant. However, the decrease in freezable water with a decrease in W/C between 0.40 and 0.45 , and 0.45 and 0.52 was found to be statistically significant. The amount of freezable moisture was also significantly reduced for pozzolanic mixes compared to

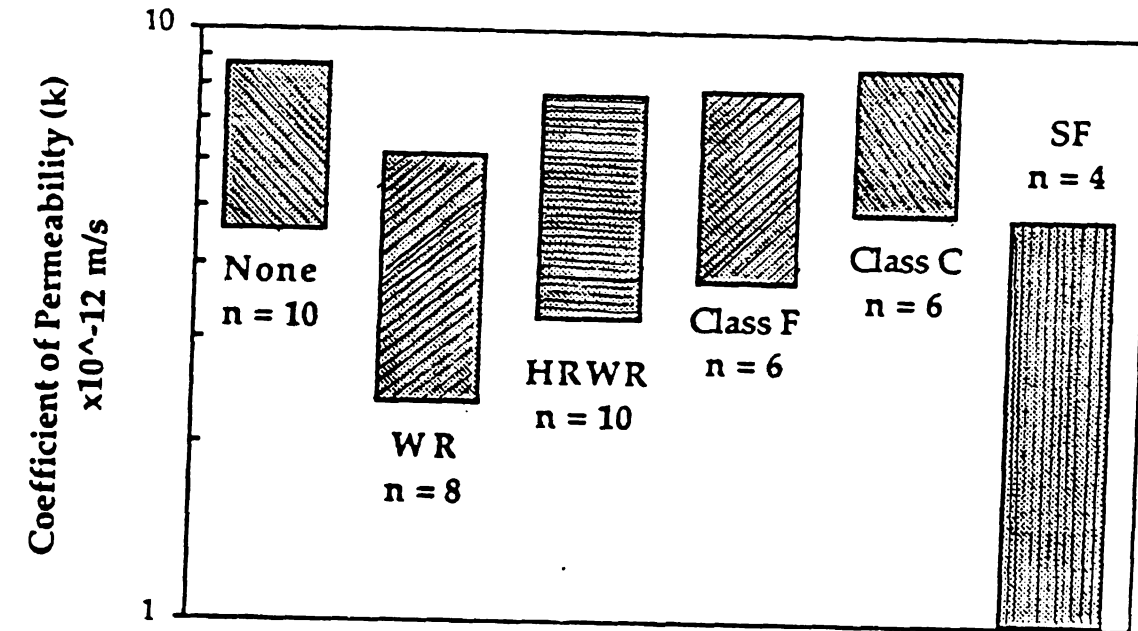


Figure 6.13. Effect of admixtures on permeability of concrete for $W/C+P = 0.40$ [190].

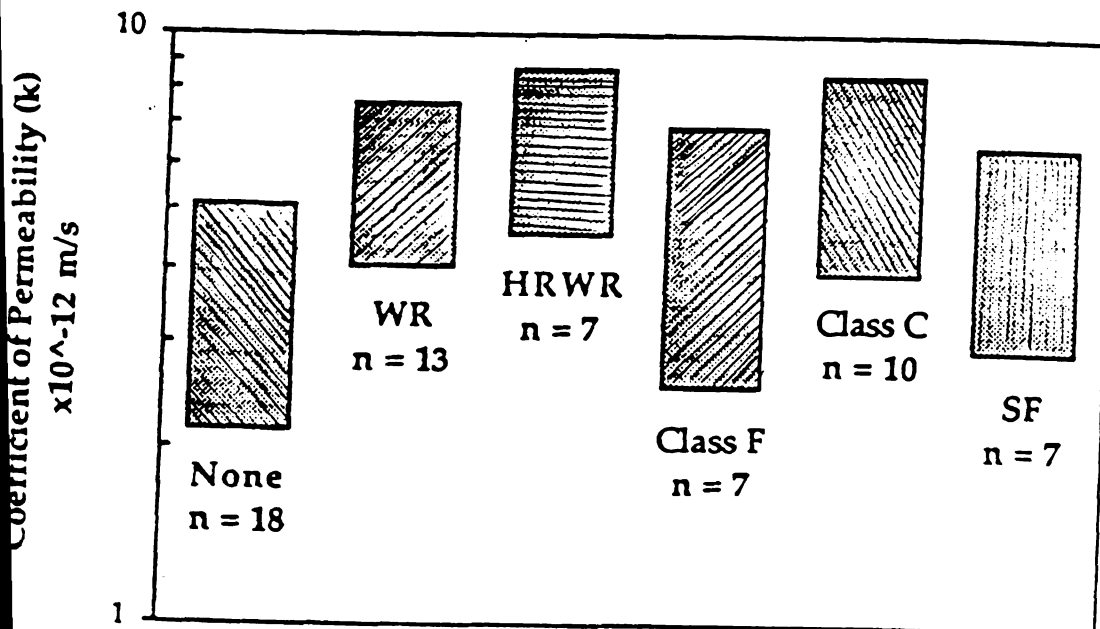


Figure 6.14. Effect of admixtures on permeability of concrete for $W/C+P = 0.45$ [190].

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non-pozzolanic mixes. This may be due to the effect of the water-reducer, or to the effect of pozzolan, or both. These will be discussed in the next section.

6.4 Effect of Pozzolans

6.4.1 Effect of Fly Ash

Cl F and C fly ashes were tested at 0%, 15%, and 30% replacement of cement (by weight) with two levels of curing period (28 and 56 days) and two levels of water-cementitious ratio (0.40 and 0.45). WR and AEA1 were used for all of these mixes. The test results are shown in tables B.1 through B.4.

Some of the air void characteristics and freeze-thaw test results for the Cl F fly ash mixes are summarized in table 6.16. The freeze-thaw test results for cells D1 through D12 are presented in figures C.1, C.29, C.2, C.30, C.5, C.31, C.6, C.32 through C.36, respectively.

It was interesting to note that for Cl F fly ash with WR, concrete made a significant reduction in frost resistance was observed with longer curing periods at all replacement levels, (see table D.5). Cl F fly ash had 24.84% of its particles retained on # 325 sieve as compared to Cl C fly ash which had 12.72% (see table A.2). This could have allowed the Cl F fly ash to form more capillaries, which could also act as escape boundaries and account for its better frost resistance performance. Since it has lower pozzolanic activity ($\text{CaO}=8.82\%$), an increased curing period might have reduced the number of capillaries, which in turn resulted in comparatively fewer escape boundaries

Table 6.16. AVC,FTD and other characteristics of Cl F fly ash.

		W/C+P	
		0.40	0.45
Amount of Cl F Fly Ash	0%	D1 2.8/2.7/1.7 0.322/0.257 154/147 56/-0.115/0.0670 43376	D3 2.7/3.8/2.1 0.315/0.238 192/182 16/0.108/0.0902 38784
	15%	D5 2.5/2.5/2.0 0.186/0.167 229/225 94/0.088/0.0114 42335	D7 2.8/2.4/2.0 0.245/0.224 187/185 89/0.206/0.0267 38846
	30%	D9 2.8/2.6/2.5 0.134/0.132 283/282 65/0.137/0.0733 30972	D11 2.5/2.7/2.4 0.148/0.139 303/300 67/0.210/0.0580 42646

KEY

Cell #

FAC%/HTA%/HEA%

SFTA(mm)/SFEA(mm)

AVTA/AVEA

DF/Wt-Chg%/L-Chg%

C-str(KPa)

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(which might be significant at marginal AC), adversely affecting frost resistance. This argument can be supported by comparing figures C.5 with C.31 (D5 vs. D6), and figures C.6 with C.32 (D7 Vs. D8), which indicate greater total elongation and gain in weight at the time of failure for samples with a greater curing period.

At a higher replacement level, the frost resistance of C1 F fly ash was observed to decrease significantly. Looking at the durability performance histories of the mixes in figures C.5, C.6, C.33, and C.35 (for cells D5, D7 and D9, D11), it was observed that, at the higher replacement level of C1 F fly ash, a much quicker drop in RDM, earlier elongation to critical value, and much larger gain in weight (ranging between 0.1% to 0.5%) took place. The average drop in DF for $W/C+P=0.40$ and 0.45 was about 25% and 31%, respectively. This can be attributed to greater ingress of water at higher replacement values.

Similarly, significant reductions in frost resistance were observed for longer curing periods (see table D.5) at the higher replacement level (see figures C.33 vs. C.34 and C.35 vs. C.36), resulting in 30.8% and 43.3% drops in DF for $W/C+P=0.40$ and 0.45 , respectively. The reason for this freeze-thaw performance for the higher replacement level with increased curing could be the same as that offered for low replacement levels.

Looking at compressive strength results (see figure 6.15), a significant drop in compressive strength was observed with increased curing at higher replacement levels for both $W/C+P$ tested. The drop in compressive strength for $W/C+P=0.40$ and $W/C+P=0.45$ was observed to be 14.6% and 19.4%, respectively. A similar drop in compressive strength is noted in the literature [106,113] between 28 and 90 days of

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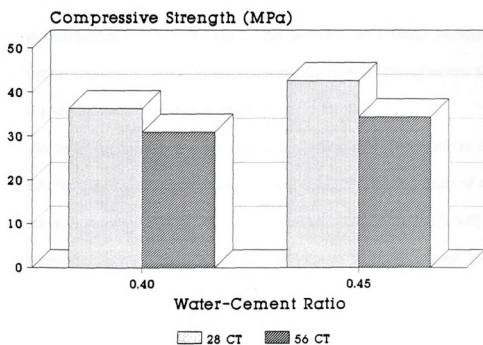


Figure 6.15. W/C+P versus C-str Cl F FA.

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curing for fly ash concrete; this phenomenon was attributed to the negative effects of the increase in fly ash particles greater than $45\text{ }\mu\text{m}$ (No. 325). This can also be a possible reason of reduced frost resistance at higher curing periods.

It can be seen that, although the number of air voids in both AVTA and AVEA were actually higher at the 30% replacement level, the frost resistance was better at the 15% replacement level. This may be caused by the effects of particle size distribution, as explained earlier. Apart from this, it could also be due to the better chemical and physical interaction of C1 F fly ash in the presence of a water reducer and AEA. Moreover, it appears that 15% is the best replacement level that produces the combined air void and pore water systems at marginal air contents.

Some of the air void characteristics, and test results for the mixes cast using C1 C fly ash, WR, and AEA1 are shown in table 6.17. The performance of C1 C fly ash concretes was strongly affected by fly ash quantities (see table D.6), with the poorest freeze-thaw performance occurring lower replacement levels. However, at a higher replacement level, significant improvements were observed. In addition, lower W/C+P generally produced lower spacing factors and improved durability at either replacement level. By itself, cure time had no significant effect on the durability of C1 C fly ash concrete (see table D.6). However, mixes with lower W/C+P performed significantly better at all replacement levels for a shorter curing period and the performance of lower W/C+P was observed to be significantly better at higher curing period and a higher replacement level. Strong 3-way and 2-way interactions between these variables were observed, which are best explained through discussions of cell to cell performance.

Comparing the test results of cells D13 and D14 with D17 and D18, it is apparent

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Table 6.17. AVC,FTD and other characteristics of Cl C fly ash.

		W/C+P	
		0.40	0.45
Amount of Cl C Fly Ash	0%	D1 2.8/2.7/1.7 0.322/0.257 154/147 56/-0.115/0.0670 43376	D3 2.7/3.8/2.1 0.315/0.238 192/182 16/0.108/0.0902 38784
	15%	D13 2.0/2.2/1.6 0.222/0.190 140/135 29/0.230/0.0888 38240	D15 2.5/2.2/1.2 0.383/0.284 113/108 15/0.227/0.0717 37323
	30%	D17 2.4/2.7/1.6 0.302/0.236 154/149 62/0.121/0.0656 25580	D19 2.0/1.3/0.6 0.433/0.302 82/77 29/0.0659/0.066 32455

KEY
Cell #
FAC%/HTA%/HEA%
SFTA(mm)/SFEA(mm)
AVTA/AVEA
DF/Wt-Chg%/L-Chg%
C-str(KPa)

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that spacing factor and durability factor both increased for higher replacement levels of Cl C fly ash, regardless of W/C + P. As discussed in the previous section, higher spacing factor values and durability factor values were also observed for some combinations of WR/HRWR and AEA at lower replacement levels. Here, too, higher spacing factor values were observed at a higher replacement level. This observation is also supported by the literature [57,58,59], which suggests the revision of the spacing factor criteria spacing factor for concrete prepared with chemical and mineral admixtures. Although the FAC was kept within the target limits, greater variation was observed in HTA, which suggests the possible loss of air at the time of casting (due to vibration, etc.).

The frost resistance histories of Cl C fly ash are presented in figures C.9, C.37, C.10, and C.38 through C.42 for 15% and 30% replacement levels, respectively for cells B13 through B20. By looking at the freeze-thaw histories in figures C.9, C.37, C.10, and C.38, a quicker drop in RDM, an increase in length, and a gain in weight (from 0.1% to 0.3%) are observed for lower replacement levels of Cl C fly ash at both curing periods. With an increase in the amount of fly ash (see figures C.39 through C.42), the frost resistance significantly improved. This is contrary to the results obtained for Cl F fly ash.

Another important observation was the increased scaling that was observed for higher replacement levels of Cl C fly ash, and is indicated by the initial drop in weight observed in figures C.39 to C.42. Continued scaling would produce a continued drop in weight, but the increase in weight due to the ingress of water is probably far greater. As a result, the net long term effect is a gain in weight. This indicates higher durability factor values with a moderate amount of scaling.

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Looking at the physical properties of the pozzolan (table A.3), we notice that at a higher replacement level, the amount of Cl C fly ash fines retained on # 325 sieve become almost equal to the amount of fines retained at lower replacement levels of Cl F fly ash (i.e., $12.72 \times 2 = 25.44\% \approx 24.84\%$). The particle size distribution combined with pozzolanic activity, could possibly be responsible for the comparable and better frost resistance performance of these two types of fly ash at different replacement levels.

Table 6.18. Freezable moisture for pozzolanic and non-pozzolanic admixtures [190].

Pozzolan	Water-cementitious ratio	
	0.40	0.45
None	0.66 (n=4, s=0.007)	0.77 (n=5, s=0.07)
15% Cl F FA	0.55 (n=1)	0.60 (n=3, s=0.04)
15% Cl C FA	0.57 (n=1)	0.66 (n=2, s=0.02)
30% Cl C FA	0.53 (n=2, s=0.11)	0.64 (n=2, s=0.06)
15% Silica Fume		0.33 (n=2, s=0.03)
Freezable Moisture (%) (n = number of samples, s = Std. Dev.)		

The results of the freezable moisture tests shown in table 6.18 (although limited in scope due to time and other constraints), do convey some message about the internal structure of the concrete. Although no significant difference exists between Cl F and C fly ashes at either replacement level, Cl F fly ash shows a lower quantity of freezable

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moisture. As the amount of C1 C fly ash increases, a trend in the reduction of freezable moisture is observed. Similarly, though not significantly, a clear trend in increased freezable moisture is also evident with the increase in the water-cementitious ratio. The significant drop in freezable moisture was observed as the pozzolans are added. This gives an indication of refinement of the WPS with the addition of pozzolans, which appears to be an important contributing factor towards the frost resistance of concrete.

The above discussion leads to the following possible conclusions:

- (1) If the quantity and type of fly ash is adjusted suitably, it can result in the production of frost-resistant concrete, even at marginal AC.
- (2) The particle size distribution of fly ash plays a vital role in making frost-resistant concrete.
- (3) Increased curing of C1 F fly ash adversely affected frost resistance for the range of curing periods examined. This trend should be validated for longer curing periods.
- (4) Fly ashes, even with spacing factors that are higher than the recommended maximum value of 0.20 mm, can still produce frost-resistant concrete, which suggests the need to modify existing air void criteria.
- (5) Fly ash concretes can exhibit high durability factor values even with moderate amounts of scaling.

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6.4.2 Effect of Silica Fume

Silica fume was tested at 0%, 8%, and 15% replacement levels, with AEA1, W/C+P of 0.40 and 0.45, and two levels of curing in this study. The pozzolan was used in the slurry form with water and HRWR. It was difficult to obtain a marginal AC in these mixes, especially at higher replacement levels. As result, AEA dosages were quite small for many of the mixes. Table D.7 shows the statistical calculations for frost resistance of silica fume mixes.

Some of the air void characteristics and freeze-thaw performance measures for the CSF concrete mixes are shown in table 6.19. The effect of silica fume dosage on frost resistance was significant, with higher replacement levels producing lower spacing factors, higher AVEA and better frost resistance. Three-way interactions between pozzolan amount, W/C+P, and pozzolan curing period were not significant, whereas two-way interactions between pozzolan amount and W/C+P, and pozzolan amount and curing period were significant (see table D.7).

The mixes cast without CSF did not show a significant difference in durability for varying W/C+P; however, the addition of 8% or 15% CSF produced increased durability with increasing W/C+P.

The mean durability factor for cell E5 (DF=47) had a coefficient of variation of 53.7%, which is out of the range for the precision statements given in reference 52. This is because the cell was cast in two batches, and two beams from one set showed a mean durability factor value of 68 (well within the specified range and consistent with similar results) while two beams from the other set showed a mean durability factor of 27, which

Table 6.19. A V

Amount of Silica Fume	KL	Ce	FAC%/HT	SFTA(mm)	AVTA	DF/Wt-Ch	C-str
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Table 6.19. AVC,FTD and other characteristics of CSF mixes.

		W/C+P	
		0.40	0.45
Amount of Silica Fume	0%	E1 2.5/1.8/1.1 0.361/0.292 103/97 26/0.131/0.081 41901	E3 2.2/1.8/1.1 0.331/0.269 106/101 28/0.103/0.0888 40887
	8%	E5 2.6/2.4/1.4 0.306/0.237 145/137 47/0.076/0.1003 46334	E7 2.7/3.5/2.2 0.339/0.274 161/153 67/0.164/0.1052 42728
	15%	E9 3.0/3.4/2.5 0.199/0.173 214/207 88/-0.071/0.043 61303	E11 3.0/2.9/2.3 0.222/0.199 216/212 93/0.004/0.0184 52443

KEY
Cell #
FAC%/HTA%/HEA %
SFTA(mm)/SFEA(mm)
AVTA/AVEA
DF/Wt-Chg%/L-Chg%
C-str(KPa)

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was probably due to poor casting practice. The value of DF given for this cell in the table 6.19 is the mean value of the whole set of beams. However, if the calculations are based on the most probable and realistic value of $DF=68$, then there is no significant difference between the durability factors observed for the two W/C+P.

At higher replacement levels, no significant difference in durability was observed between the two W/C+P for the shorter curing period, but a significant difference was observed for the longer curing period, with higher W/C+P yielding better results. Although not conclusive, this indicates a trend of better pozzolanic interaction at higher W/C+P. No significant difference was observed between the curing periods for silica fume mixes. This supports the theory of high pozzolanic reactivity and indicates that most of the pozzolanic reactions take place within the first 28 days of curing.

The mean durability factors presented in table 6.19 clearly indicate better durability performance with higher CSF replacement levels. At higher replacement levels (cells E9 and E11), the durability factors are excellent, with spacing factors close to or slightly higher than the recommended criteria of 0.20 mm. Furthermore, in cases of 8% silica fume (E5 and E7) the HEA is 41.7% and 37.1% less than HTA for W/C+P=0.40 and 0.45, respectively; at 15% replacement (E9 and E11) the difference between the two air measures is only 28.5% and 20.7%. This indicates a comparatively better and more stable AVS at the higher replacement level, which also results in lower spacing factor values and better freeze-thaw performance.

It may also be noted from the FAC values that it was more difficult to maintain the target AC as the amount of silica fume increased. This warrants more stringent mix control with increases in the quantity of the CSF because FAC is the only indicator of

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The freeze-thaw test performance history graphs for cells E1, E3, and E5 through E12) are presented in figures 6.1, 6.2, C.43 through C.46, C.21, C.47, C.22, and C.48, respectively. Comparing cells E1, E5, and E9 ($W/C+P=0.40$) or cells E3, E7, and E11 ($W/C+P=0.45$), we can clearly see how the performance of concrete improves with the amount of silica fume at either of the water-cementitious ratios. The quick drop in relative dynamic modulus values, the increase in dilation, and the gain in weight of non-pozzolanic mixes without WR/HRWR (figures 6.1 and 6.2) at a mean of less than 150 freeze-thaw cycles (for cell E1, mean cycles=133 and $s=4.22$; and for cell E3, mean cycles=143, and $s=6.83$) show the good quality control but relatively poor performance of these mixes. Silica fume mixes with 8% CSF amount (figures C.43 and C.45) showed reduction to 60% RDM with a mean of 216 (corrected value=299.5) and 300 freeze-thaw cycles, and weight gain/loss varied between + 0.2% and -0.1% for all of the beams tested. Critical dilation was not observed until failure/removal from the test. All of these results indicate good performance (although some initial scaling was observed). On the other hand, cells E9 and E11, which were cast with 15% CSF, (figures C.21 and C.22) showed excellent performance in rapid freeze-thaw testing by attaining mean durability factors of 88 and 93 (not significantly different) for the two $W/C+P$. These cells lasted an average of 300 freeze-thaw cycles ($s=0$ for both cells), gain in length of 0.0430% and 0.0184%, and weight changes of -0.071% (net loss) and 0.004% (net gain). This leads to the conclusion that high replacement levels of silica fume (15% in this study) provide potential for excellent frost resistance.

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significantly) decreased permeability coefficient was observed for silica fume mixes at $W/C+P=0.40$, $k=2.8 \times 10^{-12}$ m/s; at $W/C+P=0.45$, $k=4.7 \times 10^{-12}$ m/s, which was much higher than the permeability observed for the lower $W/C+P$, but still lower than the typical permeability of the fly ash mixes. Although a trend of decreasing permeability was seen for increasing CSF content, it was not considered conclusive [190].

It is also useful to look at the freezable moisture results in table 6.14. This table shows a significant reduction in freezable moisture for silica fume mixes as compared to fly ash mixes and non-pozzolanic mixes.

It has been postulated by Feldman [165], after observing the excellent freeze-thaw performance of silica fume non-air-entrained concrete, that CSF may create its own micro-air-void network around fine aggregate particles. The calcium hydroxide liberated by the portland cement in the transition zone during the hydration process would be used by the CSF leaving the voids. If the fine aggregate content is high enough, these voids might provide protection from frost action. In his test, the pore size distribution of CSF concrete was observed to be much finer than for the control mix, even after only 7 days, and the permeability of CSF concrete could not be measured under a differential head of 12.5 MPa after two months. The above explanation supports the significant reduction in the permeability and amount of freezable water found in silica fume mixes in this study and also gives an explanation of the superior performance of silica fume mixes, which was also observed in this research work.

The above discussion indicates:

- (1) Excellent frost resistance performance of silica fume mixes, particularly at higher replacement levels (15%) at marginal AC. This can be attributed to

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lower permeability and the development of a very refined WPS due to high pozzolanic properties and finer particle size, reducing the accumulation of freezable moisture, which is a key to the problem.

- (2) Comparatively higher spacing factor values (although not as high as in fly ash concretes), particularly at lower replacement levels, while still producing frost-resistant concrete.
- (3) Much less scaling than fly ash mixes, which could be attributed to local increases of W/C at or near surface of the fly ash mixes due to over finishing.
- (4) No significant difference in durability for varying the cure period of CSF concrete.
- (5) No significant difference in frost resistance for varying W/C+P after short periods of curing, but a trend of better durability with lower W/C+P exists. Significantly better durability was observed for lower W/C+P after longer curing periods.

6.5 Air Void, and Water Pore System and Frost Resistance

The combined use of chemical and mineral admixtures has, on one hand, brought about tremendous improvements in the performance of PCC. On the other hand, it has raised more questions regarding the complex microstructure and behavior of concrete. PCC frost resistance has also gained more attention due to the increased use of admixtures. The problem is usually addressed in small parts due to various constraints, including those of time and finances. This research was no exception. Here the scope was

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The Powers spacing factor is considered one of the most important air void parameters and indicators of the frost resistance of concrete. This is derived from the following equations [53]:

$$L = T_p/4N \quad \text{for } p/A \leq 4.342$$

$$L = 3/\alpha[1.4(p/A + 1)^{1/3} - 1] \quad \text{for } p/A > 4.342$$

where:

L	=	spacing factor
T_p	=	traverse length through paste
N	=	total number of air voids intersected
α	=	specific surface
p/A	=	paste-air ratio

It has been pointed out by Powers [28,67] and Willis [195] that these equations suffer from some limitations (already discussed in Chapter II) due to assumptions made in their derivations, and give a spacing factor which exceeds the actual mean spacing. As such, a restriction is imposed (paste to air ratio), as shown above, in order to overcome the problem. Other researchers have attempted to give their own solutions.

Philleo [62] derived equations, and Larson et al. [63] found the product to be a better indicator of frost resistance than the Powers spacing factor and named it the

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Philleo Factor. This is considered by some researchers to be a more realistic indicator because it uses the size distribution of the air voids for calculations. But the Philleo factor could not be easily and accurately determined due to the methods used in determining the air void size distribution [63]. In this study, Philleo factors for 90 and 99 percent protection (PH90 and PH99) were calculated by using the Hydrair program, as mentioned earlier. This program is based on the equations developed by Philleo [62] and assumes a lognormal air void size distribution.

A third method used for calculating a spacing factor in this study was developed by Attiogbe [66]. Looking at the problems with Powers and Philleo's factors, he developed the following equation using geometric probability concepts and stereological principles, as discussed earlier in Chapter II:

$$AMS = 2p^2/\alpha A$$

where:

AMS = Attiogbe mean spacing

p = paste content

A = air content

α = specific surface

Figure 6.16 presents plots of Powers spacing factor based on total air content and entrained air content (SFTA and SFEA), Attiogbe mean spacing (AMS), and Philleo factors (PH90 and PH99) versus durability factor (DF). This data, which is essentially based on PCC mixes prepared with different combinations of chemical and mineral

AVS Measures (mm)

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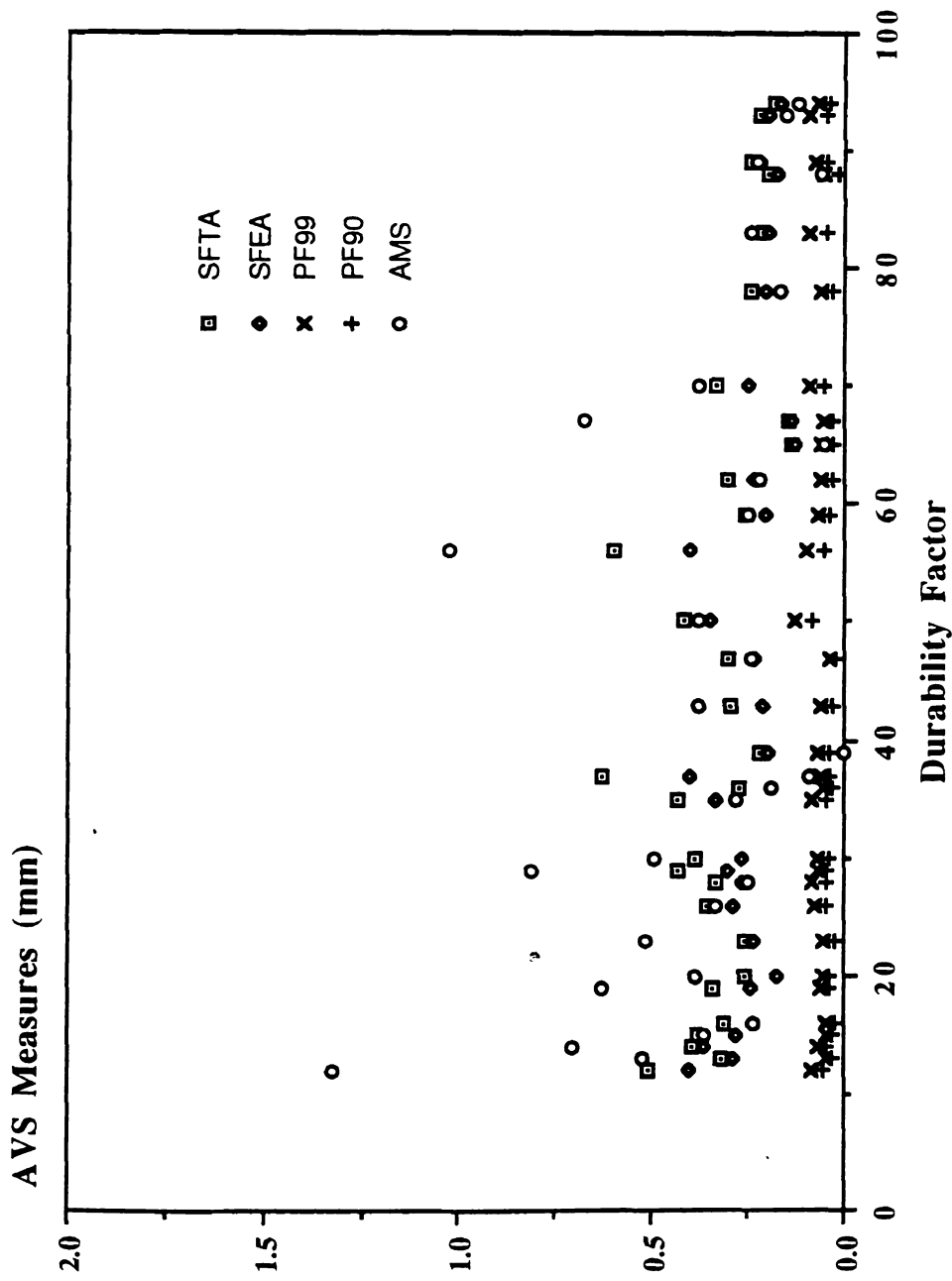


Figure 6.16. Various AVS measures versus DF.

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admixtures at marginal AC, presents some interesting results.

Attiogbe made a comparison of the Powers spacing factor and the mean spacing from his equation (AMS) for a number of mixes and found that small proportions of the durable concretes, about 40%, had standard spacing factors less than the 0.2 mm (0.008 in.) limit. A high proportion of the durable concretes, about 90%, showed AMS less than 0.2mm (0.008 in.). Figure 6.16 shows that the AMS for a number of specimens is greater than the spacing factor. The AMS also shows greater variation than the standard Powers spacing factor values, particularly where the DF is below 70. This observation is not in agreement with Attiogbe's general conclusion that his equation correctly gives smaller air void spacing when large voids (entrapped voids) are accounted for in the computation of the mean spacing. This may be due to the fact that the original comparisons were based on properly designed air-entrained concretes and the equation might not be valid for marginal AC and/or mineral admixtures present in the amounts tested in this research program. However, a comparison made between the two air void measures on mixes that yielded a durability factor of greater than 60 (which is considered durable by Attiogbe) indicated that 80% of the mixes showed smaller AMS than the Powers spacing factor, even if these were greater than the recommended ACI value {i.e., 0.2 mm (0.008 in)}. When the comparison between the Powers spacing factor based on entrained air content (SFEA) and the AMS was made on the samples tested in this research work, it was seen that AMS produced smaller values in only 36% of the cases. This shows that the spacing factor based on entrained air content (SFEA) is comparatively more useful in determining the frost resistance of PCC at least than the standard spacing factor and the Attiogbe mean spacing for admixtures-rich concretes at marginal

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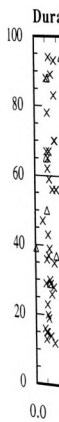
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AC. This is also supported by the work of Pleau et al. [196]. This, of course, leads to the question of subjective size criterion for entrained and entrapped air voids. With some validation of experimental results, this can be agreed upon for future work. This would also require no extra effort because, with simple modifications of standard test programs, both the spacing factors (SFTA, SFEA) can be obtained in the same linear traverse run.

The Philleo factor, PF90 resulted in a range of 0.018 to 0.086 mm (mean=0.0387, s=0.01334, n=36), whereas PF99 resulted in a range of 0.036 to 0.096 (mean=0.0678, s=0.01879, n=36), which shows values that are too low and too close. This may still be due to the problems in calculating the of number of voids per unit volume. Comparatively, SFTA ranged from 0.134 to 0.630 mm (mean=0.31572, s=0.11139, n=36) and SFEA ranged from 0.132 to 0.405 (mean=0.24972, s=0.07144, n=36). The Philleo factor, PF99, calculated here are about 64% to 90% and 60% to 85% lower than the spacing factors based on total air and entrapped air, respectively. On the basis of the study of five air void spacing measurements on the tests conducted in this research work as discussed above, this author recommends the use of a standard spacing factor based on entrained air content (SFEA). This needs to be further verified using a variety of mix designs and various size limits on the definition of entrained air voids limit.

Figure 6.17 presents a summary of various air void measurements versus the observed durability factor. A horizontal line at a durability factor of 60 is shown as the arbitrary dividing line between durable and non-durable concretes. This arbitrary definition is based on reference 66, and could be moved up or down, depending on



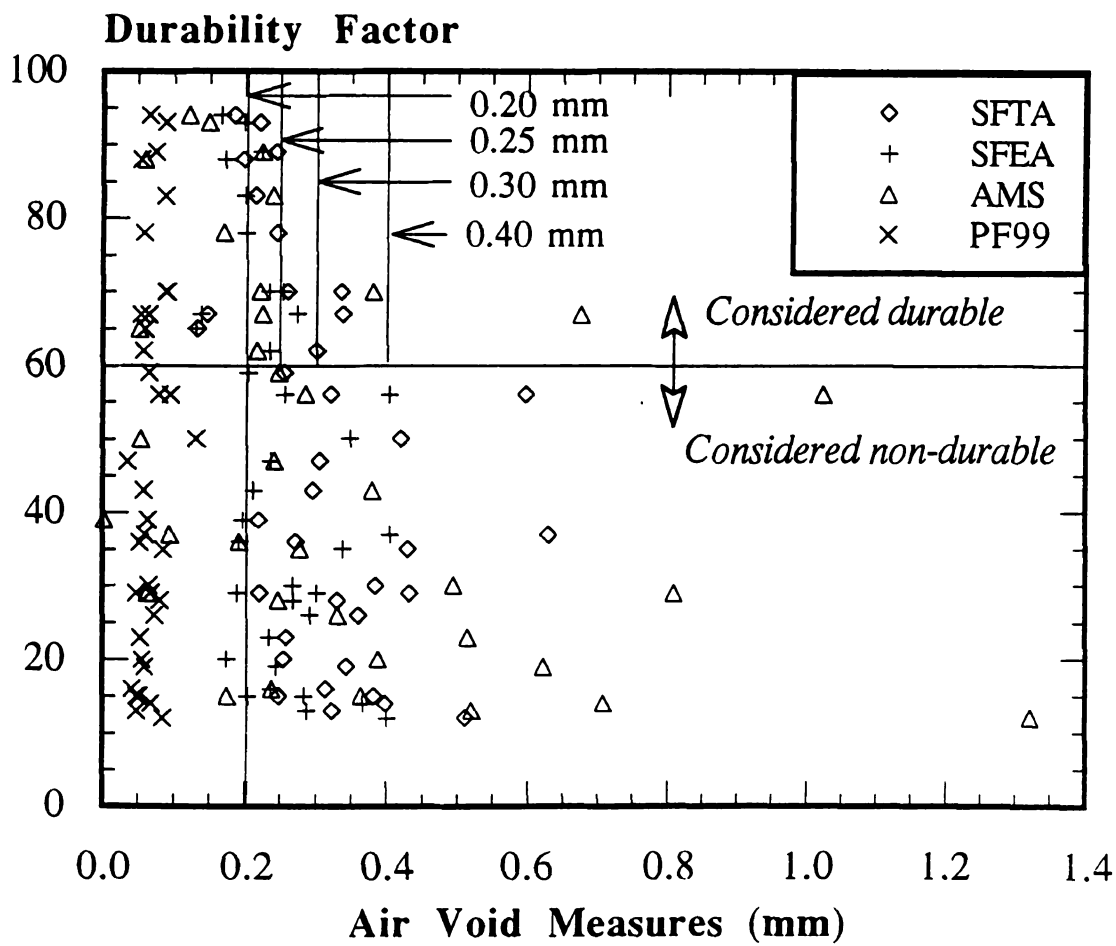


Figure 6.17. Comparison of various AVS measures.

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environmental conditions. A vertical line at 0.2 mm (0.008 in.) shows the recommended maximum value of the spacing factor for durable concrete, as established by the ACI and ASTM specifications. Note that only 25% and 33% of the mixes that have a DF greater than 60 fall within the 0.2 mm limit in the cases of SFTA and SFEA, respectively. When we consider 0.25 mm as the acceptable limit with DF greater than 60, then the percentages of points increase to 66% and 83% respectively. At 0.3 mm limit, 75% and 100% of the mixes for a spacing factor with total AC and entrained air content fall within the limit. This suggests the validity of the concept of increasing the limit of the spacing factor for concretes prepared with chemical and mineral admixtures, particularly in the case of the fly ash mixes made with HRWR. The silica fume mixes with HRWR are still very close to or slightly higher than the spacing factor limit.

Spacing factor alone is not adequate for predicting concrete durability; note that a number of mixes that have a $DF < 60$ also fall within the acceptable spacing factor limits. Other air void parameters were studied, but none gave a consistently good correlation. Specific surface shows a good correlation with durability to some extent, but it also violates the standard limit for specific surface of greater than or equal to $24 \text{ mm}^2/\text{mm}^3$ (see table B.3). The specific surfaces based on entrained air content obviously showed higher values, but these are also poorly correlated to frost resistance. For example, B5 and B6 have a DF/SSE of 94/39.8 and 89/32.6 and B10 and B11 have DF/SSE of 39/42.2 and 43/43.2 for same W/C+P. These observations lead to the possibility of combining the air void and water pore system measurements to predict durability.

The permeability and freezable moisture testing that was described earlier produces some of the water pore system parameters that are usually referred to in the

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literature. For the reasons discussed in section 6.1, the permeability test results were not found to be an effective means of assessing differences between different mixes. On the other hand, the freezable moisture estimates did provide more useful information about the pore structure of concrete. The freezable moisture results are presented in table 6.18.

As discussed earlier, a significant increase in the freezable moisture was observed with an increase in the water-cement ratio for non-pozzolanic mixes; no significant difference was observed for fly ash mixes, although an increasing trend in freezable moisture was observed with an increase in water-cementitious ratio. The addition of fly ash and silica fume did significantly reduce the freezable moisture when compared to non-pozzolanic mixes at both levels of the water-cementitious ratio tested. An increase in the amount of C1 C fly ash provide some reduction in FM although the reduction was not considered significant. The addition of silica fume showed a tremendous reduction in the amount of freezable moisture. The possible reasons for these observations have been discussed previously.

Although the freezable moisture data was available for only a few selected mixes, an effort was made to study the combined effect of the AVS and WPS on the freeze-thaw performance characteristics.

In research, the primary purpose of determining a realistic relationship between variables depends upon the objective of the analysis. The least square results present only a correlational structure for the data being analyzed. The consistency of the resulting model to the present knowledge must be carefully and critically studied by the researcher. A problematic aspect of the variable selection process is the relative importance of the variables as manifested in the sample, which may not reflect their

relative importance of each factor. The total research is based on the constraints; this is the development of the work. This encourages the development of work that will be discussed.

For the purpose of performance comparison, a fresh analysis of the air content (H₂O) (SFEA), compared (FM) were also and number of variables.

The results were carefully independent regression tests of the data, is a combination of the data were also analyzed SFTA, C-st, dependent variables.

relative importance in the population. Another major problem encountered in experimental research is the lack of adequate test data due to financial, time, and project-related constraints; this may limit the scope of the developed relationship. On the other hand, the development of some limited relationship or guidelines is always helpful for future work. This endeavor helped in determining the relative importance of various variables that will be discussed later.

For the development of a relationship between various AVS, the WPS and performance characteristics, a personal computer version of SPSS/PC+ was used for the analysis. Fresh air content (FAC), hardened total air content (HTA), hardened entrained air content (HEA), spacing factor based on HTA (SFTA), spacing factor based on HTA (SFEA), compressive strength (C-str), permeability (PERM), and freezable moisture (FM) were all considered for use as independent variables. The durability factor (DF) and number of freeze-thaw cycles to failure (FTC) were used as alternate dependent variables.

The relationships of all the independent variables with the dependent variables were carefully checked. The nature of the data (definite relationships between independent and dependent variables were not easily observed) suggested that a linear regression technique be used for the analysis. This type of regression, if not imposed by the data, is otherwise often preferred to keep the model simple. However, after the major combinations of the variables were identified, a number of non-linear transformations were also analyzed. Table E.1 shows the results of some of the combinations analyzed. SFTA, C-str, and FM were finally selected as the independent variables with DF as dependent variable.

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The regression analyses were carried out using forward, backward, and stepwise techniques, all of which gave exactly the same results. Table 6.20 presents a summary of the variability of durability explained by all of the variables, in order of priority, through a stepwise regression. About seventy three percent of the variation in durability was explained by SFTA and twenty seven percent was explained by FM. The inclusion of compressive strength improved the R square value in the third decimal place. This apparently indicates that, if it is not included, it would not make any significant difference, but it does affect the R square value (see table E.2),. This means the combined effect of the three variables is greater than only SFTA and FM. The overall significance of the 'F test' observed was 0.0472 with an R square = 0.90642.

Keeping any two of the variables independent at a time and using DF as the dependent variable, all three combinations were then drawn in three dimensions using a statistical/graphic program (PC version of AXUM). These graphs illustrates how the two variables are related to the DF. The values of R square (RSq) and adjusted R square (ARSq) are shown in table E.2 for these combinations. The graphs for the three combinations are presented in figures 6.18 through 6.20.

Figure 6.18 shows the proposed relationship between SFTA, C-str and DF. The overall effect is shown with the response surface (obtained from regression of variables), which clearly indicates that, as the spacing factor is reduced, the durability factor increases. The overall DF increases as the SFTA decreases and the compressive strength increases, but the effect of compressive strength is much smaller than the effect of SFTA.

Figure 6.19 shows the effect of the spacing factor and freezable moisture on the



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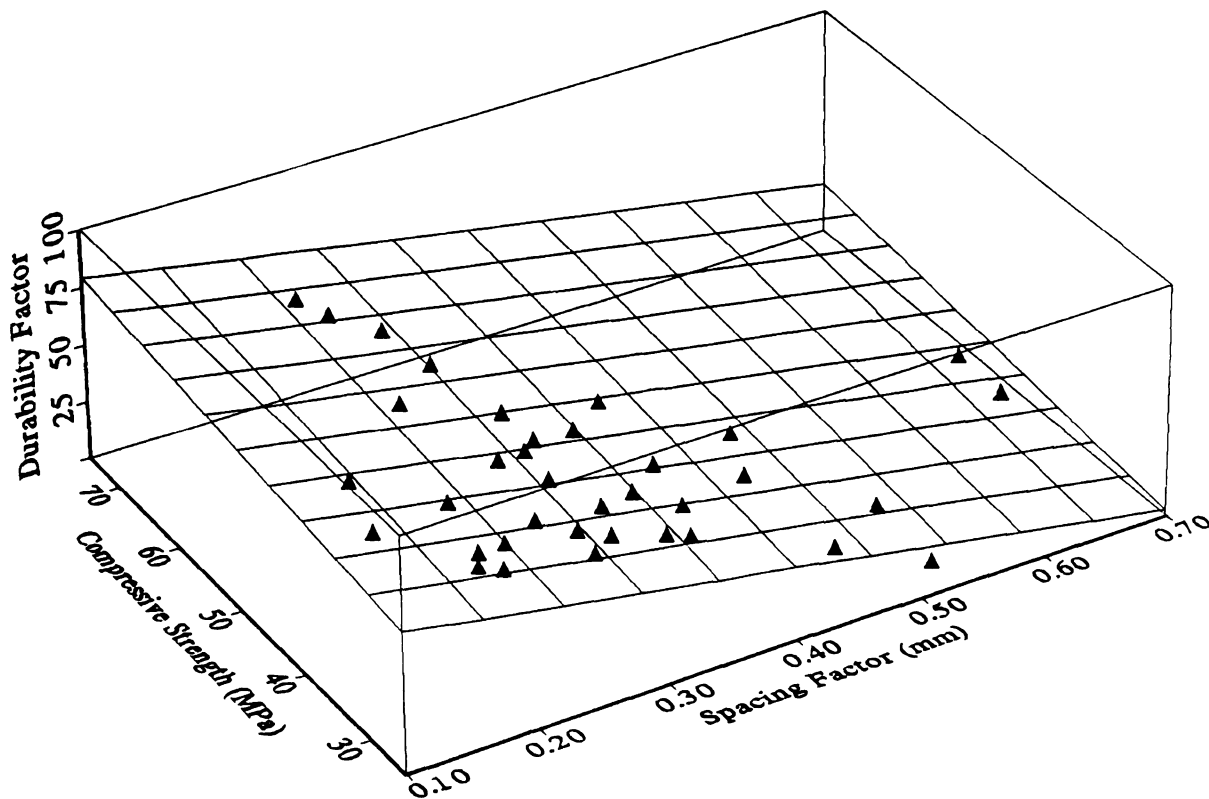


Figure 6.18. Relationship of FM and C-str with DF.

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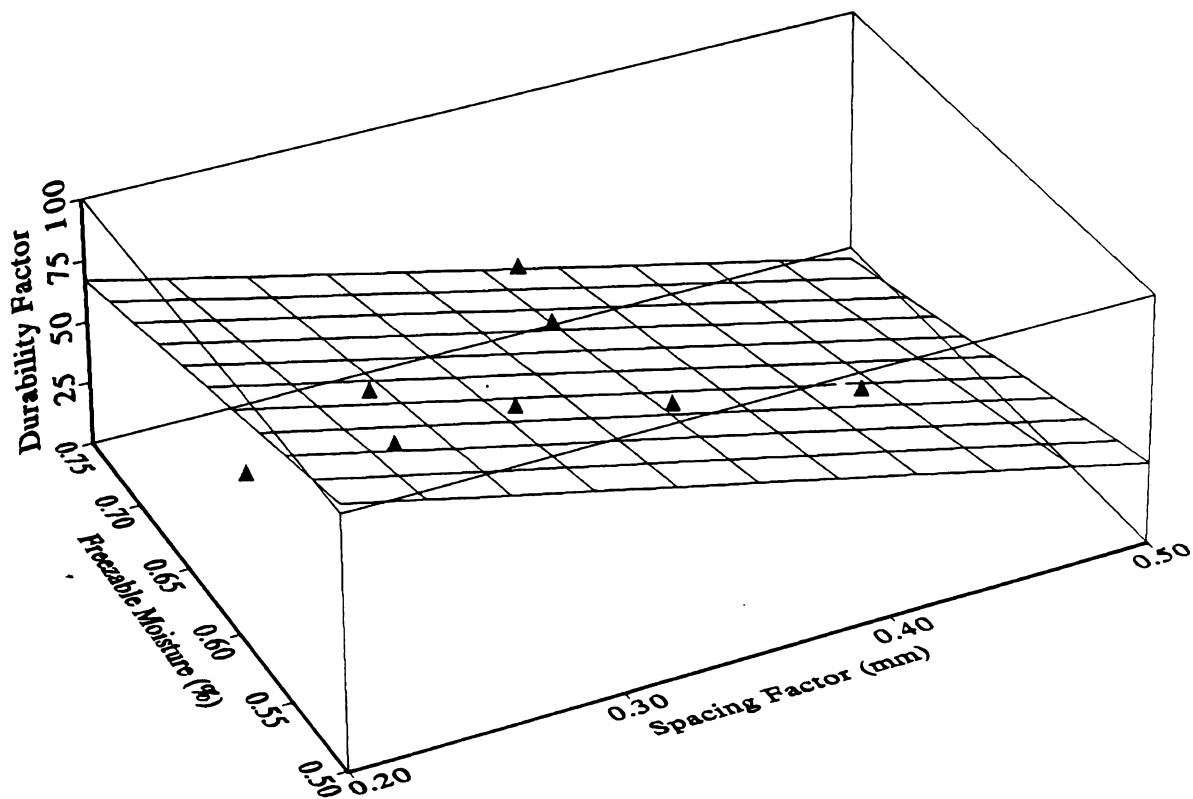


Figure 6.19. Relationship of SFTA and FM with DF.

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Figure 6.20 presents the effect of FM and C-str on the frost resistance of concrete. This clearly shows the greater effectiveness of freezable moisture as compared to compressive strength.

Figure 6.21 shows a plot of actual and predicted DF values. A relationship of this kind based on a more extensive data base would be an excellent predictor of the frost resistance of concrete.

This research has identified certain key variables and their relative importance with respect to each other. These results can be further evaluated or broadened with further testing.

The major conclusions and the recommendations drawn from this laboratory study are summarized in the next chapter.



FM, C-STR, and DF

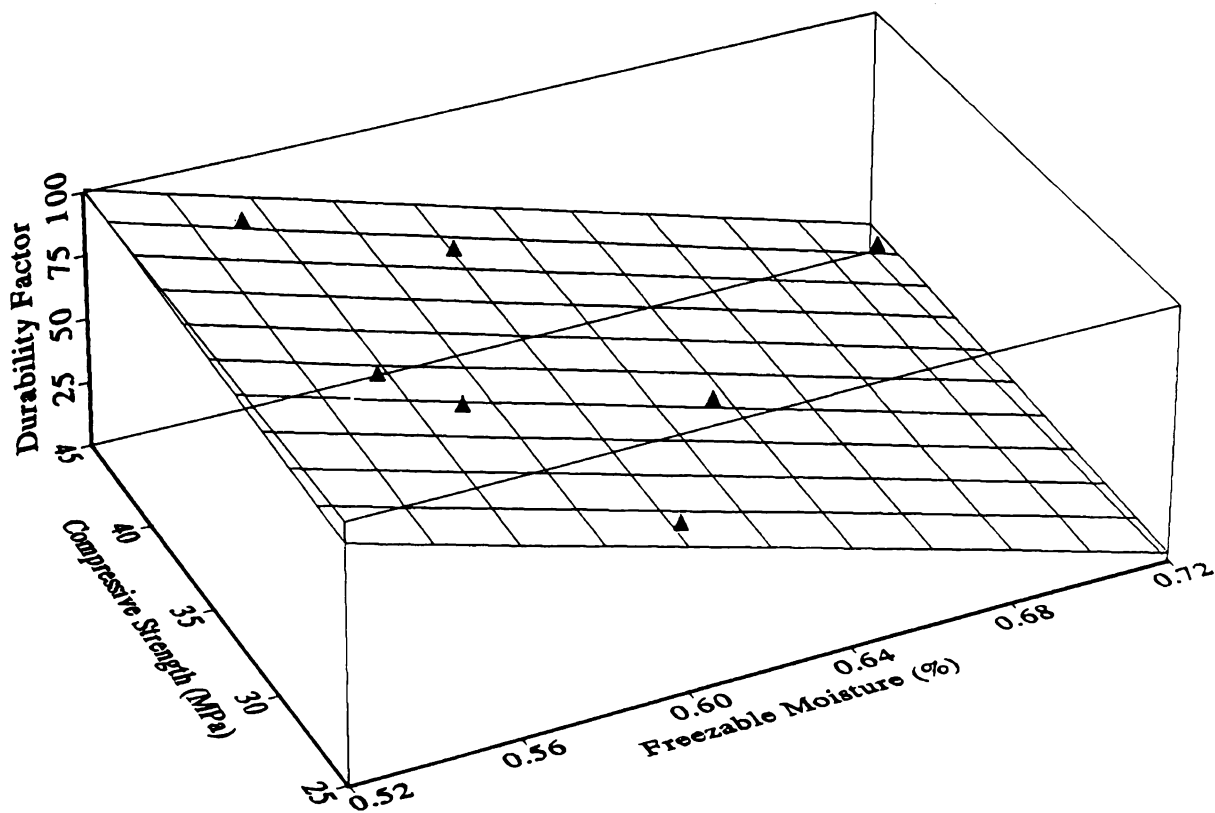
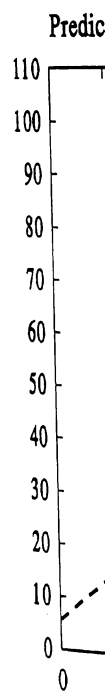


Figure 6.20. Relationship of SFTA and C-str with DF.



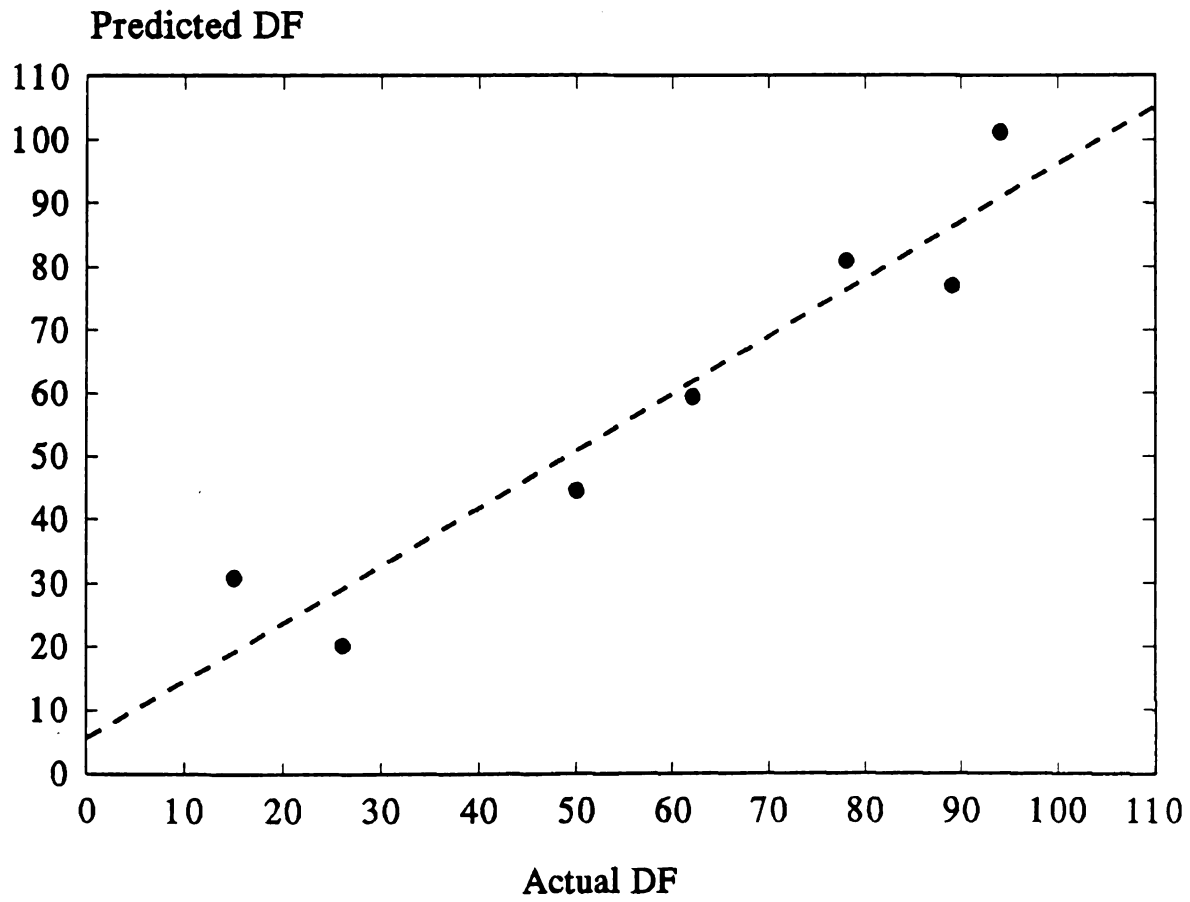


Figure 6.21. Plot showing actual versus predicted DF.

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CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 General

This research work, which was based on a laboratory study that continued for about three years, involved an extensive program of casting and testing concrete mixes with marginal air content that included various types and amounts of chemical and mineral admixtures. The resulting conclusions and observations are described herein and should be field tested for validation and verification. Further studies are warranted in certain areas, as indicated, to continue to advance the state of the art on the subject of concrete frost resistance.

7.2.1 Primary Conclusions

- (1) The Powers spacing factor, which is considered to be one of the most important criteria for the frost resistance of PCC, was compared with Philleo factors and Attiogbe's

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mean spacing for a variety of concrete mixes. The Attiogbe mean spacing, which is based on paste content, air content, and specific surface measurements obtained from linear traverse tests, showed greater variation for mixes prepared at marginal air content than the standard Power's spacing factor, particularly at durability factors lower than seventy. The results indicate that, unless a more accurate method is determined for calculating the number of voids per unit volume, as required by Philleo factor, the Powers spacing factor remains the better indicator of concrete frost resistance.

The standard spacing factor, which is based on total hardened air content, yields high values, especially for mixes that include HRWR; but, when calculations of spacing factor are based only on entrained air voids, as shown in this study, the resulting values are closer to the recommended criteria. However, for mixes with superplasticizers, the existing spacing factor criteria of 0.2 mm (0.008 in.) needs to be increased to 0.30 mm (0.012 in.) based on entrained air content, especially for fly ash concretes.

2) The combined effects of the pozzolanic and cementitious properties of certain types of mineral and chemical admixtures make it possible to produce frost-resistant concrete at marginal air contents. This will allow a reduction in the amount of entrained air required to produce frost-resistant concrete, resulting in the improvement of the mechanical properties of concrete. As seen from the literature, each additional percent of air entrainment reduces the concrete compressive strength from two to ten percent, which may be important under certain conditions. This research determined that at a marginal air content of $2.5\% \pm 0.5\%$, frost-resistant concrete can be produced with 8% and 15% silica fume and superplasticizer, or 15% class F fly ash with water-reducer and vinsol resin-based air entraining admixture.

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The use of either 15% class C fly ash WR/HRWR or 40% GGBF slag with WR failed to produce frost-resistant concretes at marginal air contents. This may have been due to inferior particle size distributions and/or interaction of chemical and mineral admixtures.

The use of 30% class C fly ash with WR and air entrainment provided better results. This can be further investigated at varying fly ash replacement levels and/or air contents to look for improved frost resistance.

3) Freezable moisture (as determined by reference 190), is a very effective and useful indicator of the internal air void/water pore structure of concrete and, hence, its frost resistance. It is recommended that this be added to concrete design specifications as an indicator of frost resistance after verification on a statistically reasonable number of tests and a variety of mix designs.

4) A relationship between concrete durability and spacing factor, freezable moisture, compressive strength has been established. This model needs to be further verified so that it can serve as a useful indicator of frost resistance allowing engineers to make adjustments between these factors to design durable concrete without sacrificing strength, quality, and workability.

3.2 Secondary conclusions

1) It has been observed that none of the air entraining admixtures or water-reducing admixtures used in this study with fly ash can be considered universally better than the

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2) Fly ash and silica fume mixes, even those with excellent and good durability factors, did show some scaling. Durability factors were generally unrelated to scaling.

4) Adherence to standard practices is essential at the time of preparation, casting, consolidating, and testing of portland cement concrete to achieve the reliable results. It is particularly important to maintain strict control of the air content of concrete placed at marginal air contents, which is more difficult for concretes prepared with silica fume in slurry form (with HRWR and water) at higher replacement levels.

7.3 Recommendations

1) The spacing factor based on entrained air content should be put to more tests, particularly using mixes with chemical and mineral admixtures at marginal air content. This will also require the consensus of researchers concerning the selection of the boundary between entrained and entrapped air voids, which is a subjective limit. It would be much easier and economical to use spacing factor based on total air content, as only minor modifications to most linear traverse analysis programs will allow the computation of this parameter.

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c) More work should be directed towards identifying and using the properties of chemical and mineral admixtures for producing frost-resistant concrete at lower air contents. The past two decades have seen a continuous trend in increasing the air content. This can be avoided as shown in this work, and an improvement in the mechanical properties of concrete can be achieved without sacrificing the frost resistance of concrete.

d) More testing should be directed towards establishing the freezable moisture as a criteria for the production of a frost-resistant concrete.

e) A quantitative relationship between concrete durability and measurements of the air void and water pore systems, and performance characteristics, as developed and demonstrated in this research work would be very useful and needs to be further pursued to advance the state of the art.

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APPENDIX A
(Properties of Materials)

Table A.1: P

1. Coarse Agg

a. Type

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Table A.1: Properties of aggregates used.**1. Coarse Aggregate****a. Type:** Dolomite, crushed limestone**b. Nominal size:** 1.25 inch**c. Bulk Specific Gravity (SSD):** 2.64**d. Absorption:** 0.9%**e. Durability factor:** 92 (determined using MDOT modification of ASTM C 666 procedure B)**f. Gradation of 6A crushed limestone:**

Sieve Size	Total % Passing	MDOT Gradation 6A Specification
1.25 in.	100	100%
1.0 in.	98	95-100%
0.75 in.	84	
0.5 in.	38*	30-60%
0.375 in.	10	
No. 4	2	0.0-0.8%

(* Gradation test run in the lab show only 16% passing 1/2 in. sieve)

g. Chemical analysis:

Oxide	Percentage
CaCO ₃	95.90%
MgCO ₃	2.55%
SiO ₂	0.80%
Al ₂ O ₃	0.17%
Fe ₂ O ₃	0.10%
S	1.02%

Table A.1 (c)

2. Fine Aggreg

a. Bull

b. Fin

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Table A.1 (cont'd)**2. Fine Aggregate****a. Bulk Specific Gravity (SSD): 2.64****b. Fineness modulus: 2.70****c. Absorption: 2.1%****d. Gradation Analysis:**

Sieve Size	Total % Passing (Average of 15 samples)	ASTM C 33 Specification
3/8	100	100
4	99.86	95-100
8	90.67	80-100
16	71.19	50-85
30	45.45	25-60
50	20.01	10-30
100	5.49	2-10
200	1.57	0.3

Table A.2. C

Pozzolan Type & S
Class F F Centralia
Class C Laramie

Table A.2. Chemical properties of fly ash.

Pozzolan Type & Source	Chemical Composition	ASTM C 618-89 Specifications	Actual Percent
Class F Fly Ash Centralia	Silicon Dioxide Aluminum Oxide Iron Oxide * * * Total Sulfur Trioxide Calcium Oxide Moisture Content Loss of Ignition	70.0 Min 05.0 Max 03.0 Max 06.0 Max	48.87 23.23 6.14 78.24 1.16 8.82 0.04 0.13
Class C Fly Ash Laramie River	Silicon Dioxide Aluminum Oxide Iron Oxide * * * Total Sulfur Trioxide Calcium Oxide Moisture Content Loss of Ignition	50.0 Min 05.0 Max 03.0 Max 06.0 Max	33.68 18.47 6.37 58.52 2.48 27.23 0.06 0.30

Table A.3. 1

Pozzolan Type & Source
Class F Fly Ash Centralia
Class C Fly Ash Laramie

Table A.3. Physical properties of fly ash.

Pozzolan Type & Source	Properties	ASTM C 618-89 Specifications	Actual Percent
Class F Fly Ash Centralia	Fineness Retained on #325 Sieve (%) Pozzolanic Activity Index With Portland Cement Ratio to Control @ 28 days With Lime @ 7 days (psi) Water Requirement, % of Control Soundness Autoclave Expansion (%) Specific Gravity	34 Max 75 Min 800 Min 105 Max 0.8 Max	24.84 90.70 1020.00 88.00 -0.037 2.29
Class C Fly Ash Laramie River	Fineness Retained on #325 Sieve (%) Pozzolanic Activity Index With Portland Cement Ratio to Control @ 28 days With Lime @ 7 days (psi) Water Requirement, % of Control Soundness Autoclave Expansion (%) Specific Gravity	34 Max 75 Min No Limit 105 Max 0.8 Max	12.72 124.30 890.00 86.40 -0.013 2.6

APPENDIX B

(Mix Designs, Freeze-Thaw Durability, and Air Void Characteristics)

Table B.1. Mix design and concrete characteristics for Matix B through E.

	AFC	FAC (%)	k (m/s) $\times 10^{12}$
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Table B.1. Mix design and concrete characteristics for Matix B through E.

Cell #	C-str (KPa)	CA-SSD (#/cyd)	FA-SSD (#/cyd)	H-water (#/cyd)	Cement (#/cyd)	Pozz (#/cyd)	WR/HRWR (Type)	AEA (Type)	FAC (%)	k (m/s)x10 ⁻¹² /FH (%)
B1/D1	43376	2078	1090	244	610	-	WR	AEA1	2.8	2.3
B2/D3	38784	2079	1185	236	525	-	WR	AEA1	2.7	1.8
B3	49623	2093	1101	246	615	-	WR	AEA2	2.0	4.2
B4	41866	2072	1147	243	541	-	WR	AEA2	3.0	13.0
B5/D5	42335	-	-	-	-	-	WR	AEA1	-	1.4/0.55
B6/D7	38846	2091	1152	242	467	70	WR	AEA1	2.8	2.2/0.59
B7	39488	2076	1021	255	555	83	WR	AEA2	2.6	13.0
B8	32144	2092	1223	226	438	66	WR	AEA2	2.8	18.0
B9	41549	2084	1120	237	516	77	HRWR	AEA1	2.2	7.6
B10	34123	2073	1115	247	478	72	HRWR	AEA1	2.8	10.0
B11	32862	2070	1132	232	504	75	HRWR	AEA2	2.8	5.5
B12	41604	2079	1136	244	472	71	HRWR	AEA2	2.5	3.2
B13/D13	38240	2109	1078	251	547	83	WR	AEA1	2.0	-
B14/D15	37323	2092	1177	242	468	70	WR	AEA1	2.5	2.0/0.65
B15	38502	2105	1096	250	538	81	WR	AEA2	2.0	9.9/0.57
B16	-	2108	1226	232	448	68	WR	AEA2	2.0	2.5/0.68

Table B.1. (Cont'd).

[illegible]

Table B.1. (Cont'd).

Cell #	C-str (kPa)	CA-SSD (#/cyd)	FA-SSD (#/cyd)	H-water (#/cyd)	Cement (#/cyd)	Pozz (#/cyd)	WR/HRWR (Type)	AEA (Type)	FAC (%)	k (m/s)x10 ⁻¹² /FH (%)
B17	25643	2071	1206	217	472	71	HRWR	AEA1	3.0	9.8
B18	24925	2076	1117	248	479	72	HRWR	AEA1	2.9	7.2
B19	31069	2074	1207	215	472	71	HRWR	AEA2	3.0	9.9
B20	42501	2089	1141	245	474	71	HRWR	AEA2	2.3	6.3
B21/E9	61303	2071	1158	224	488	73	HRWR	AEA1	3.0	3.2
B22/E11	52443	2039	1210	243	419	63	HRWR	AEA1	3.0	2.2
B23	59456	2076	1118	233	505	76	HRWR	AEA2	2.9	7.3
B24	53092	2078	1300	206	398	60	HRWR	AEA2	2.8	2.6
C1	53312	2099	1017	258	461	184	-	AEA1	2.2	9.0
C2	43301	2085	1038	264	419	168	-	AEA1	2.8	14.0
C3	43742	2094	1071	246	439	176	WR	AEA1	2.4	8.9
C4	43073	2093	1131	246	390	156	WR	AEA1	2.4	6.0
D9	36268	2092	1093	237	458	137	WR	AEA1	2.8	-
D10	30972	2092	1093	237	458	137	WR	AEA1	2.8	-
D11	42646	2099	1156	238	409	123	WR	AEA1	2.5	-
D12	34380	2099	1156	238	409	123	WR	AEA1	2.5	-

Table B.1 (Cont'd).

Cell #	C-str (KPa)	CA-SSD (#/cyd)	FA-SSD (#/cyd)	H-water (#/cyd)	Cement (#/cyd)	Pozz (#/cyd)	WR/HRWR (Type)	AEA (Type)	FAC (%)	k (m/s) $\times 10^{12}$ /FH (%)
D15	30917	2109	1078	251	547	83	WR	AEA1	2.0	-
D16	30834	2092	1177	242	468	70	WR	AEA1	2.5	3.0/0.65
D17	25580	2100	1082	247	474	142	WR	AEA1	2.4	6.1/0.6
D18	32455	2100	1082	247	474	142	WR	AEA1	2.4	9.3/0.45
D19	38681	2109	1183	239	411	123	WR	AEA1	2.0	37.0
D20	38700	2107	1182	239	411	123	WR	AEA1	2.0	5.7/0.59
E1	41889	1899	1266	253	633	-	-	AEA1	2.5	4.3/0.71
E2	46783	1894	1352	251	559	-	-	AEA1	2.2	3.4/0.58
E3	38864	2078	1090	244	610	-	-	AEA1	-	-/0.68
E4	40900	2079	1185	236	525	-	-	AEA1	-	-
E5	46334	2080	1229	214	495	40	HRWR	AEA1	2.6	2.2
E6	53491	2080	1229	214	495	40	HRWR	AEA1	2.6	1.2
E7	42728	2146	1190	225	463	37	HRWR	-	2.7	5.1
E8	40632	2146	1190	225	463	37	HRWR	-	2.7	8.5
E10	53381	2072	1158	224	488	73	HRWR	AEA1	3.0	-
E12	52898	2162	1214	207	398	60	HRWR	AEA1	3.5	4.1/0.35

Table B.2. Freeze-thaw durability test results for Matrix B through E.

Matrix	Test Results	Actual/Recomm. Range (D2S)
B		
C		
D		
E		

Table B.2. Freeze-thaw durability test results for Matrix B through E.

Cell #	L-Chg (%)	Wt-Chg (%)	# Cyc Endured	Std. Dev. (s)	DF	Std. Dev. (s)	Actual/Recomm Range (D2s)
B1/D1	0.0670	-0.115	268	29.43	56	11.33	27.0/25.5
B2/D3	0.0902	0.108	78	19.46	16	3.85	9.0/10.3
B3	0.0878	0.099	99	20.51	20	4.09	11.0/13.3
B4	0.0263	0.015	257	46.68	59	19.31	24.0/25.5
B5/D5	0.0114	0.088	300	0	94	2.08	5.0/4.9
B6/D7	0.0267	0.206	300	0	89	5.03	13.0/11.1
B7	0.0754	0.128	173(300, 105)	95.60(0.71, 8.5)	36(55, 21)	22.18(7.07, 2)	(5)50.0/19.5, (2)10.0/40.2, (3)4.0/17.2
B8	0.0610	0.203	300	0	78	6.88	17.0/25.5
B9	0.099	0.295	73	11.34	14	2.19	6.0/10.3
B10	0.0514	-0.020	203	51.73	39	7.91	8.0/19.5
B11	0.0964	0.188	235	35.59	43	9.81	25.0/19.5
B12	0.0634	0.065	117	17.41	23	3.32	8.0/13.3
B13/D13	0.0888	0.230	146	21.51	29	4.55	11.0/13.3
B14/D15	0.0717	0.227	75	20.35	15	4.06	11.0/10.3
B15	0.0766	0.210	242	43.45	50	12.34	(4)29.0/28.5
B16	0.0774	0.218	300	0	70	2.05	(2)3.0/34.2

Note: + sign indicates increase in length/weight compared to initial reading
 - sign indicates decrease in length/weight compared to initial reading

Table B.2. (Cont'd).

	Actual/Recomm Range (02S)		
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Table B.2. (Cont'd).

Cell #	L-Chg (%)	Wt-Chg (%)	# Cys Endured	Std. Dev. (s)	DF	Std. Dev. (s)	Actual/Recomm Range (D2S)
B17	0.0927	0.106	61	25.72	12	5.13	13.0/10.3
B18	0.0804	0.275	178	47.78	35	1.95	30.0/19.5
B19	0.0761	0.077	276	33.37	56	7.26	19.0/25.5
B20	0.0842	0.083	185	49.40	37	9.86	23.0/13.3
B21/E9	0.0430	-0.071	300	0	88	8.29	20.0/11.1
B22/E11	0.0184	0.004	300	0	93	1.79	4.0/4.9
B23	0.0118	-0.194	300	0	83	3.97	9.0/11.1
B24	0.0287	-0.169	300	0	70	3.56	8.0/25.5
C1	0.0843	0.247	97	24.27	19	4.83	13.0/10.3
C2	0.0871	0.039	153	13.03	30	2.51	13.0/13.3
C3	0.0702	0.185	75	11.69	15	2.39	6.0/10.3
C4	0.0738	0.258	67	11.39	13	2.39	6.0/10.3
D6	0.0340	0.019	300	0	83	1.15	(3)2.0/14.4
D8	0.0434	0.130	300	0	80	2.42	(6)6.0/10.2
D9	0.0733	0.137	300	0	65	7.98	19.0/10.3
D10	0.1059	0.157	231	60.34	45	18.03	(3)25.0/25.1
D11	0.058	0.21	282	25.23	67	14.29	27.0/10.3
D12	0.109	0.161	191	21.77	38	4.45	11.0/17.8

Note: + sign indicates increase in length/weight compared to initial reading
- sign indicates decrease in length/weight compared to initial reading

Table B.2: (Cont'd).

1990-1999 Range (D2S)

Table B.2: (Cont'd).

Cell #	L-Chg (%)	Wt-Chg (%)	# Cys Endured	Std. Dev. (s)	DF	Std. Dev. (s)	Actual/Recomm Range (D2S)
D14	0.0842	0.163	124	15.60	24	5.85	12.0/17.8
D16	0.0840	0.140	65	29.53	13	3.70	15.0/10.3
D17	0.0656	0.121	297	6.26	62	4.47	10.0/25.5
D18	0.0764	0.083	293	11.26	61	3.08	12.0/10.3
D19	0.0659	0.066	139	16.17	29	3.08	5.0/13.3
D20	0.0574	0.157	293	0	70	6.26	15.0/25.5
E1	0.0871	0.131	133	21.56	26	4.22	(9)13.0/12.2
E2	0.0716	0.14	250	34.36	51	8.83	19.0/13.3
E3	0.0888	0.103	143	27.26	28	6.83	13.0/13.3
E4	0.0806	0.654	264	39.26	55	10.09	28.0/23.2
E5	0.1003	0.076	216(300, 132)	99.24(0.71, 39.6)	47(68, 27)	25.24(11.13, 7.78)	(4)55.0/21.8, (2)16.0/40.2, (2)11.0/21.0
E6	0.1256	0.063	235	49.38	47	9.73	25.0/19.5
E7	0.1052	0.164	300	0	67	2.79	6.0/25.5
E8	0.1151	0.033	300	0	67	3.85	9.0/25.5
E10	0.0604	0.024	285	33.09	72	17.98	47.0/11.5
E12	0.0246	0.042	300	0	92	0.71	2.0/4.9

Note: + sign indicates increase in length/weight compared to initial reading
 - sign indicates decrease in length/weight compared to initial reading

Table B.3. Air void characteristics of Matrix B through E set 1.

Cell #	FAC (%)	NTA (%)	HEA (%)	P/A-T	P/A-E	ACLT A (mm)	ACLEA (mm)	#AVTA	#AVEA	VPNTA	VPNEA	SFTA (mm)	SFEA (mm)	SST (mm ² /mm ³)	SSE (mm ² /mm ³)
B1/D1	2.8	2.7	1.7	10.21	16.2	0.201	0.130	154	147	0.135	0.129	0.322	0.257	19.9	30.9
B2/D3	2.7	3.8	2.1	7.41	13.5	0.227	0.131	192	182	0.168	0.159	0.315	0.238	17.6	30.4
B3	2.0	2.5	1.2	7.20	15.3	0.186	0.091	154	148	0.035	0.148	0.255	0.175	21.5	43.8
B4	3.0	3.3	2.1	9.47	15.1	0.165	0.108	230	221	0.201	0.193	0.256	0.205	24.2	37.1
B5/D5	2.5	2.5	2.0	8.90	11.1	0.123	0.101	229	225	0.200	0.197	0.186	0.167	32.4	39.8
B6/D7	2.8	2.4	2.0	11.50	13.8	0.145	0.123	187	185	0.164	0.162	0.245	0.224	27.6	32.6
B7	2.6	2.9	1.4	8.48	17.3	0.185	0.095	179	170	0.157	0.149	0.272	0.192	21.6	42.0
B8	2.8	2.6	1.8	8.88	13.2	0.164	0.112	183	179	0.160	0.157	0.246	0.202	24.6	35.6
B9	2.2	1.8	1.5	20.44	24.8	0.184	0.156	113	110	0.099	0.096	0.399	0.367	21.7	25.7
B10	2.8	2.3	1.9	15.26	18.8	0.116	0.095	229	227	0.200	0.199	0.221	0.198	34.5	42.2
B11	2.8	3.0	1.5	12.27	23.6	0.171	0.093	199	191	0.074	0.167	0.297	0.213	23.4	43.2
B12	2.5	3.5	1.5	11.86	27.6	0.210	0.096	190	181	0.166	0.158	0.259	0.235	19.0	41.7
B13/D13	2.0	2.2	1.6	5.50	7.9	0.183	0.133	140	135	0.122	0.118	0.222	0.190	21.9	30.1
B14/D15	2.5	2.2	1.2	12.56	23.0	0.218	0.125	113	108	0.099	0.090	0.383	0.284	18.3	32.0
B15	2.0	1.3	0.9	21.90	31.8	0.189	0.134	76	74	0.066	0.065	0.421	0.349	21.2	29.9
B16	2.0	2.5	1.4	12.92	22.2	0.189	0.113	148	144	0.129	0.126	0.336	0.254	21.1	35.3
B17	2.3	1.6	1.0	28.22	46.5	0.206	0.131	89	85	0.078	0.074	0.512	0.400	19.4	30.6
B18	2.9	3.7	2.2	10.94	19.3	0.261	0.163	163	155	0.143	0.136	0.430	0.338	15.4	24.5

Table B.3. (cont'd)

Cell #	FAC (%)	HTA (%)	HEA (%)	P/A-T	P/A-E	ACLTa (mm)	ACLEA (mm)	#AVTA	#AVEA	VPMTA	VPNEA	SFTA (mm)	SFEA (mm)	SST (mm ² /mm ³)	SSE (mm ² /mm ³)
B19	3.0	3.4	1.5	13.3	31.3	0.332	0.156	118	107	0.103	0.094	0.598	0.404	12.0	25.7
B20	2.3	2.8	1.1	14.1	35.3	0.342	0.149	94	86	0.082	0.075	0.630	0.405	11.7	26.9
B21/E9	3.0	3.4	2.5	4.4	6.0	0.183	0.138	214	207	0.187	0.181	0.199	0.173	21.9	29.0
B22/E11	3.0	2.9	2.3	8.4	10.6	0.151	0.122	216	212	0.189	0.185	0.222	0.199	26.4	32.7
B23	2.9	3.4	3.0	10.2	11.8	0.135	0.117	290	288	0.254	0.252	0.215	0.200	29.7	34.2
B24	2.8	3.3	2.7	8.7	10.8	0.176	0.143	217	213	0.190	0.186	0.261	0.235	22.8	27.9
C1	2.2	1.6	0.9	22.3	42.2	0.153	0.084	122	118	0.107	0.103	0.344	0.245	26.2	47.2
C2	2.8	3.7	1.8	10.8	22.6	0.234	0.119	178	169	0.156	0.148	0.385	0.268	17.1	33.7
C3	2.4	2.1	1.4	10.6	15.9	0.153	0.105	155	150	0.136	0.131	0.249	0.205	26.1	37.9
C4	2.4	1.7	1.3	20.6	26.3	0.149	0.119	129	126	0.113	0.110	0.323	0.287	26.9	33.6
D9	2.8	2.6	2.5	6.0	6.3	0.106	0.103	283	282	0.248	0.247	0.134	0.132	37.6	38.8
D11	2.5	2.7	2.4	8.2	9.3	0.102	0.091	303	300	0.265	0.262	0.148	0.139	39.2	44.0
D17	2.4	2.7	1.6	9.1	15.1	0.198	0.124	154	149	0.135	0.130	0.302	0.236	20.2	32.2
D19	2.0	1.3	0.6	27.1	55.7	0.177	0.092	82	77	0.072	0.067	0.433	0.302	22.6	43.5
E1	2.5	1.8	1.1	13.2	21.4	0.201	0.132	103	97	0.090	0.085	0.361	0.292	19.9	30.2
E3	2.2	1.8	1.1	12.2	19.1	0.192	0.128	106	101	0.093	0.088	0.331	0.269	20.9	31.3
E5	2.6	2.4	1.4	10.3	18.0	0.191	0.116	145	137	0.127	0.120	0.306	0.237	21.0	34.6
E7	2.7	3.5	2.2	7.3	11.8	0.245	0.161	161	153	0.141	0.134	0.339	0.274	16.3	24.9

Table B.4. Air void characteristics of Matrix B through E set 2.

	HTA (%)	HEA (%)	AMS (mm)	PF90 (mm)	PF99 (mm)	ACLTA (mm)	VPMTA
						0.111	0.244

Table B.4. Air void characteristics of Matrix B through E set 2.

Cell #	FAC (%)	HTA (%)	HEA (%)	AMS (mm)	PF90 (mm)	PF99 (mm)	ACLTA (mm)	VPMTA
B1/D1	2.8	2.7	1.7	0.286	0.045	0.080	0.111	0.244
B2/D3	2.7	3.8	2.1	0.239	0.021	0.042	0.079	0.481
B3	2.0	2.5	1.2	0.389	0.027	0.056	0.081	0.311
B4	3.0	3.3	2.1	0.248	0.036	0.066	0.079	0.423
B5/D5	2.5	2.5	2.0	0.122	0.035	0.066	0.077	0.319
B6/D7	2.8	2.4	2.0	0.225	0.043	0.075	0.080	0.296
B7	2.6	2.9	1.4	0.192	0.027	0.052	0.066	0.438
B8	2.8	2.6	1.8	0.171	0.031	0.059	0.089	0.296
B9	2.2	1.8	1.5	0.709	0.044	0.069	0.062	0.294
B10	2.8	2.3	1.9	0.003	0.039	0.065	0.063	0.367
B15	2.8	3.0	1.5	0.380	0.034	0.059	0.069	0.430
B12	2.5	3.5	1.5	0.515	0.031	0.054	0.061	0.574
B13/D13	2.0	2.2	1.6	0.064	0.021	0.048	0.106	0.212
B14/D15	2.5	2.2	1.2	0.365	0.028	0.048	0.051	0.424
B15	2.0	1.3	0.9	0.055	0.086	0.133	0.104	0.121
B16	2.0	2.5	1.4	0.381	0.053	0.089	0.083	0.295
B17	2.3	1.6	1.0	1.322	0.056	0.085	0.064	0.252
B18	2.9	3.7	2.2	0.278	0.048	0.086	0.125	0.298

Table B.4. (cont'd)

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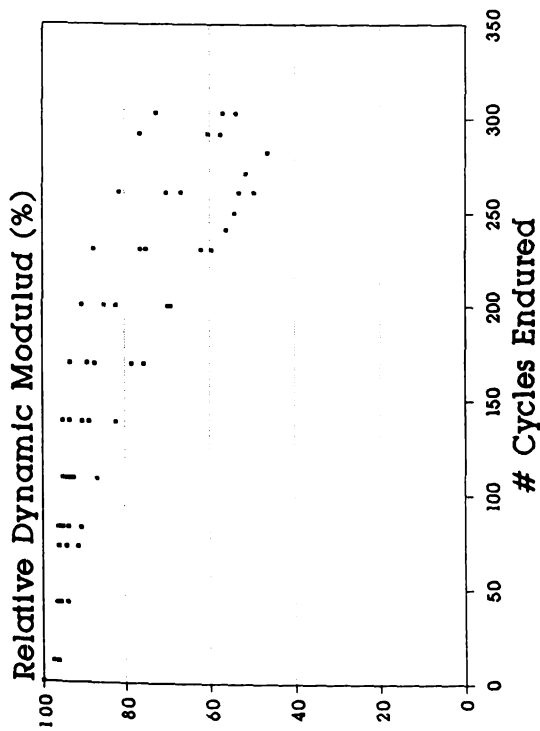
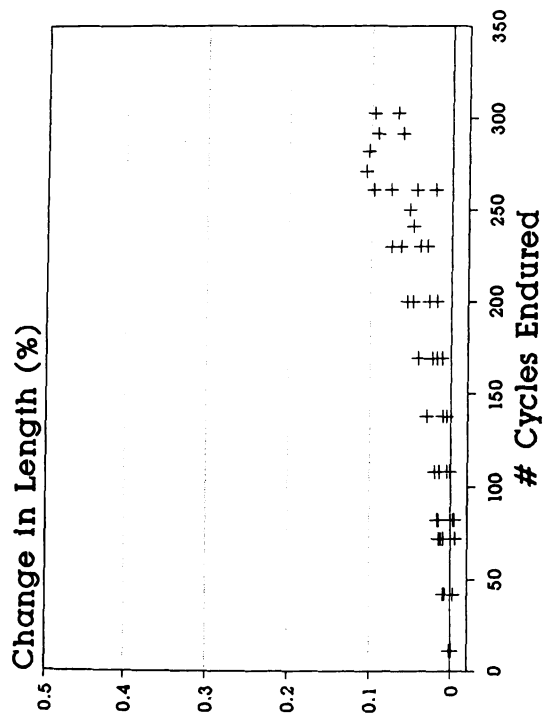
Table B.4. (cont'd)

Cell #	FAC (%)	HTA (%)	HEA (%)	AMS (mm)	PF90 (mm)	PF99 (mm)	ACLTa (mm)	VPMTA
B19	3.0	3.4	1.5	1.024	0.057	0.096	0.124	0.278
B20	2.3	2.8	1.1	0.095	0.036	0.060	0.067	0.421
B21/E9	3.0	3.4	2.5	0.060	0.018	0.055	0.121	0.282
B22/E11	3.0	2.9	2.3	0.150	0.047	0.089	0.118	0.242
B23	2.9	3.4	3.0	0.240	0.049	0.088	0.106	0.322
B24	2.8	3.3	2.7	0.222	0.048	0.091	0.159	0.213
C1	2.2	1.6	0.9	0.632	0.039	0.060	0.056	0.289
C2	2.8	3.7	1.8	0.495	0.037	0.066	0.104	0.353
C3	2.4	2.1	1.4	0.176	0.030	0.053	0.066	0.315
C4	2.4	1.7	1.3	0.521	0.031	0.048	0.052	0.323
D9	2.8	2.6	2.5	0.052	0.027	0.061	0.101	0.261
D11	2.5	2.7	2.4	0.677	0.029	0.055	0.072	0.375
D17	2.4	2.7	1.6	0.218	0.032	0.059	0.076	0.349
D19	2.0	1.3	0.6	0.810	0.045	0.069	0.040	0.319
E1	2.5	1.8	1.1	0.332	0.044	0.074	0.087	0.208
E3	2.2	1.8	1.1	0.248	0.048	0.082	0.099	0.180
E5	2.6	2.4	1.4	0.245	0.020	0.036	0.052	0.465
E7	2.7	3.5	2.2	0.226	0.033	0.066	0.133	0.262

(Freeze-thaw)

APPENDIX C

(Freeze-thaw Test Data - Dilation, Mass Loss and Relative Dynamic Modulus)



Change in Weight (%)

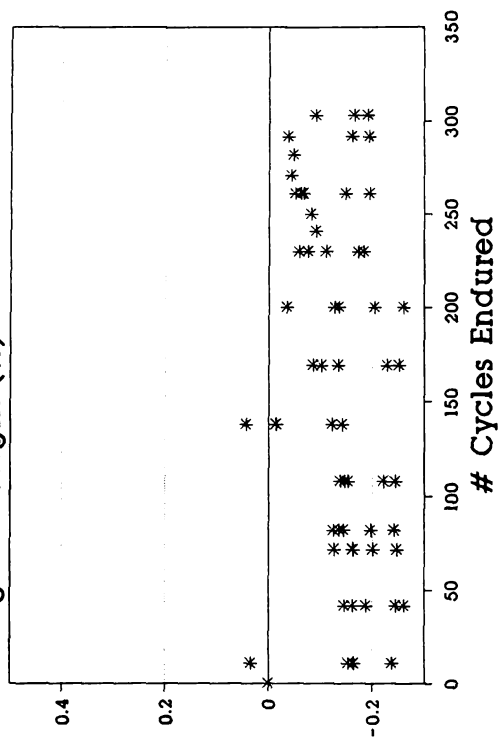
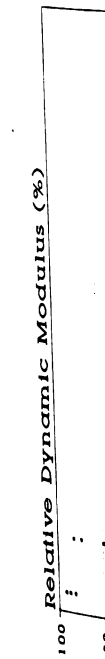


Figure C.1. RDM, change in length, weight versus no. of freeze-thaw cycles endured for PCC with W/C=0.40, AEA1 and WR.



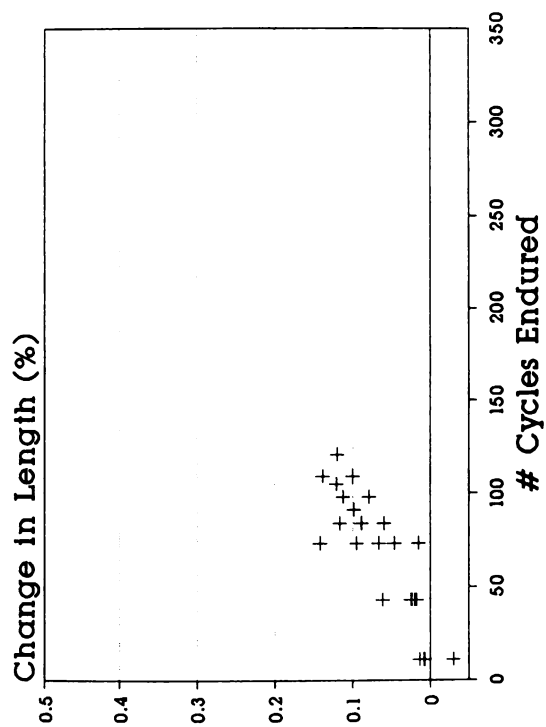
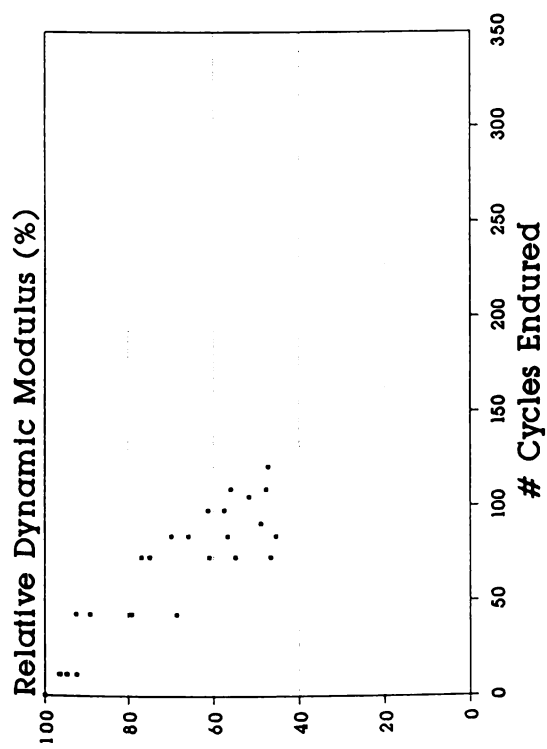
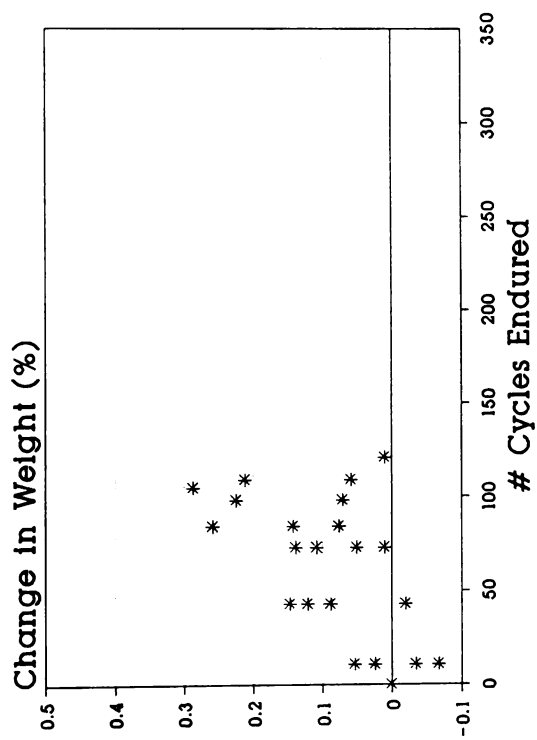
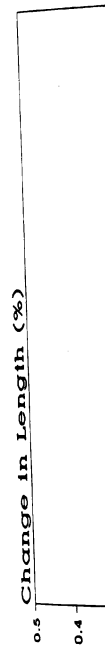
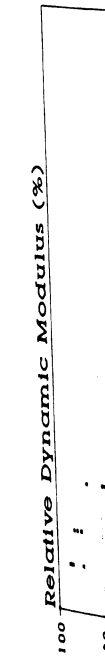


Figure C.2. RDM, change in length, weight versus no. of freeze-thaw cycles endured for PCC with W/C=0.45, AEAl and WR.





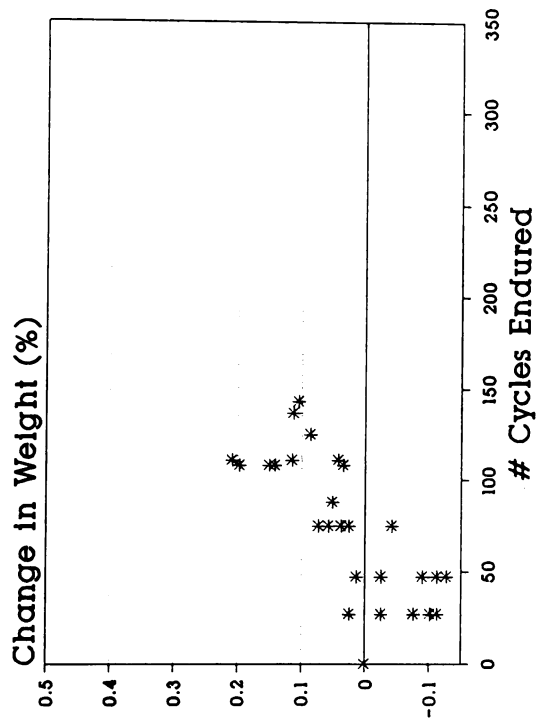
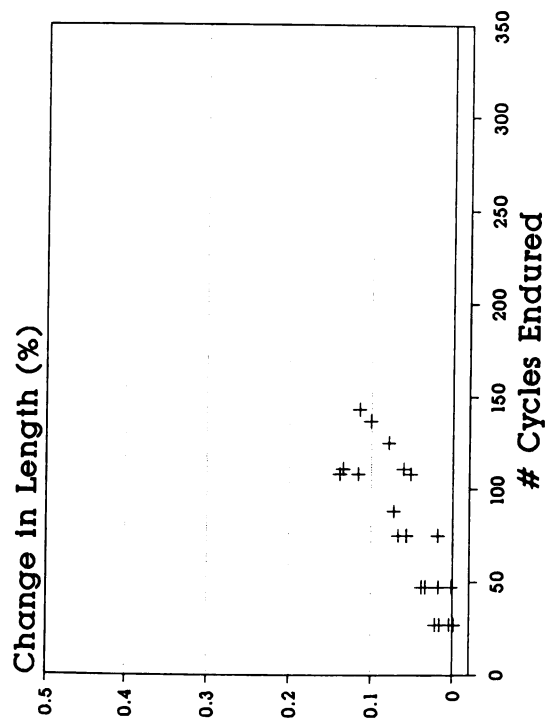
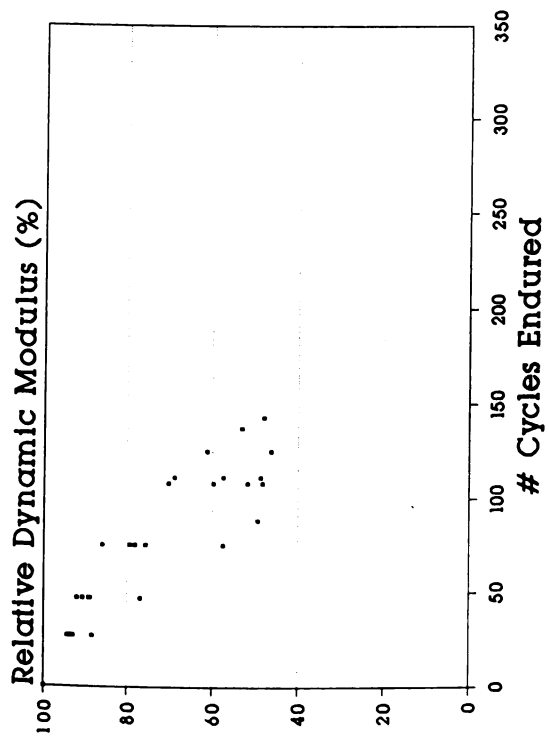
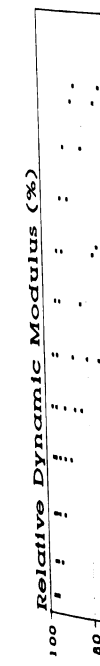
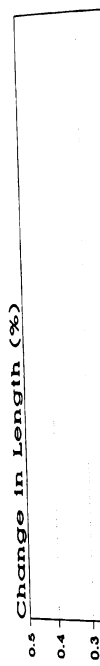


Figure C.3. RDM, change in length, weight versus no. of freeze-thaw cycles endured for PCC with WR, W/C=0.40 and AEA2.



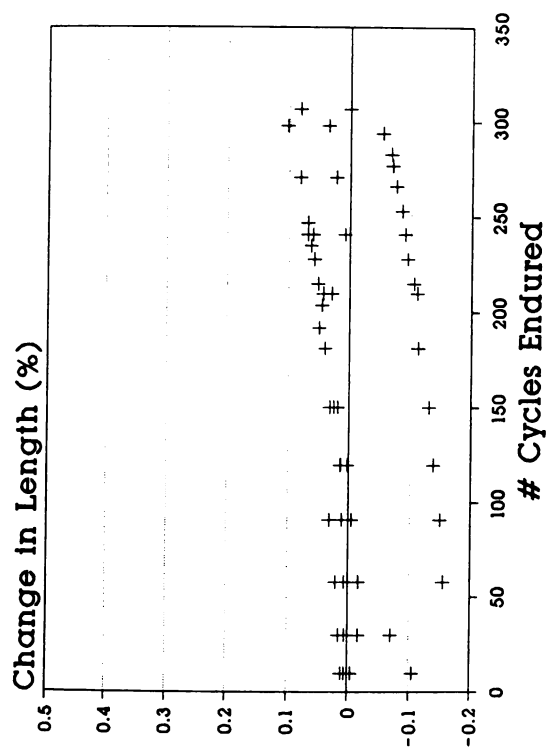
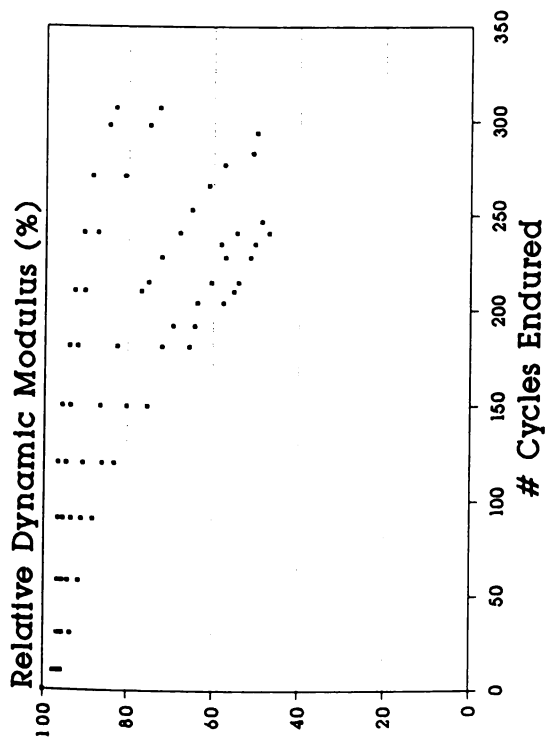
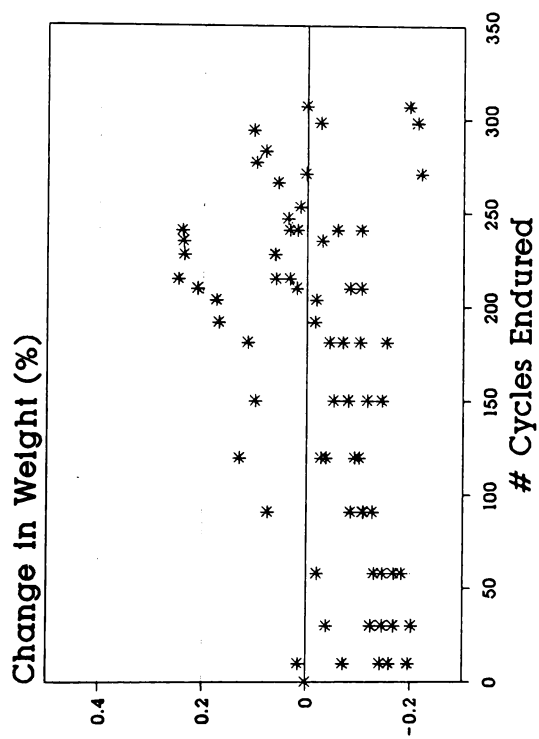
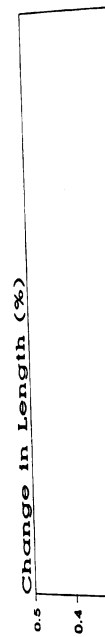
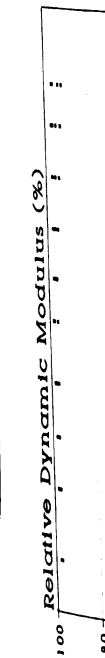


Figure C.4. RDM, change in length, weight versus no. of freeze-thaw cycles endured for PCC with WR, W/C=0.45, AEA2.





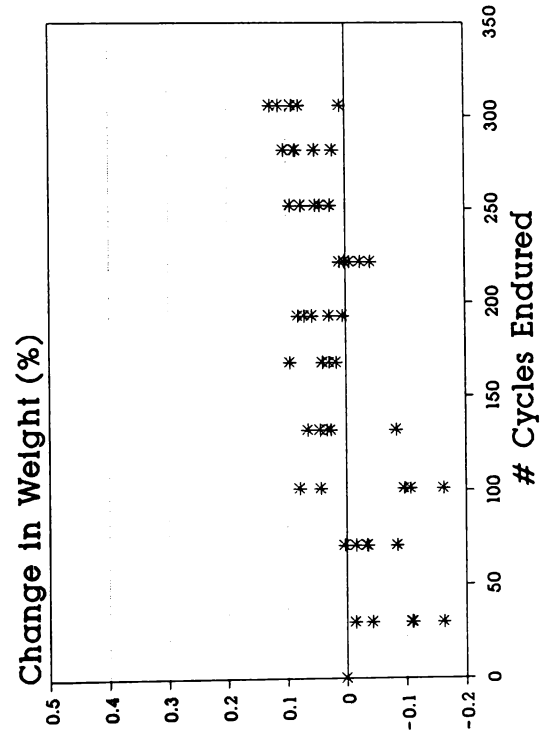
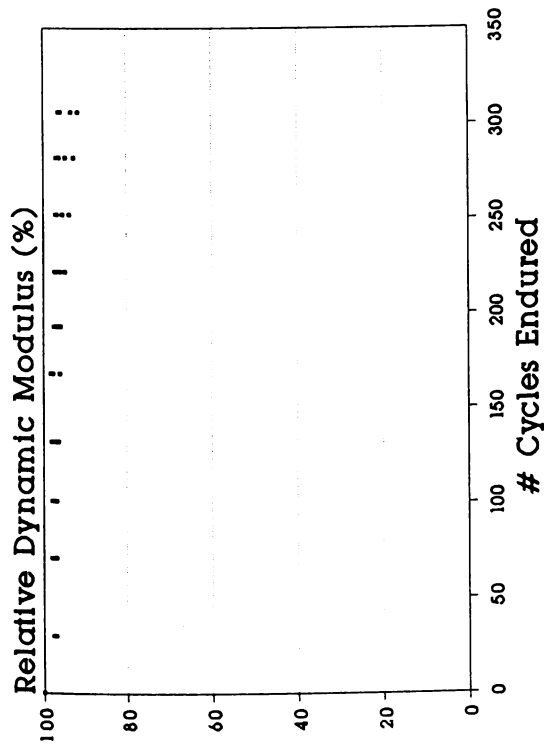
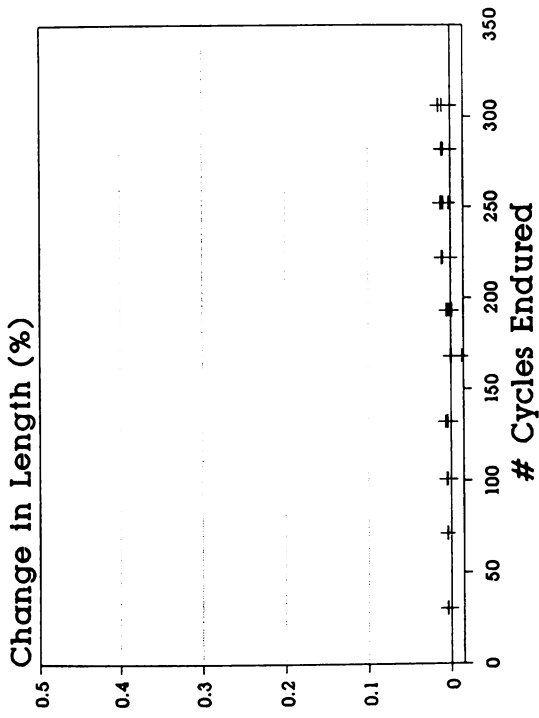
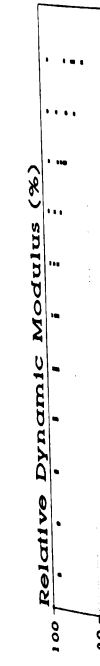
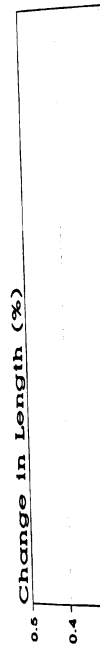


Figure C.5. RDM, change in length, weight versus no. of freeze-thaw cycles endured with $W/C+P=0.40$, AEAl, and Cl F FA.



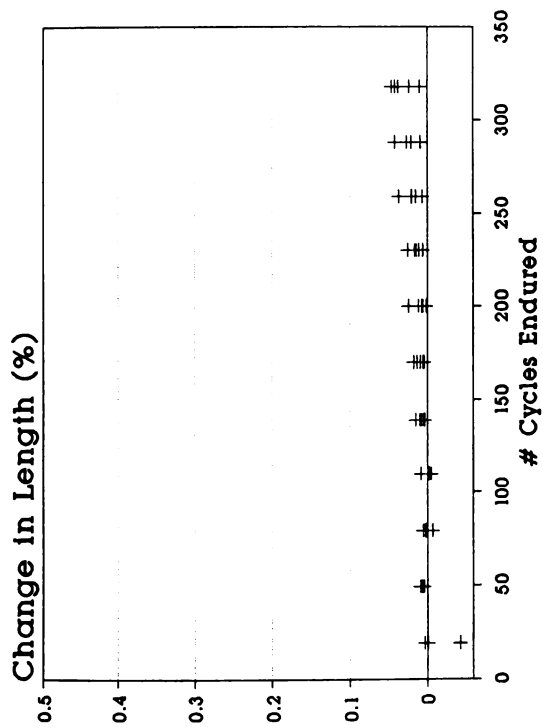
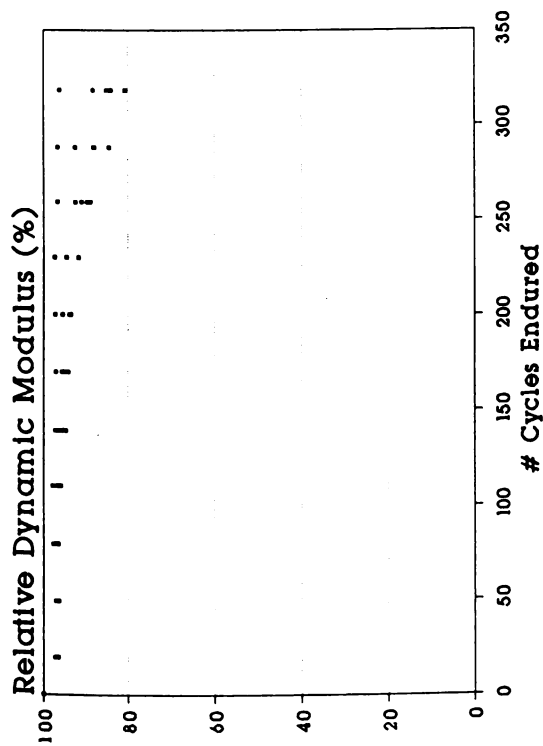
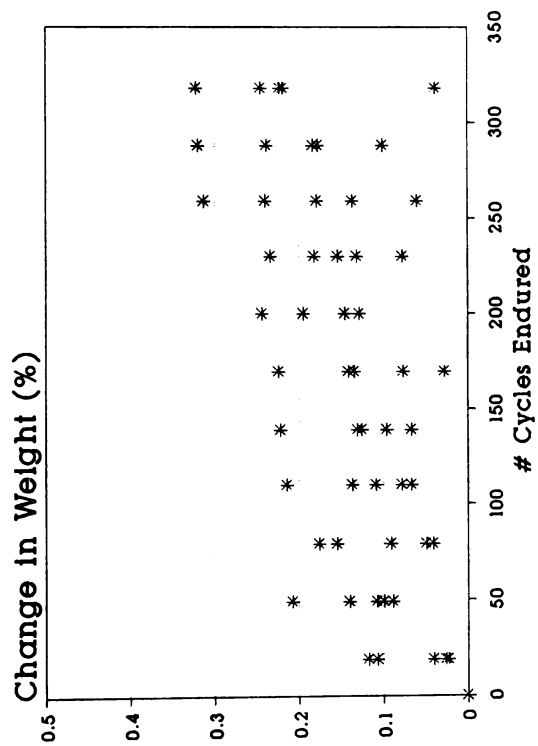
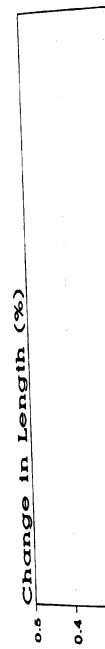
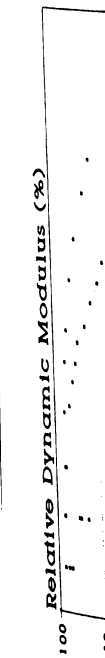


Figure C.6. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.45, AEAl, and Cl F FA.





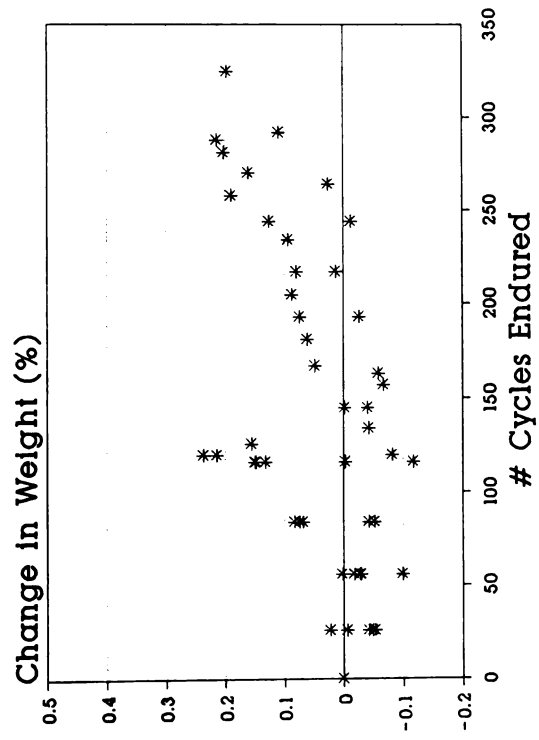
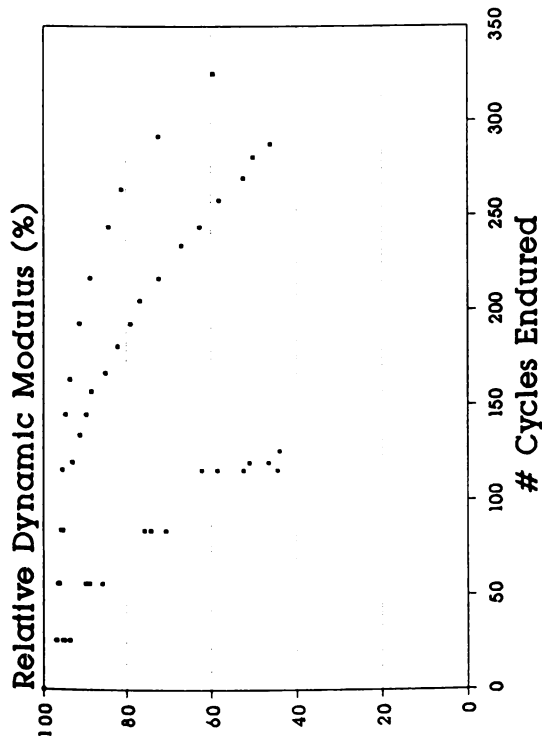
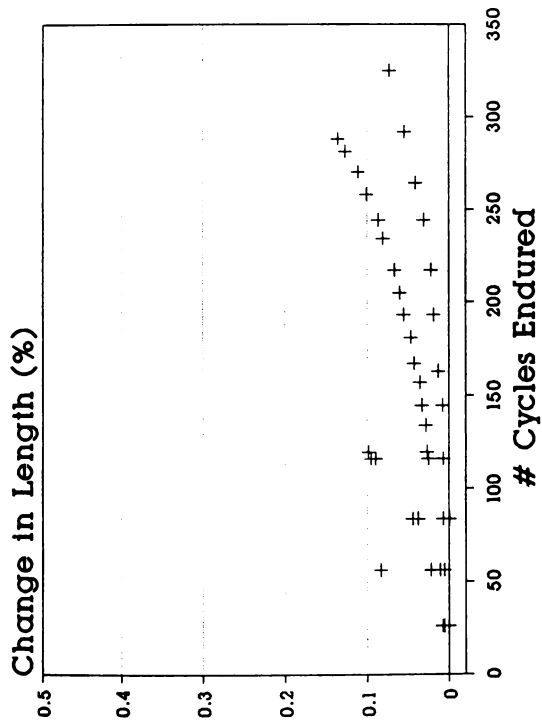
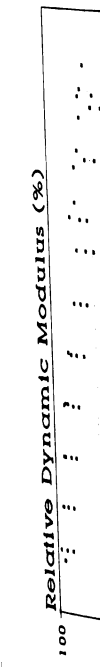


Figure C.7. RDM, change in length, weight versus no. of freeze-thaw cycles endured with $W/C+P=0.40$, AEA2, C1 F FA.



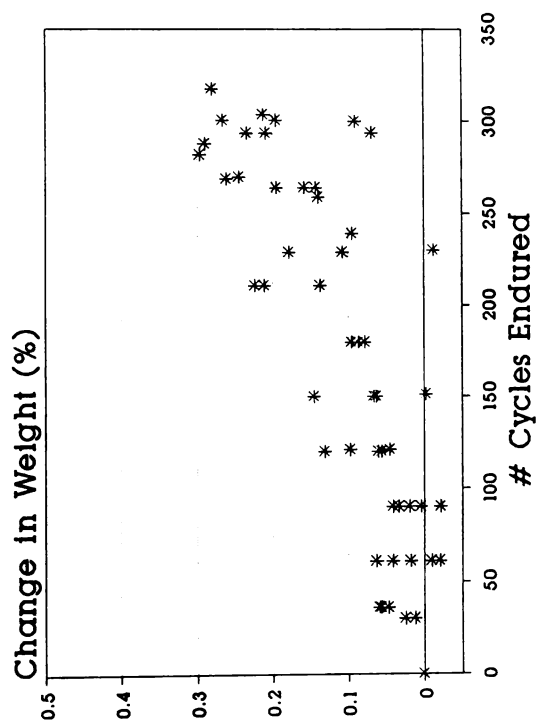
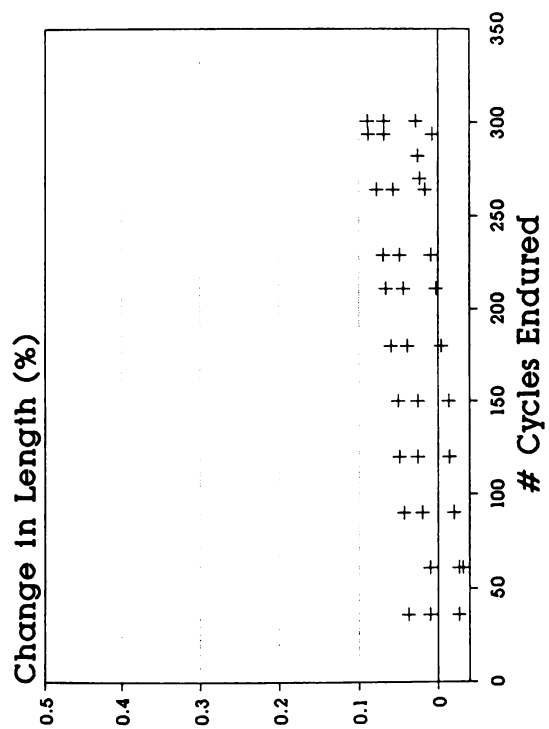
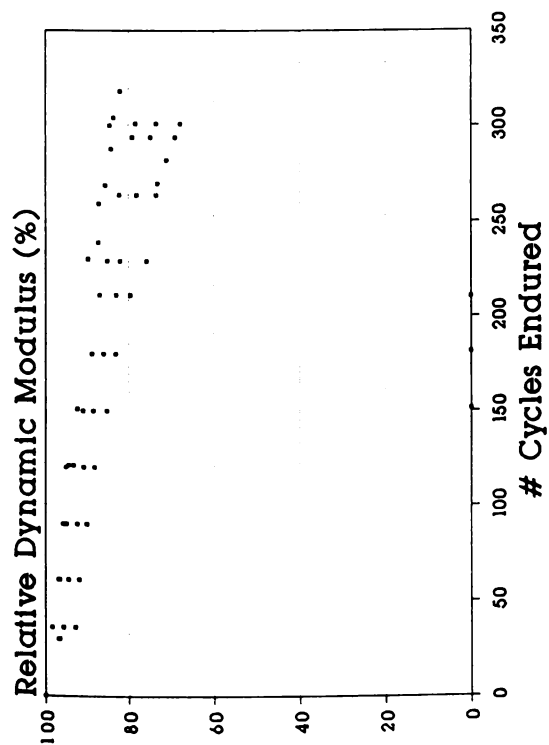


Figure C.8. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.45, AEA2, and Cl F FA.

Change in Length (%)

0.5

0.4

Relative Dynamic Modulus (%)

100

1

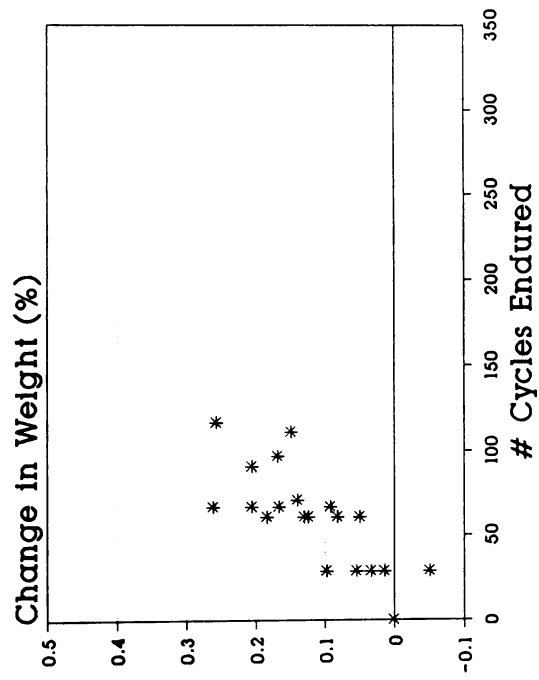
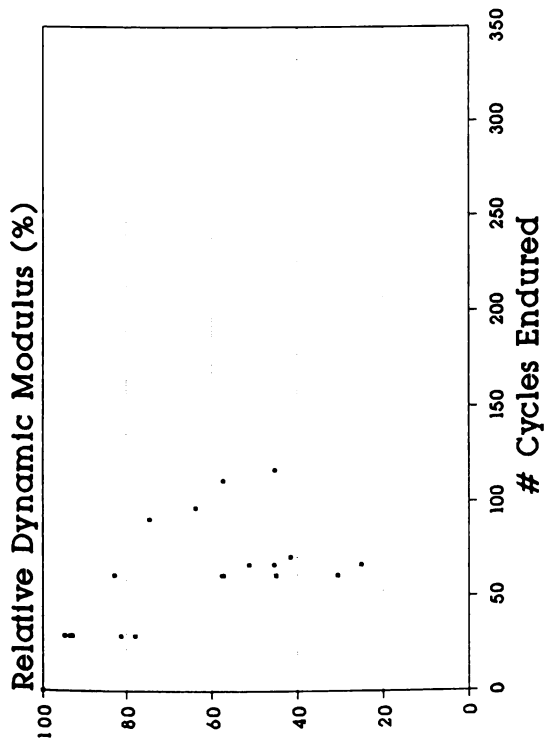
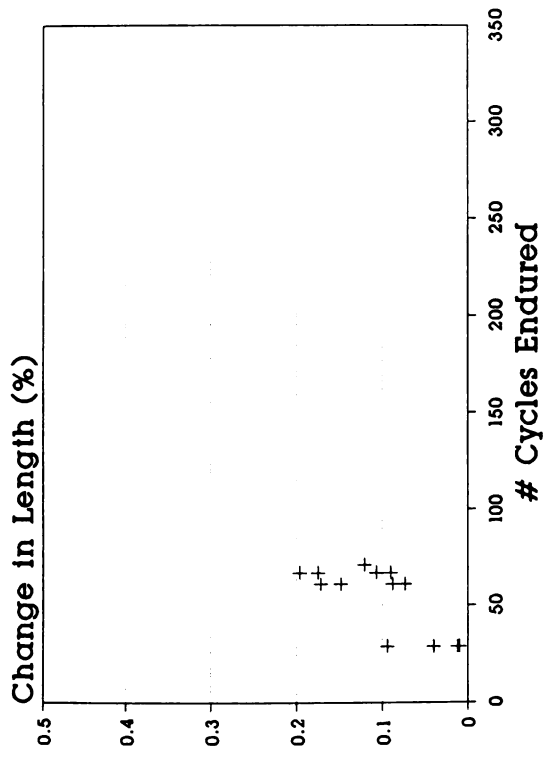


Figure C.9. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.40, AEI, and 15% CI C FA.

Change in Length (%)

0.6

0.4

Relative Dynamic Modulus (%)

100

i

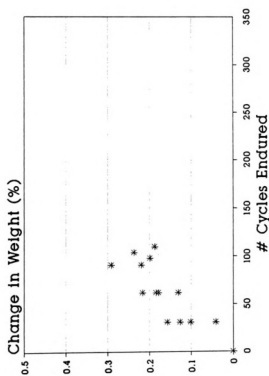
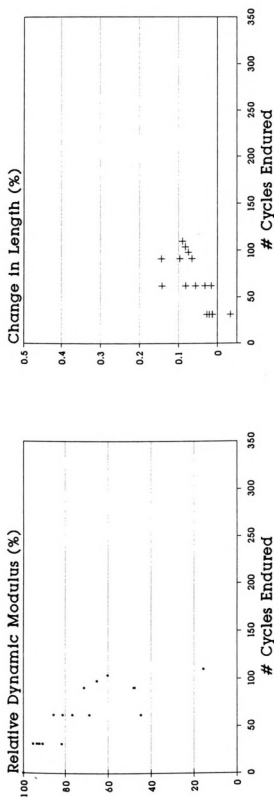


Figure C.10. RDM, change in length, weight versus no. of freeze-thaw cycles endured with $W/C+P=0.45$, AEI, and 15% CI C FA.

Change in Length (%)

0.5

0.4

Relative Dynamic Modulus (%)

100

1

1

1

1

1

1

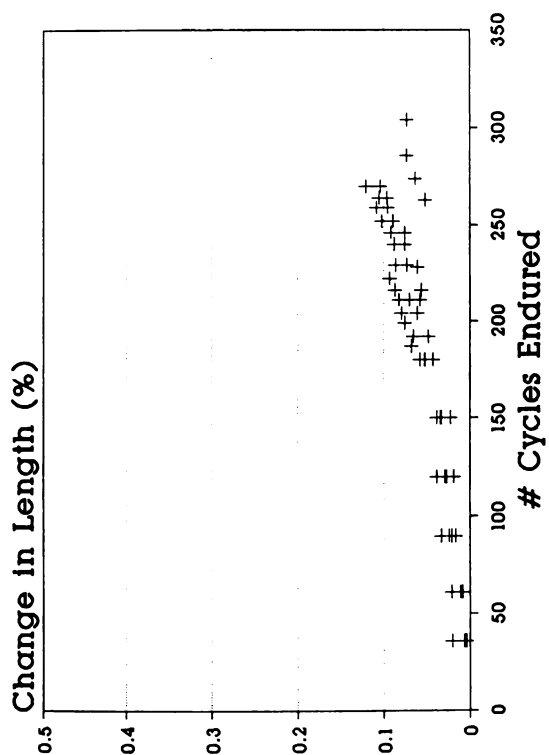
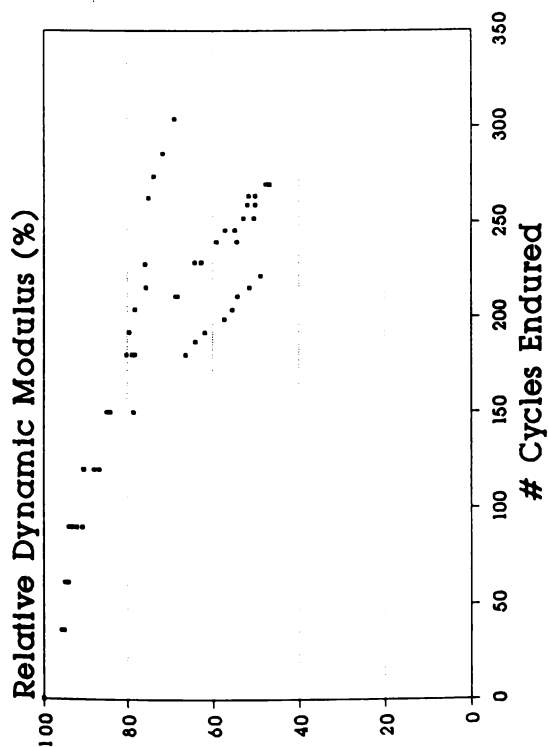
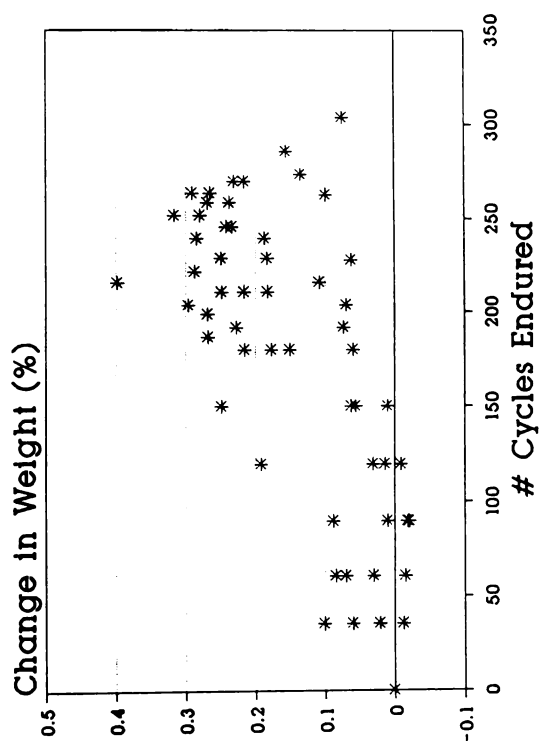
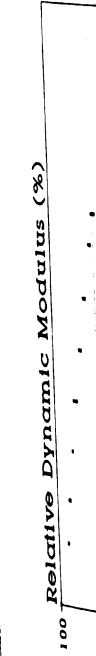


Figure C.11. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.40, AEA2, and 15% CI C FA.





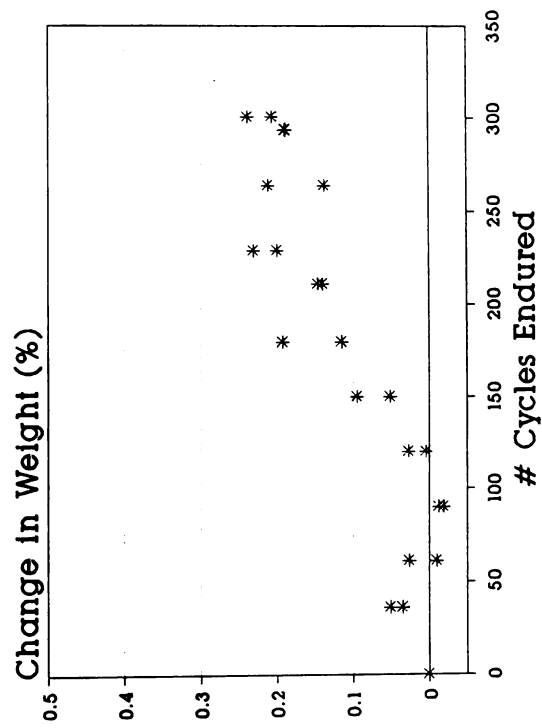
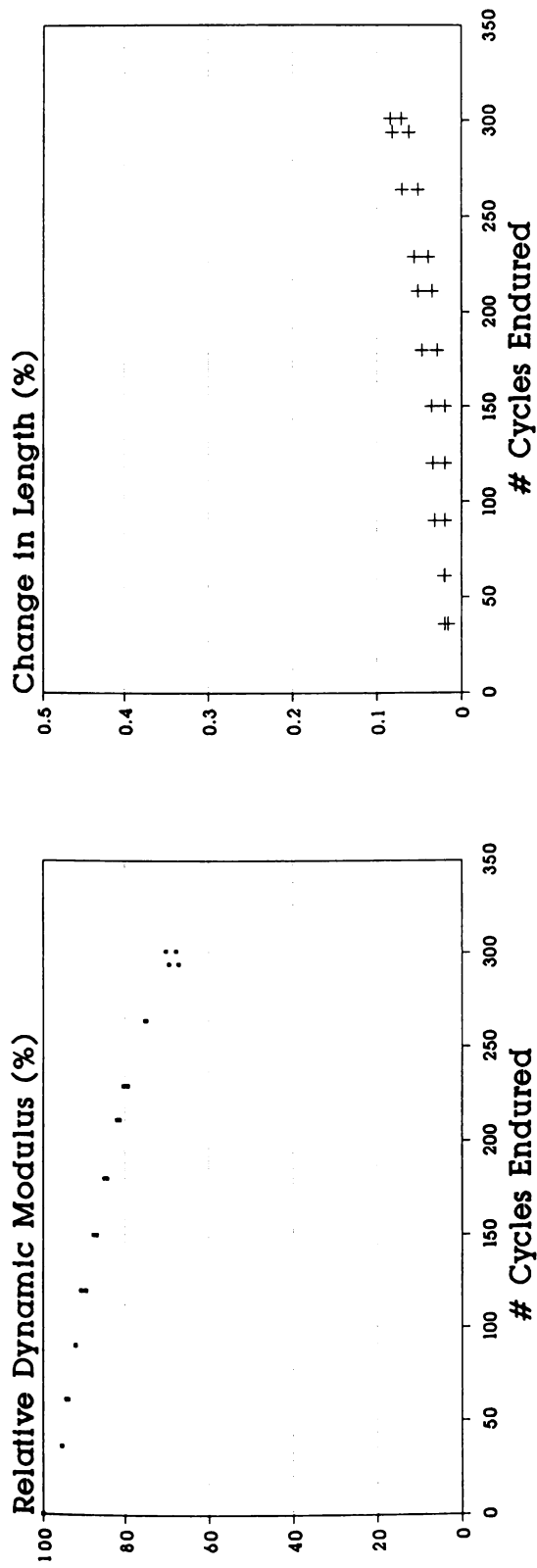


Figure C.12. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.45, AEA2, and 15% CI C FA.

100
:
Relative Dynamic Modulus (%)

0.5
0.4
Change in Length (%)

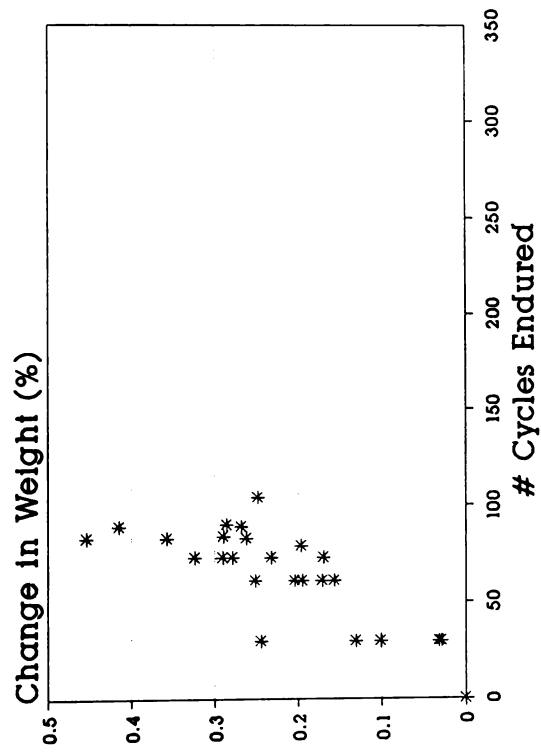
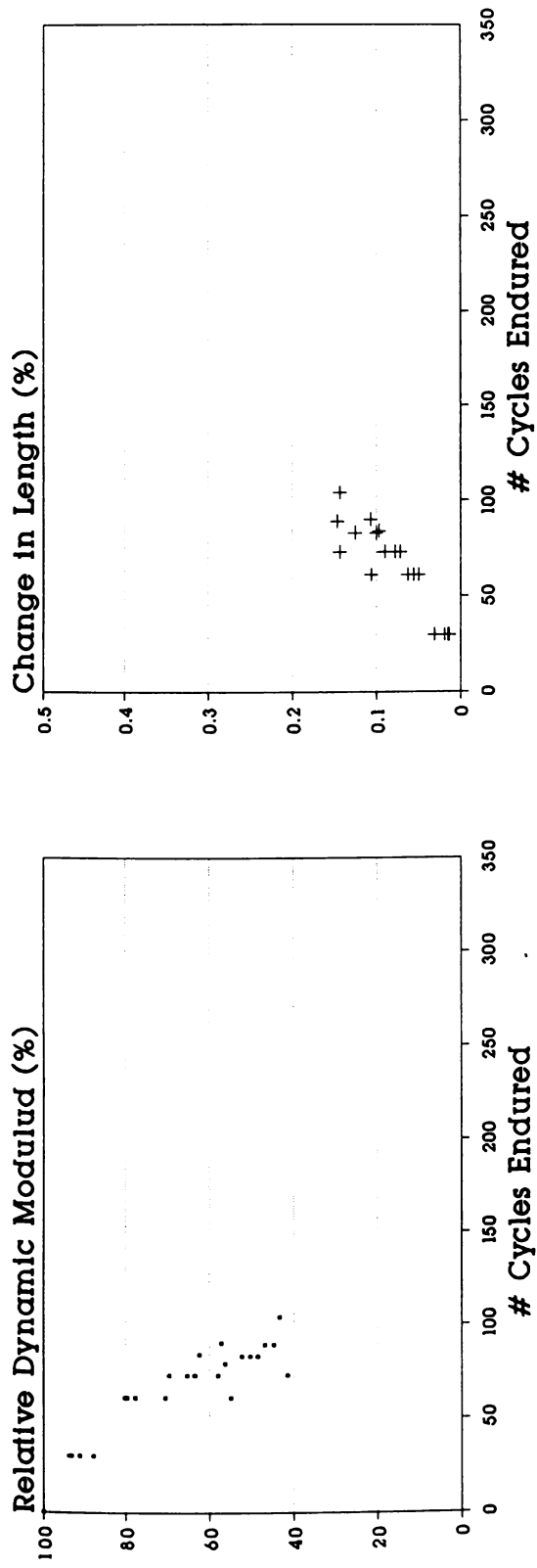


Figure C.13. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.40, AEAl, HRWR, and 15% Cl F FA.

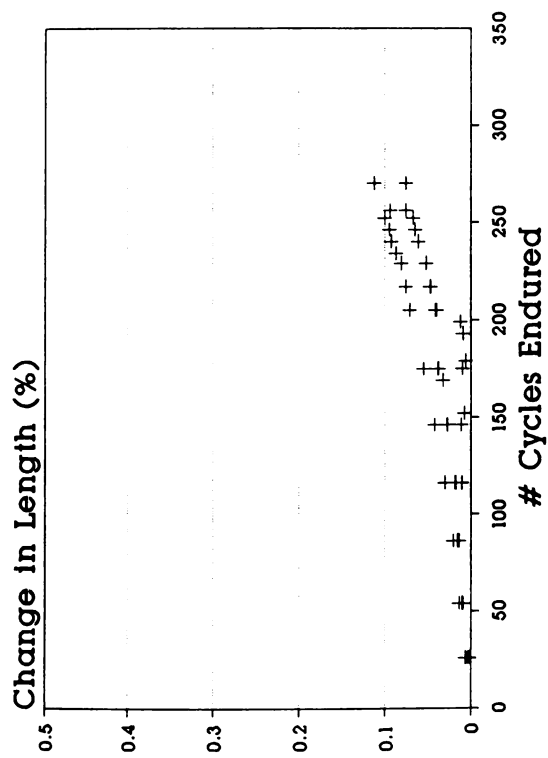
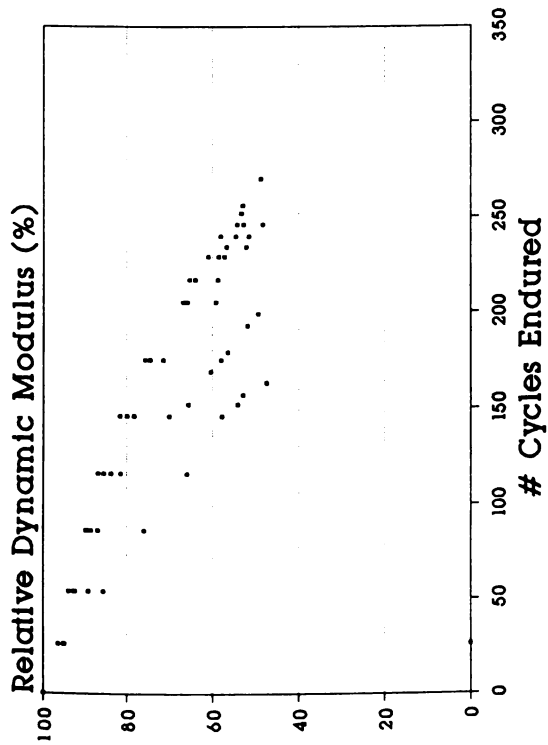
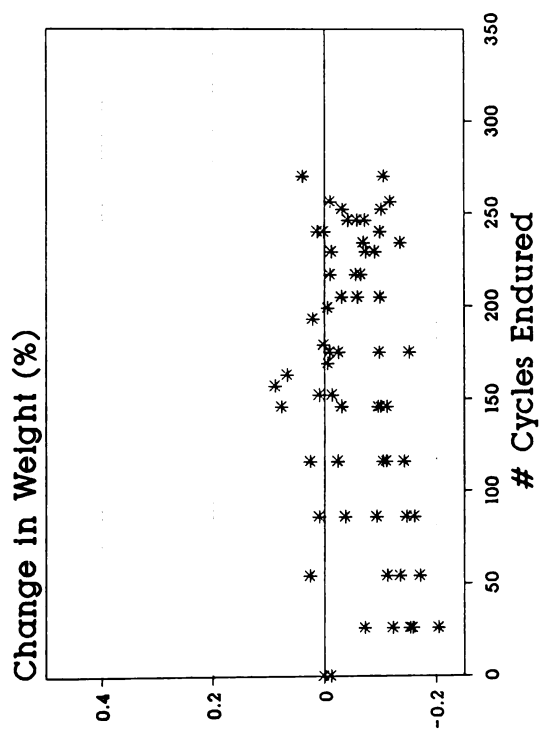


Figure C.14. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.45, AEAl, HRWR, and 15% CI C FA.



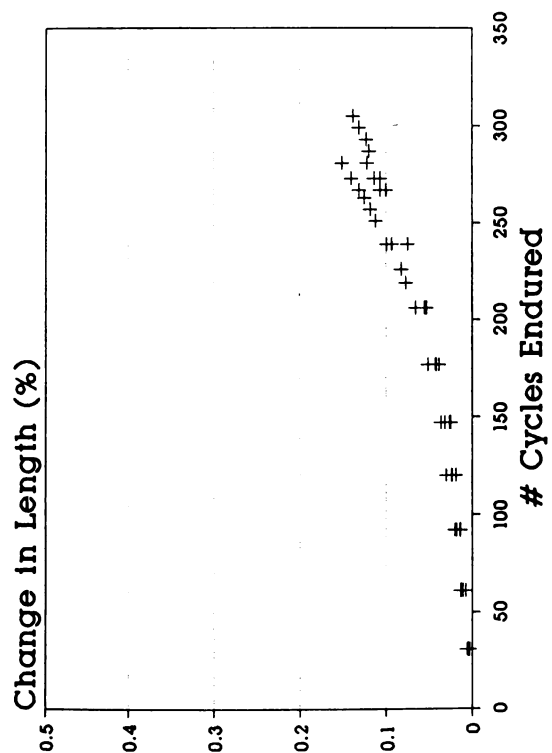
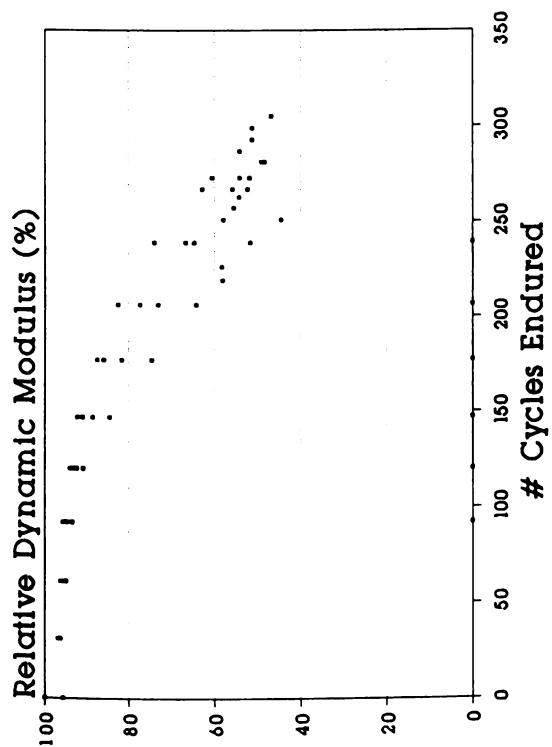
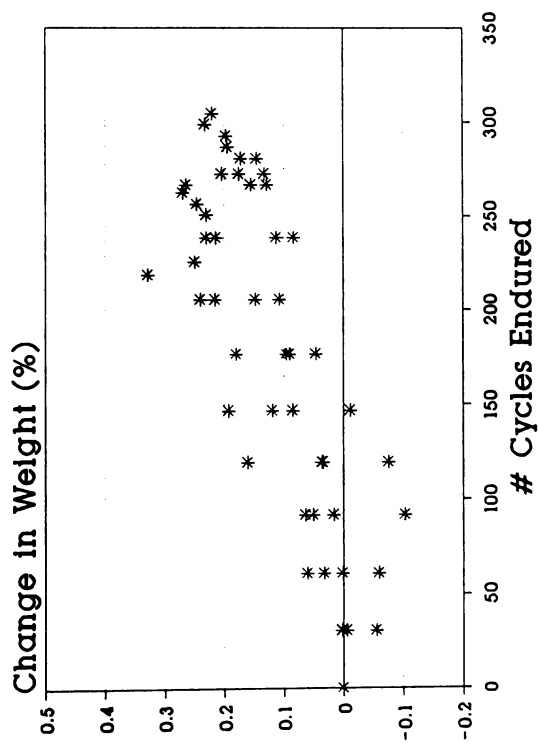


Figure C.15. RDM, change in length, weight versus no. of freeze-thaw cycles endured with $W/C+P=0.40$, AEA2, HRWR, and 15% CI F FA.



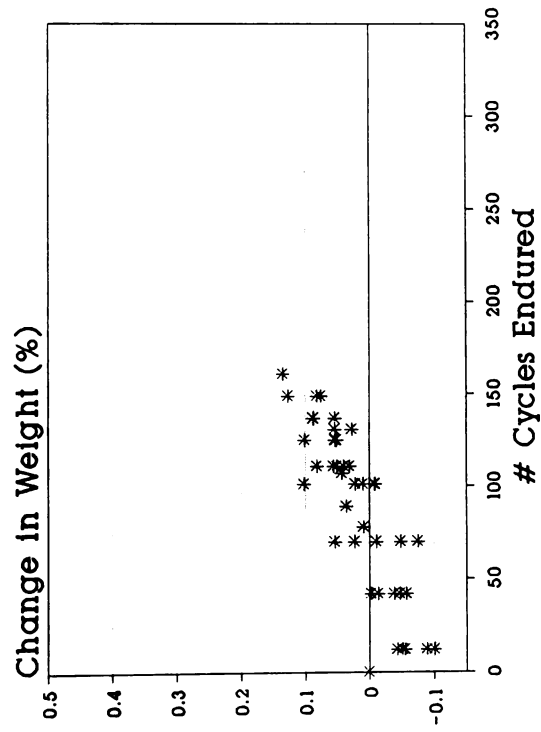
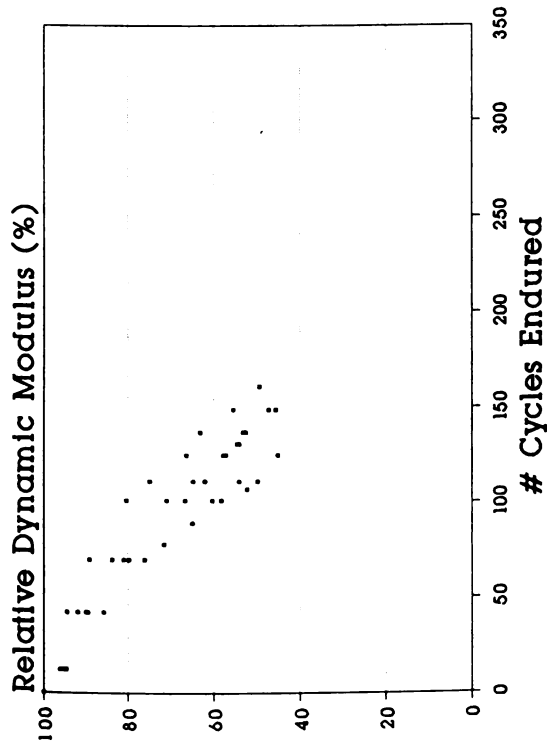
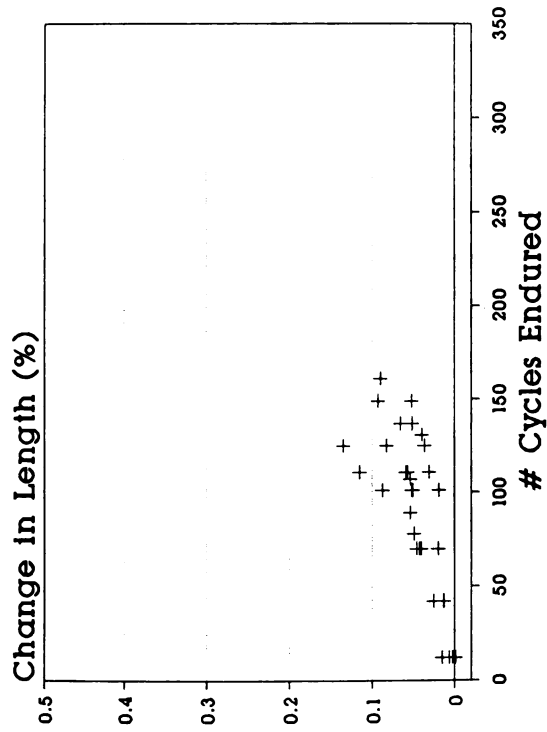


Figure C.16. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.45, AEA2, HRWR, and 15% CI F FA.

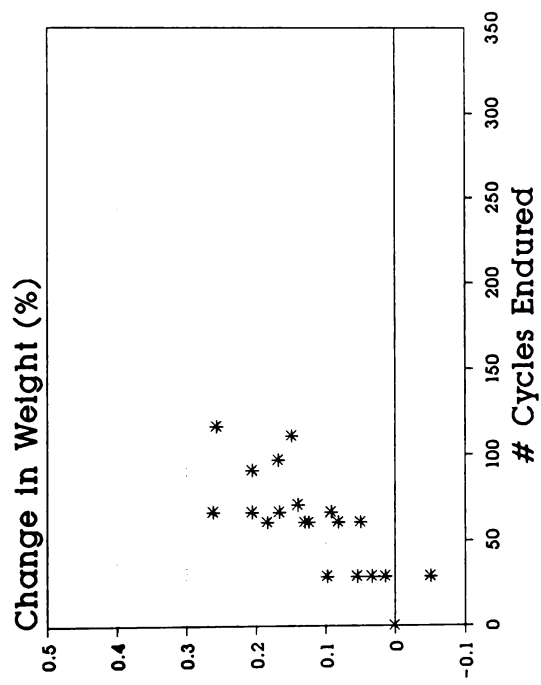
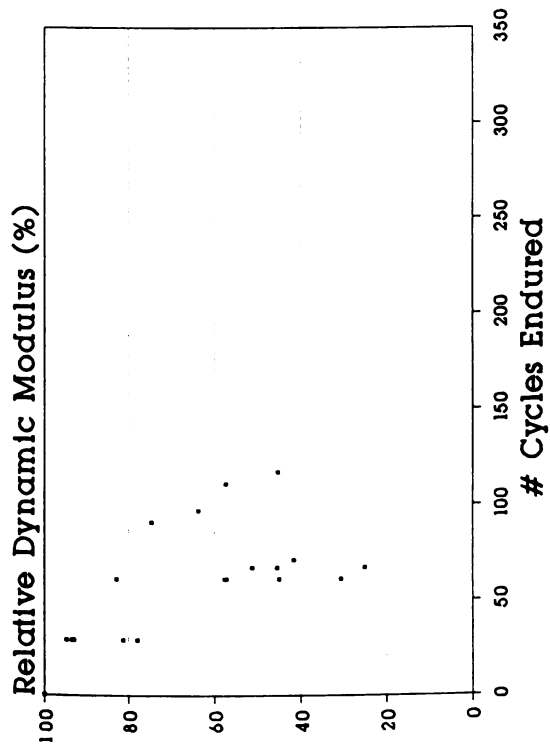
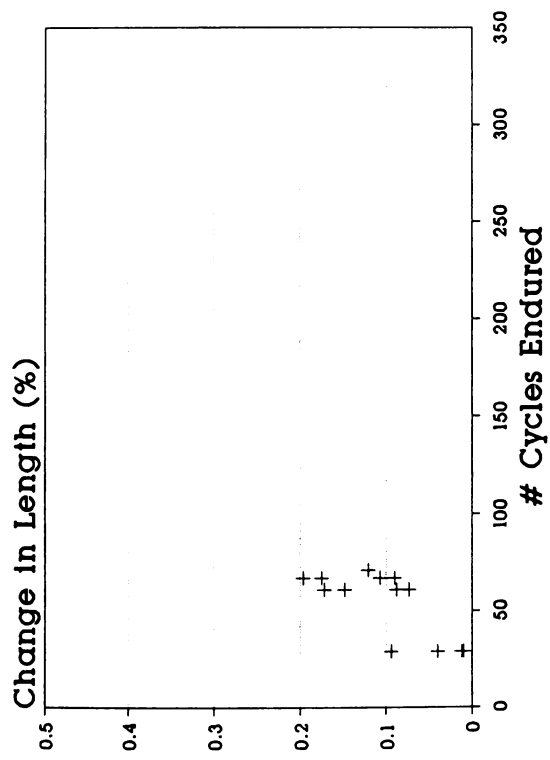


Figure C.17. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.40, AEAl, HRWR, and 15% Cl C FA.

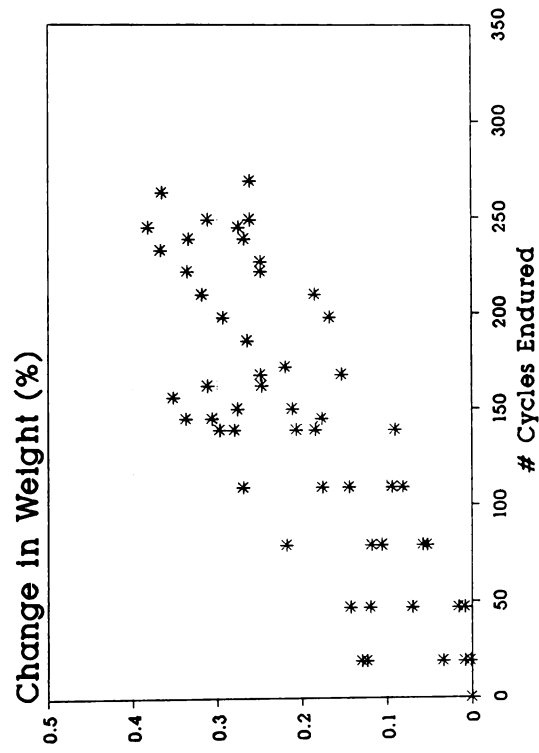
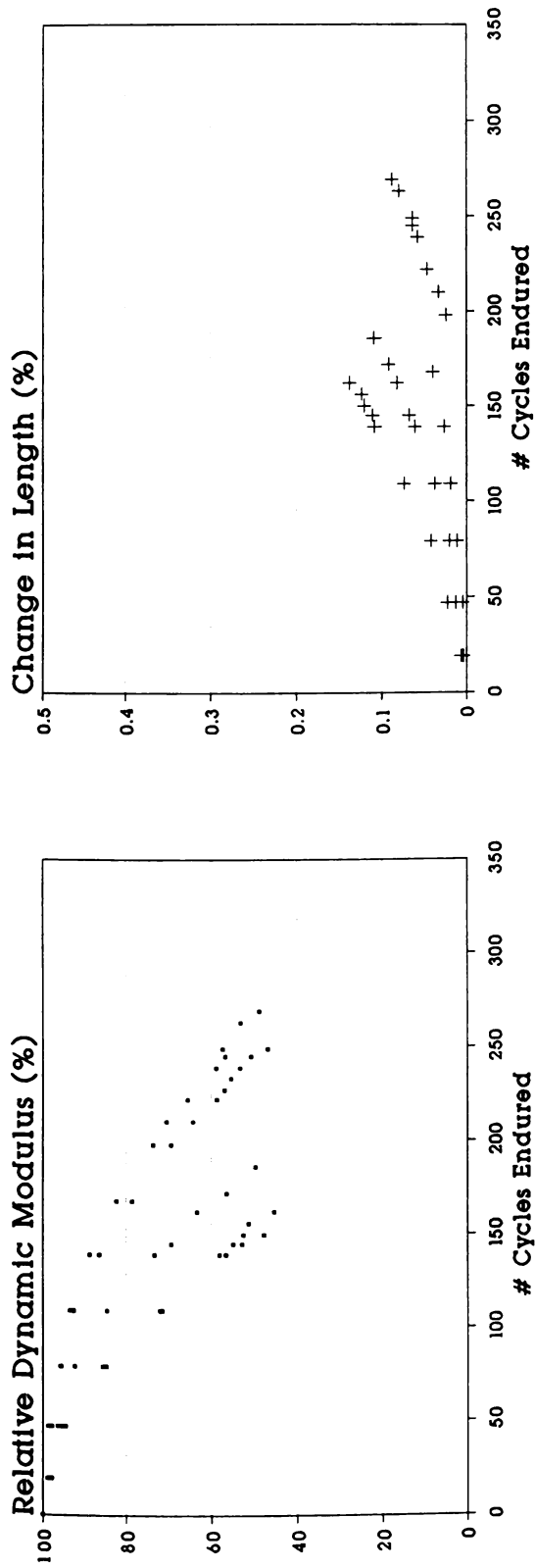


Figure C.18. RDM, change in length, weight versus no. of freeze-thaw cycles endured with $W/C=0.45$, AEI, HRWR, and 15% CI C FA.

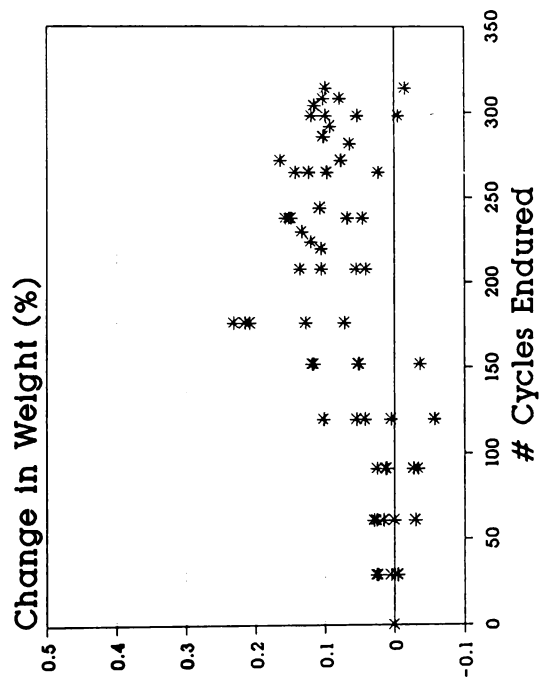
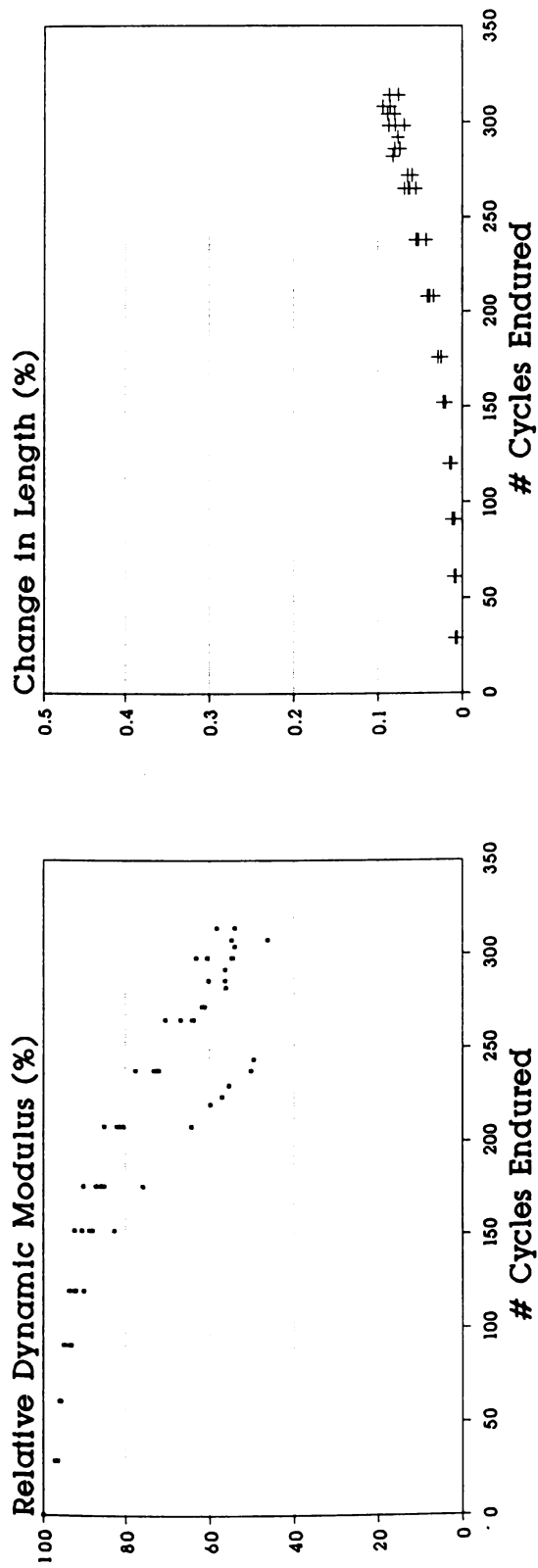


Figure C.19. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.40, AE A2, HRWR, and 15% CI C FA.

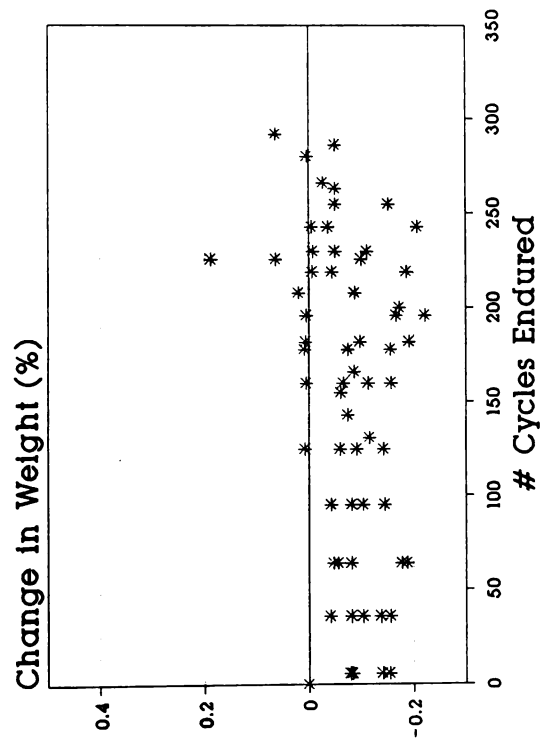
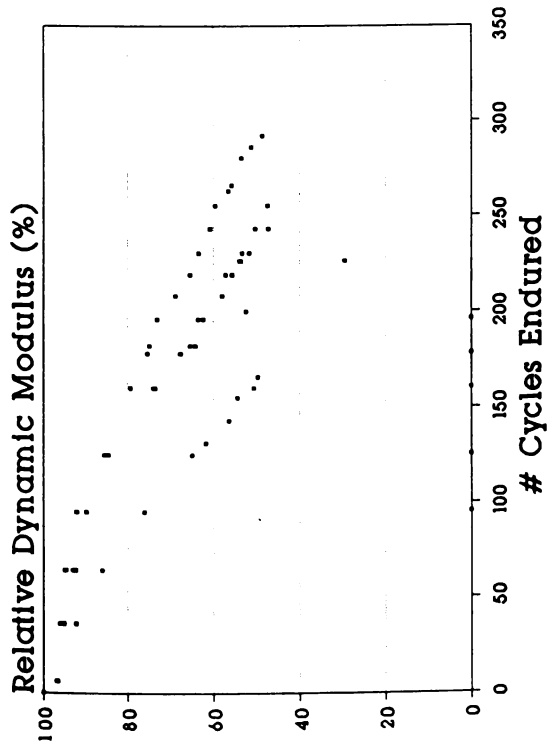
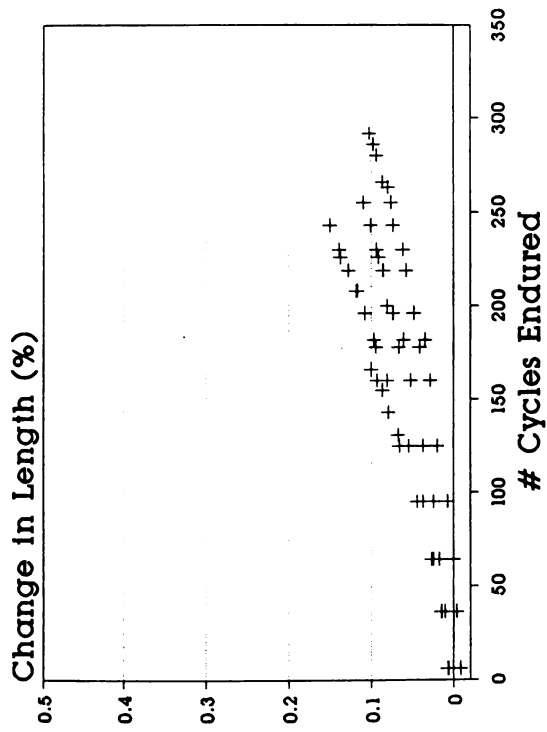


Figure C.20. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.45, AEA2, HRWR, and 15% CI C FA.

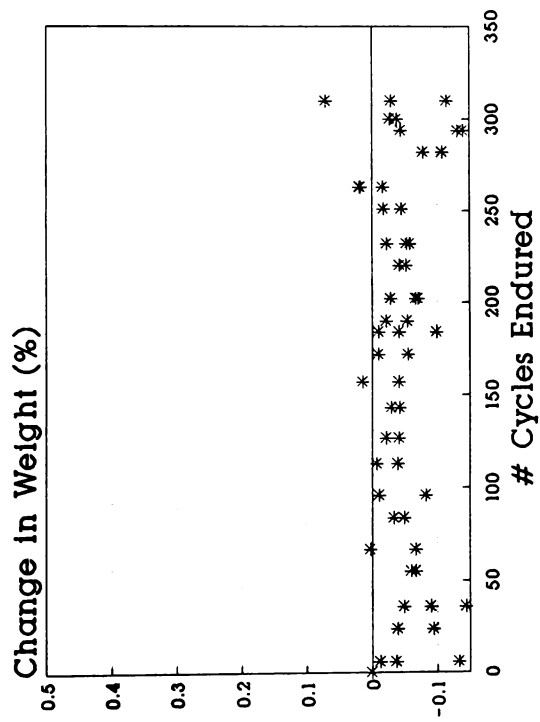
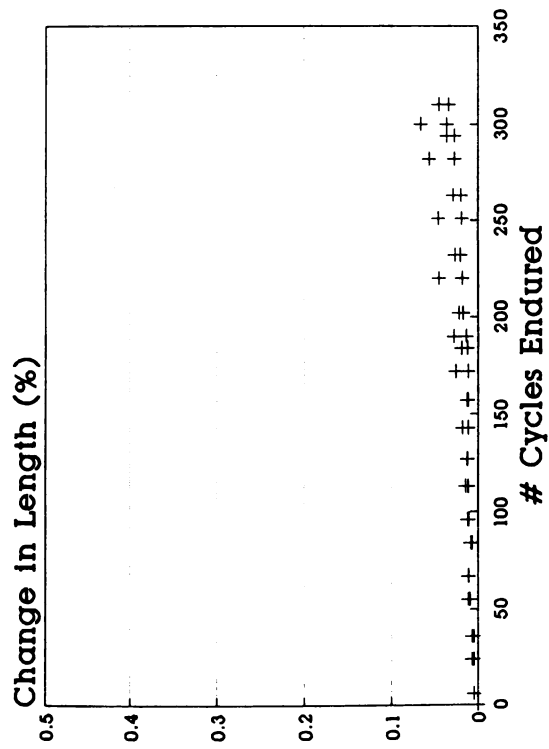
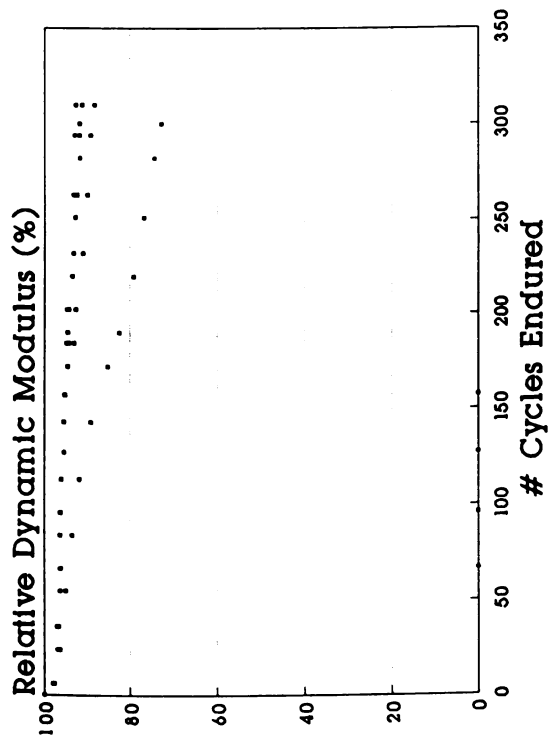


Figure C.21. RDM, change in length, and weight versus no. of freeze-thaw cycles endured with W/C+P=0.40, AEAl, HRWR, and 15% silica fume.

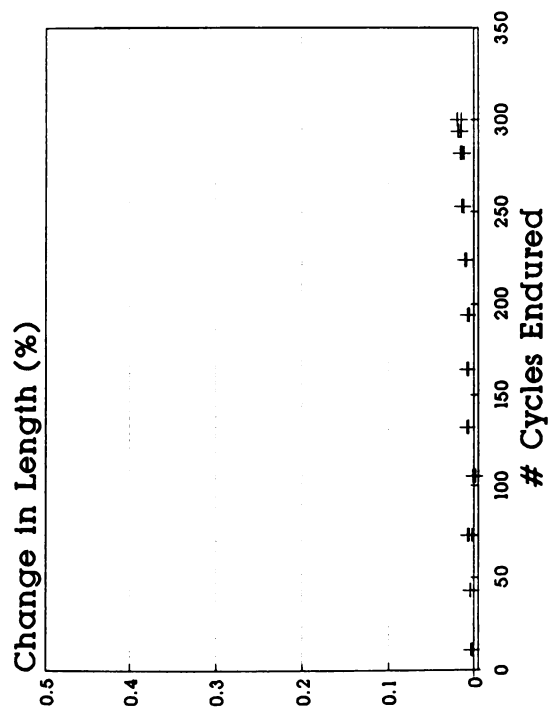
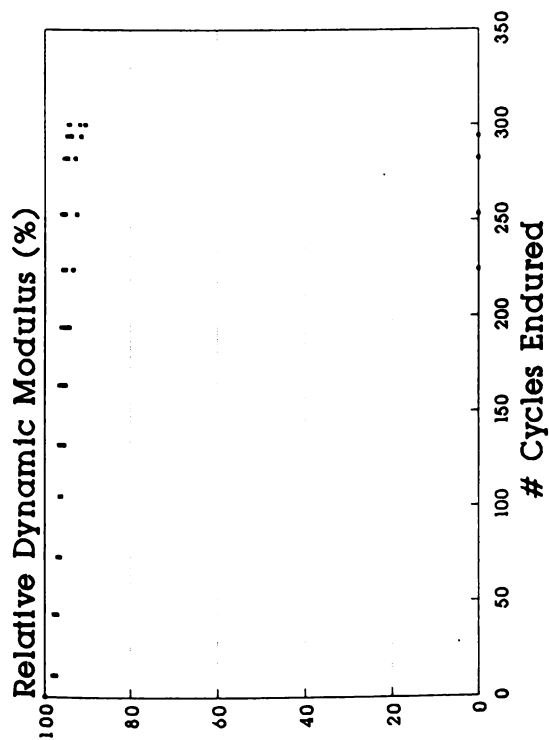
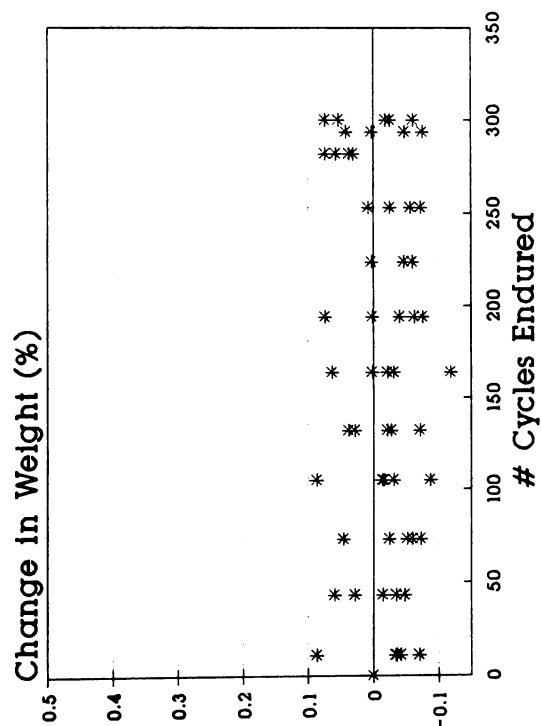


Figure C.22.RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.45, AEAl, HRWR, and 15% silica fume.



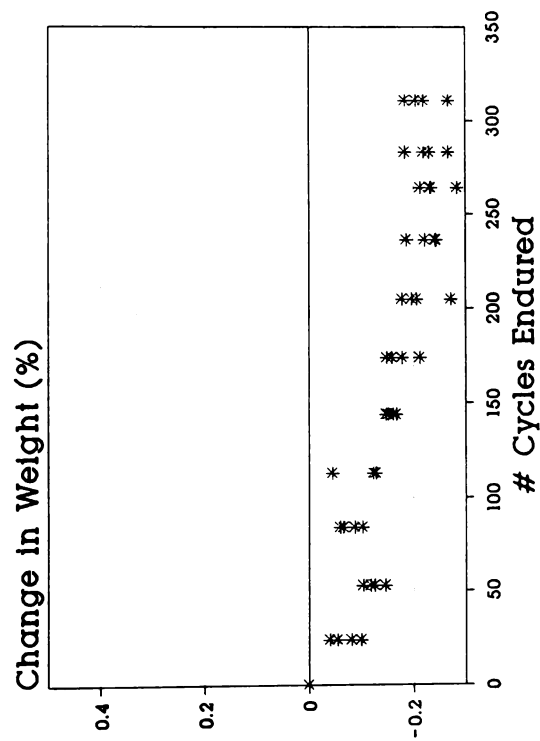
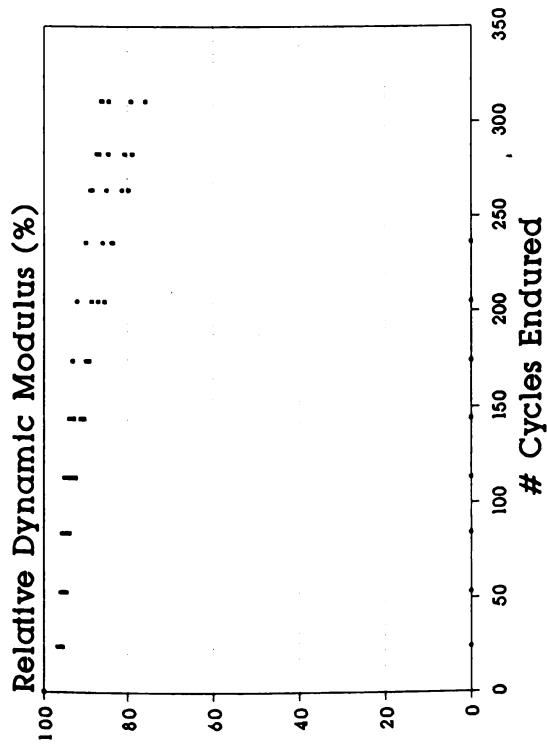
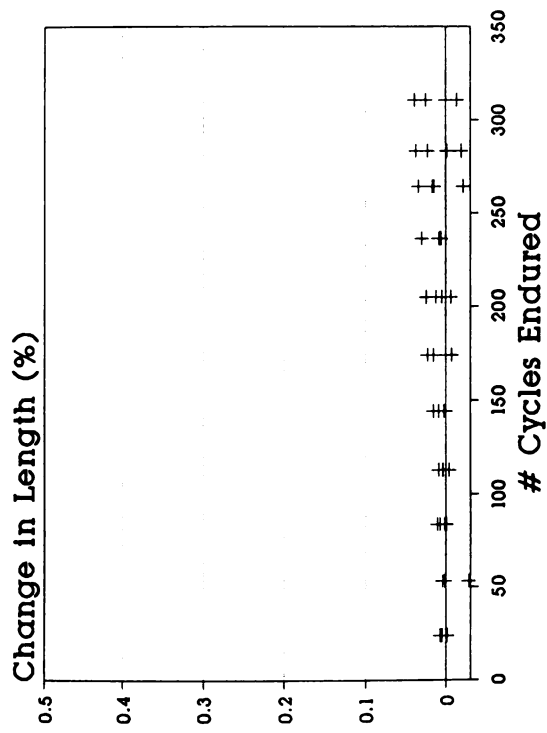


Figure C.23. RDM, change in length, weight versus no. of freeze-thaw cycles endured with W/C+P=0.40, AEA2, HRWR, and 15% silica fume.

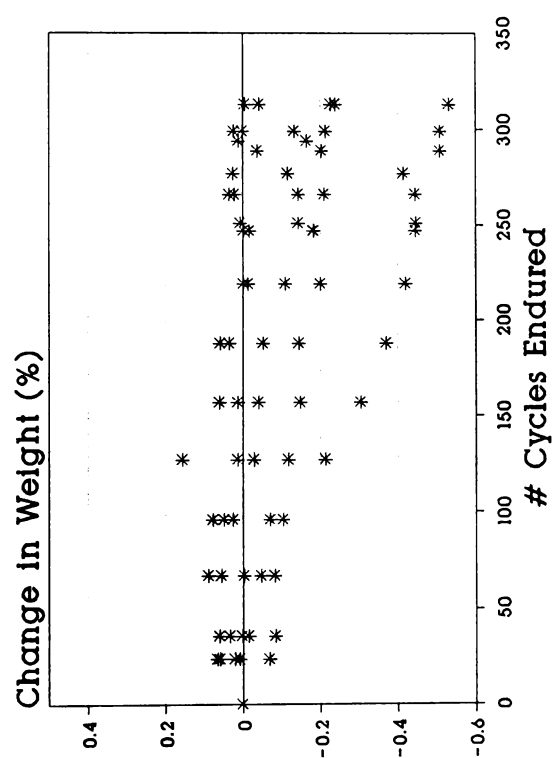
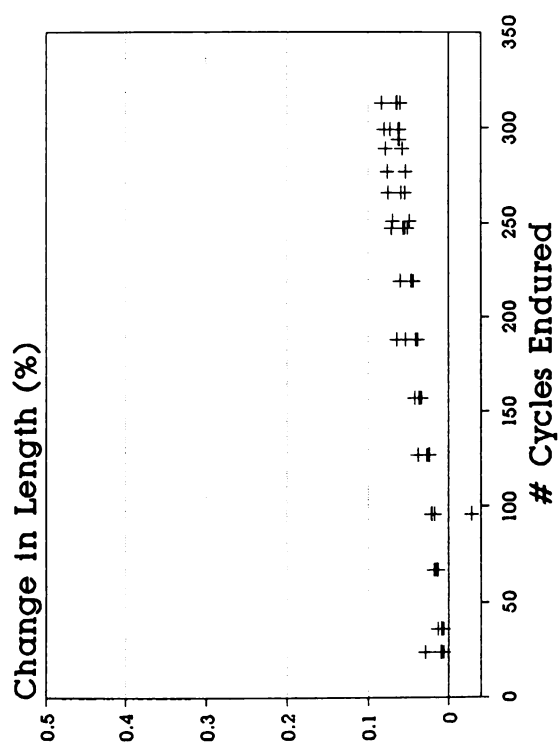
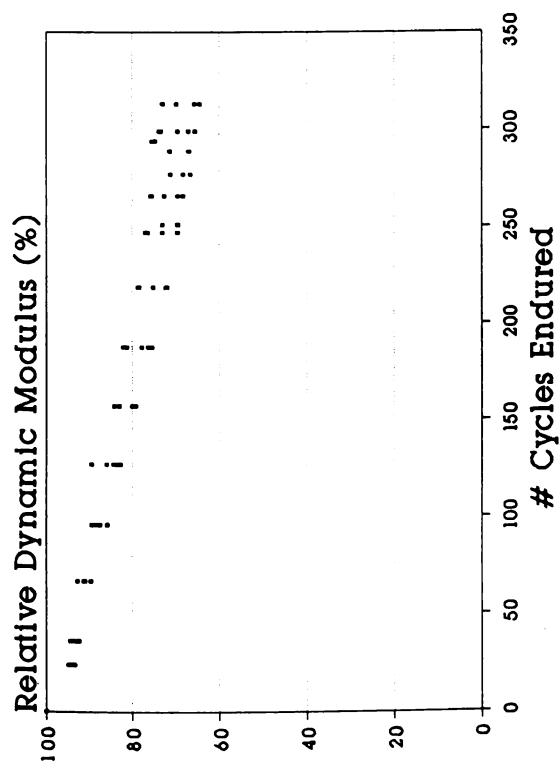


Figure C.24. RDM, change in length, weight versus no. of freeze-thaw cycles endured with $W/C+P=0.45$, AEA2, HRWR, and 15% silica fume.

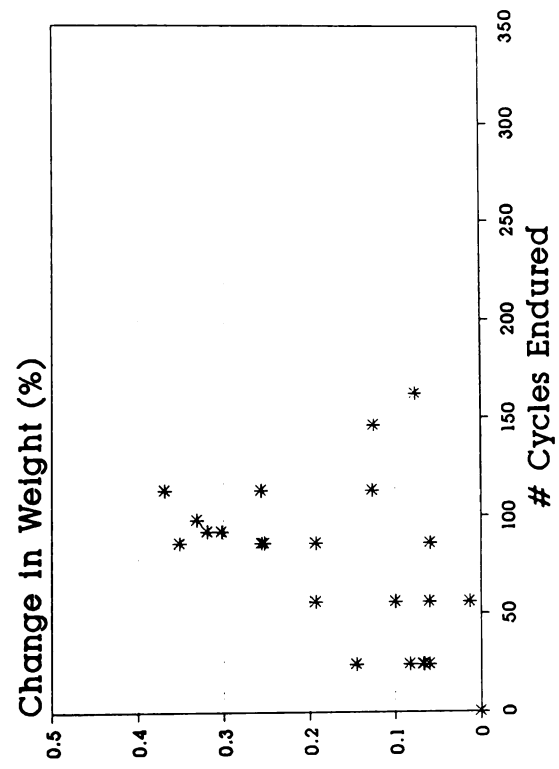
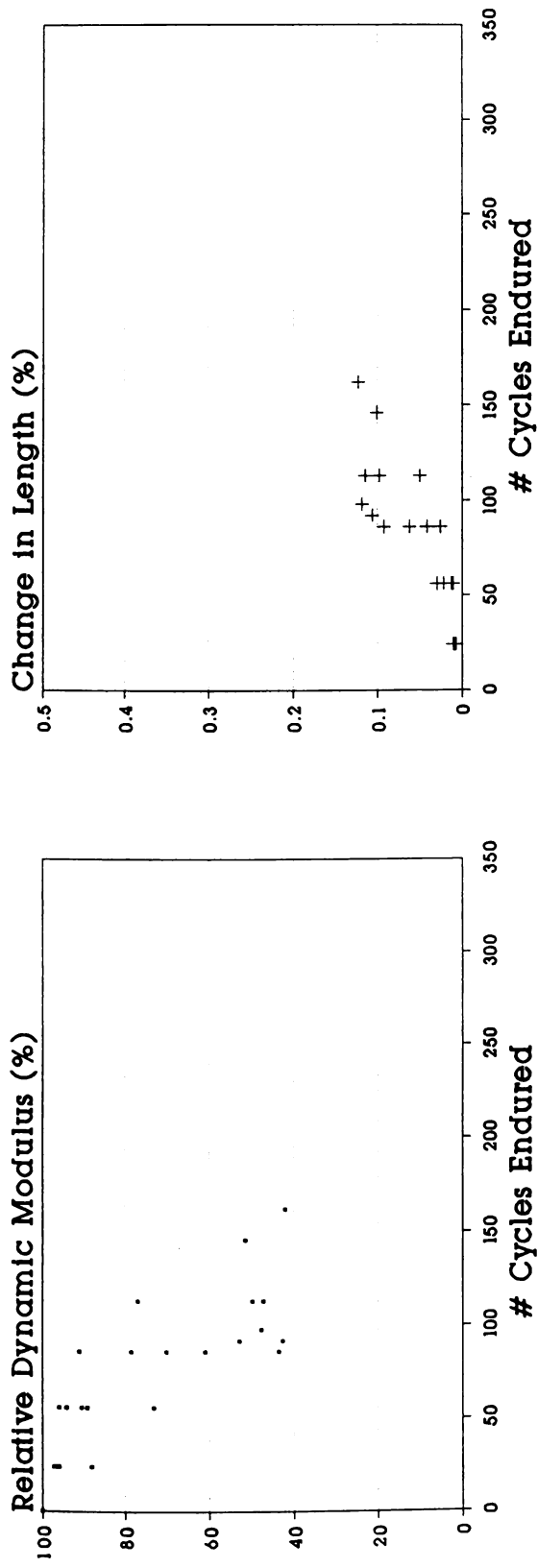


Figure C.25. RDM, change in length, weight versus no. of freeze-thaw cycles endured without WR, W/C+P=0.40, and 40% GGBF slag.

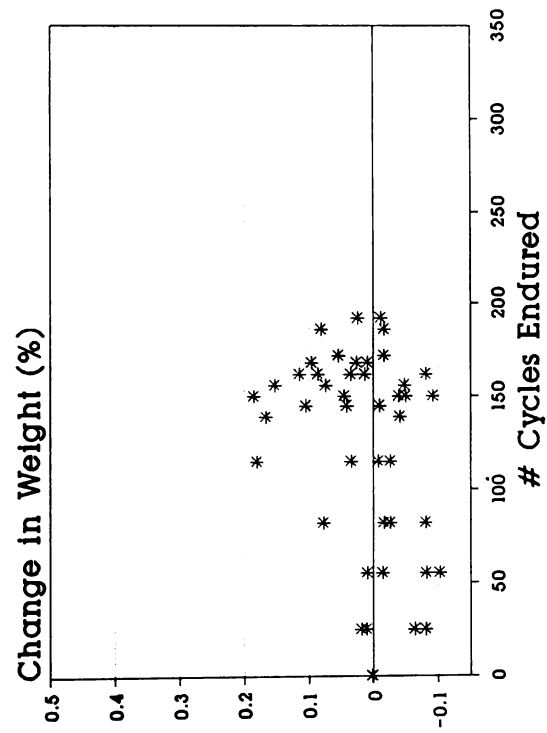
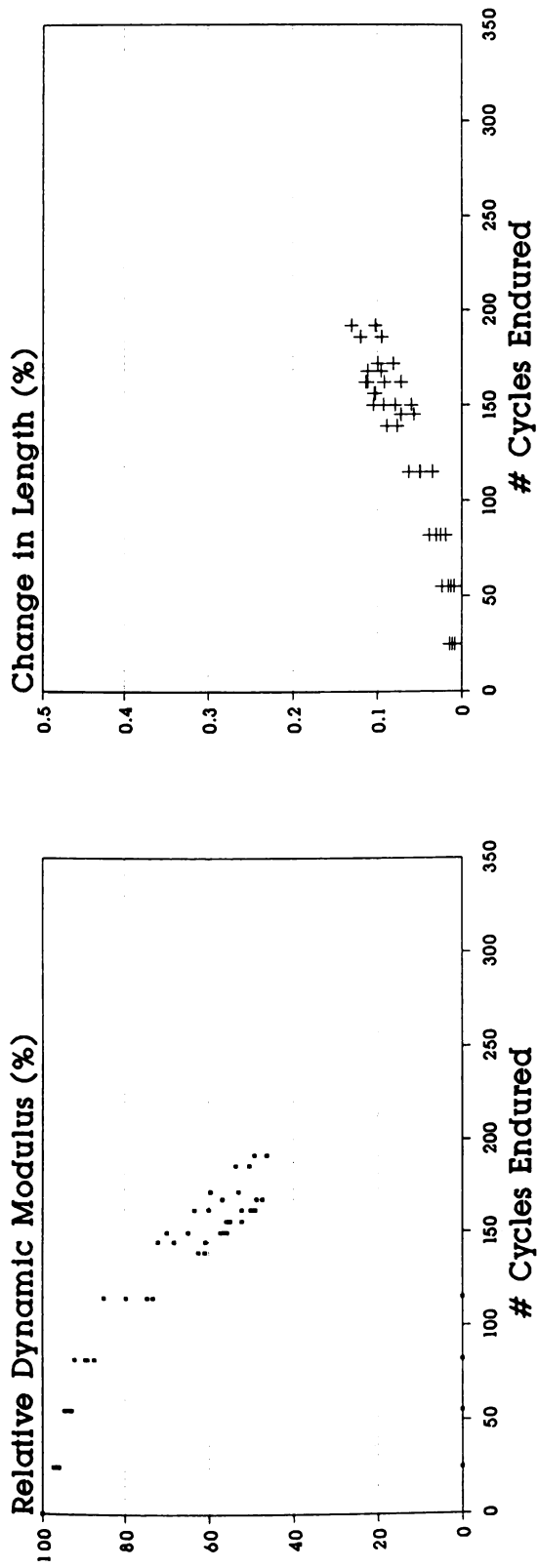


Figure C.26. RDM, change in length, weight versus no. of freeze-thaw cycles endured without WR, W/C+P=0.45, and 40% GGBF slag.

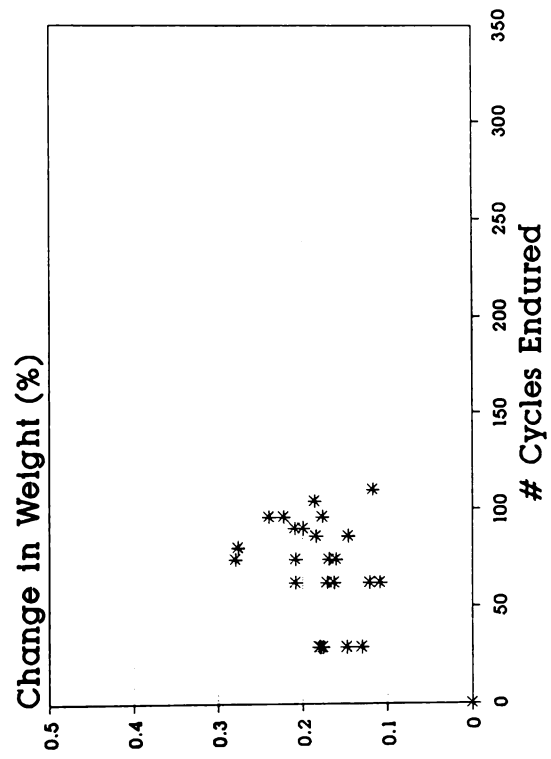
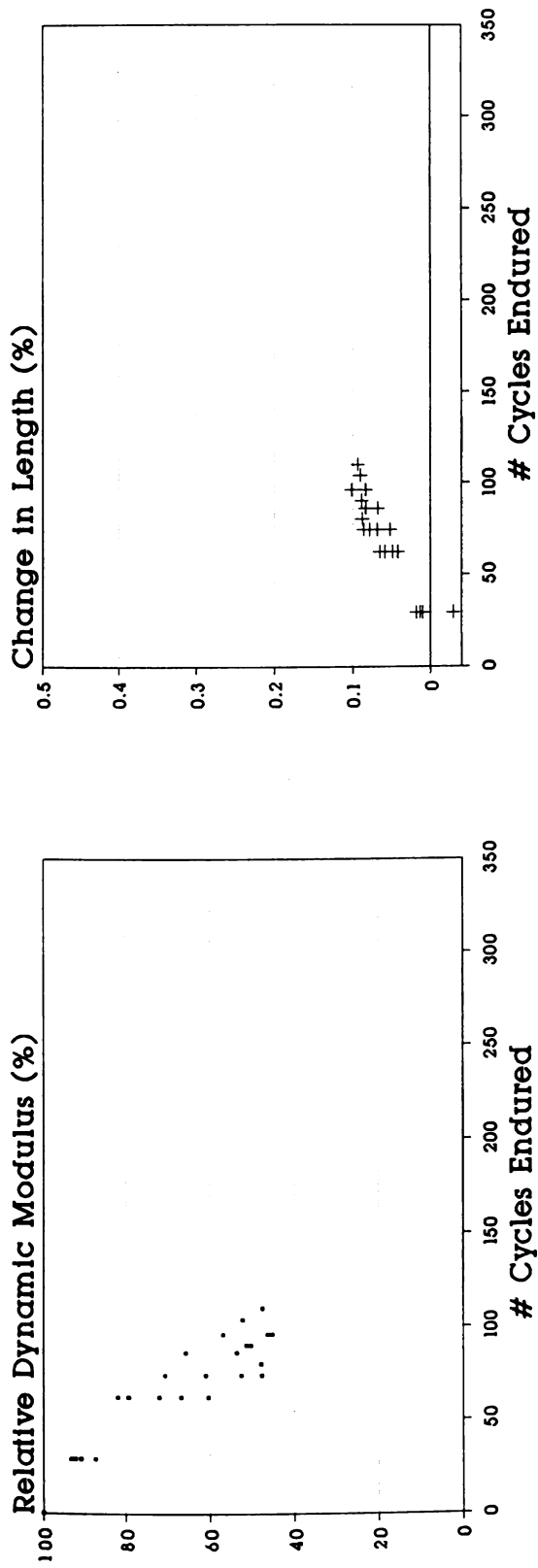


Figure C.27. RDM, change in length, weight versus no. of freeze-thaw cycles endured with WR, W/C+P=0.40, and 40% GGBF slag.

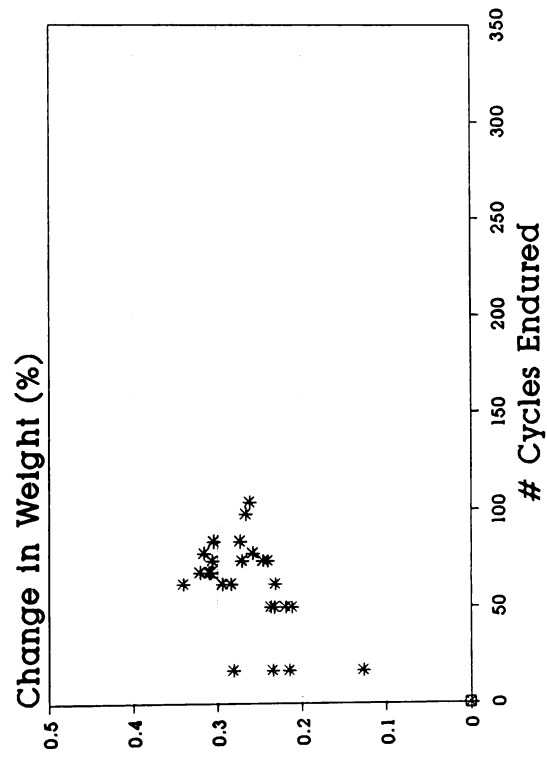
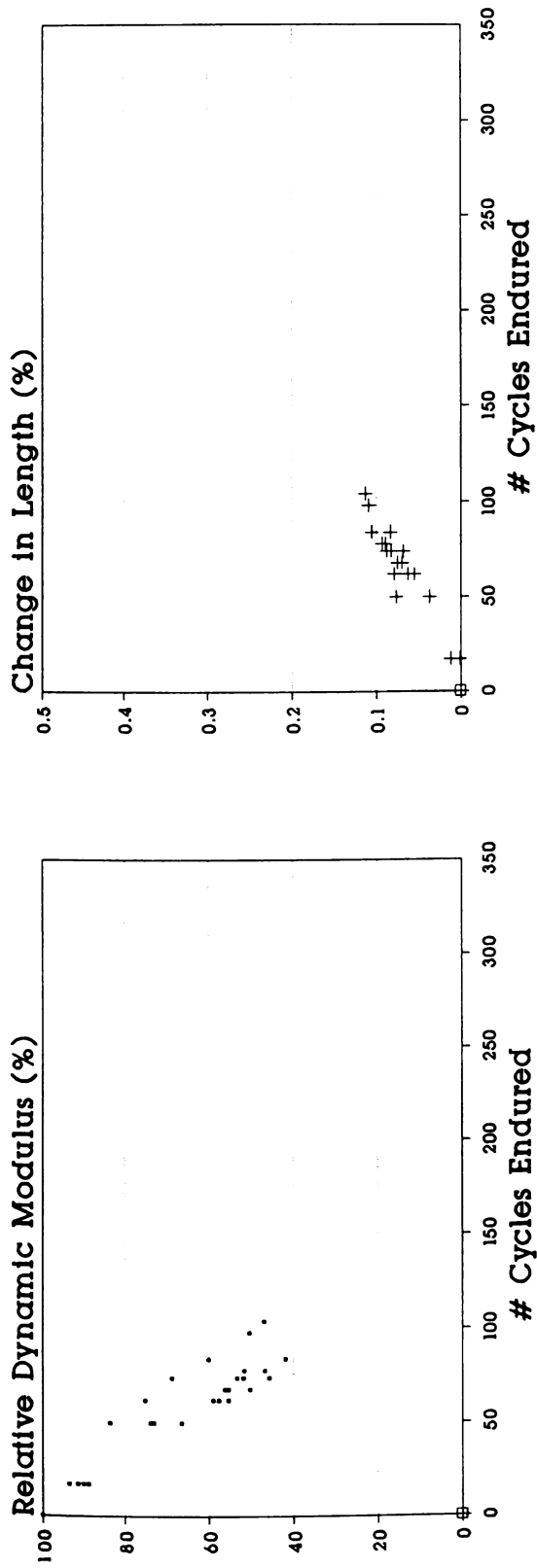


Figure C.28. RDM, change in length, weight versus no. of freeze-thaw cycles endured with WR, W/C+P=0.45, and 40% GGBF slag.

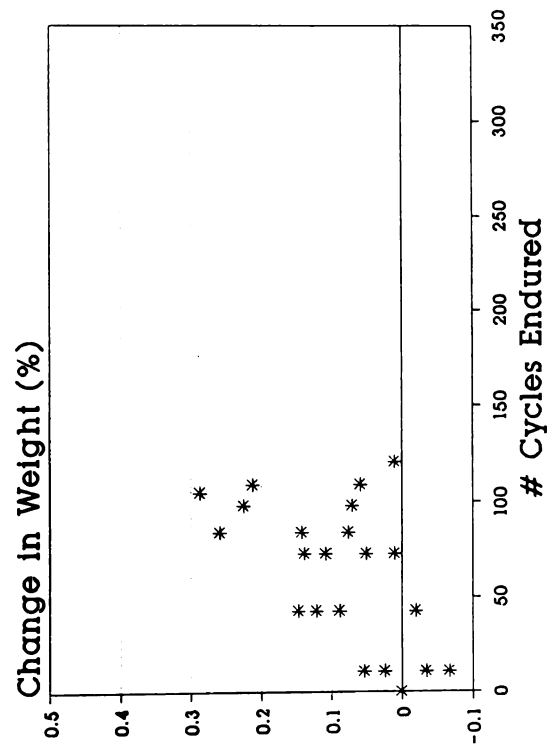
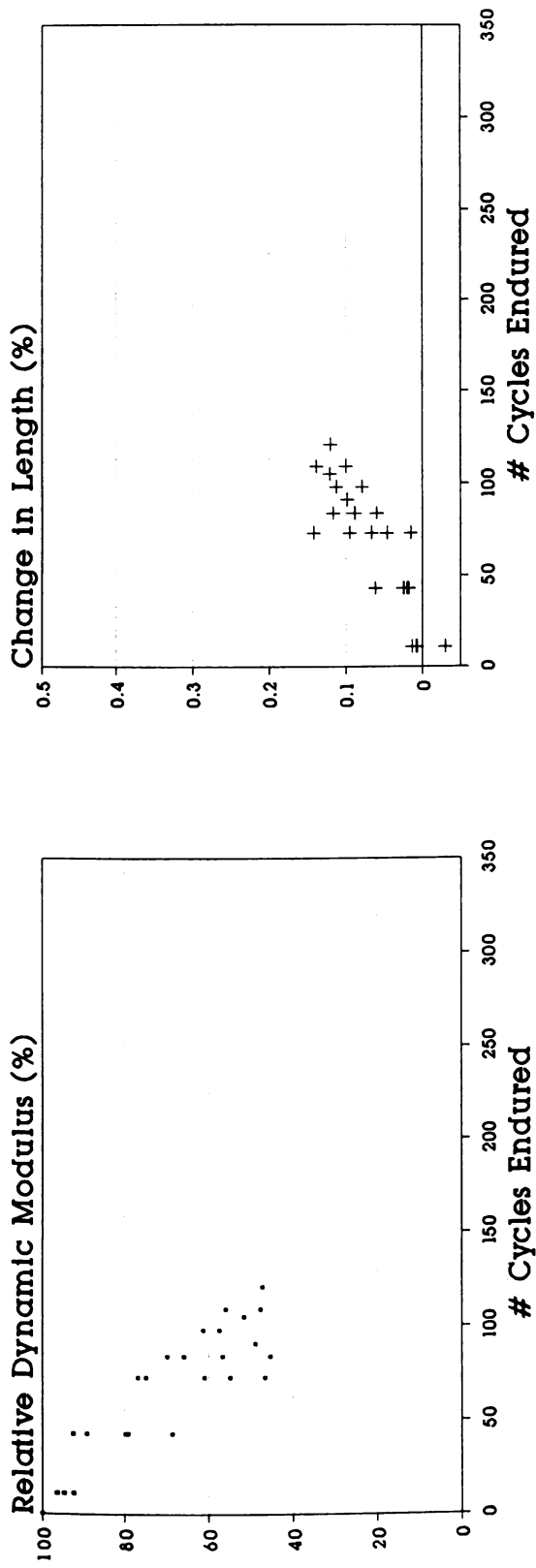


Figure C.29. RDM, change in length, and weight versus freeze-thaw cycles endured for PCC with WR, W/C=0.40, and 56 day curing period.

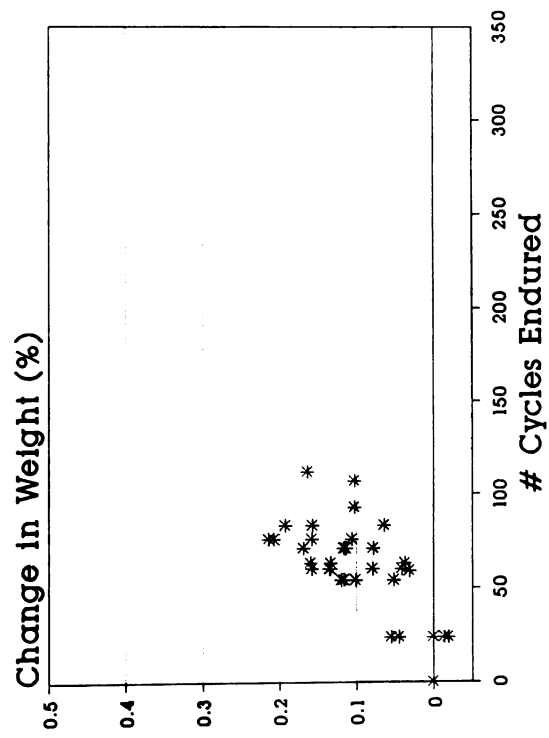
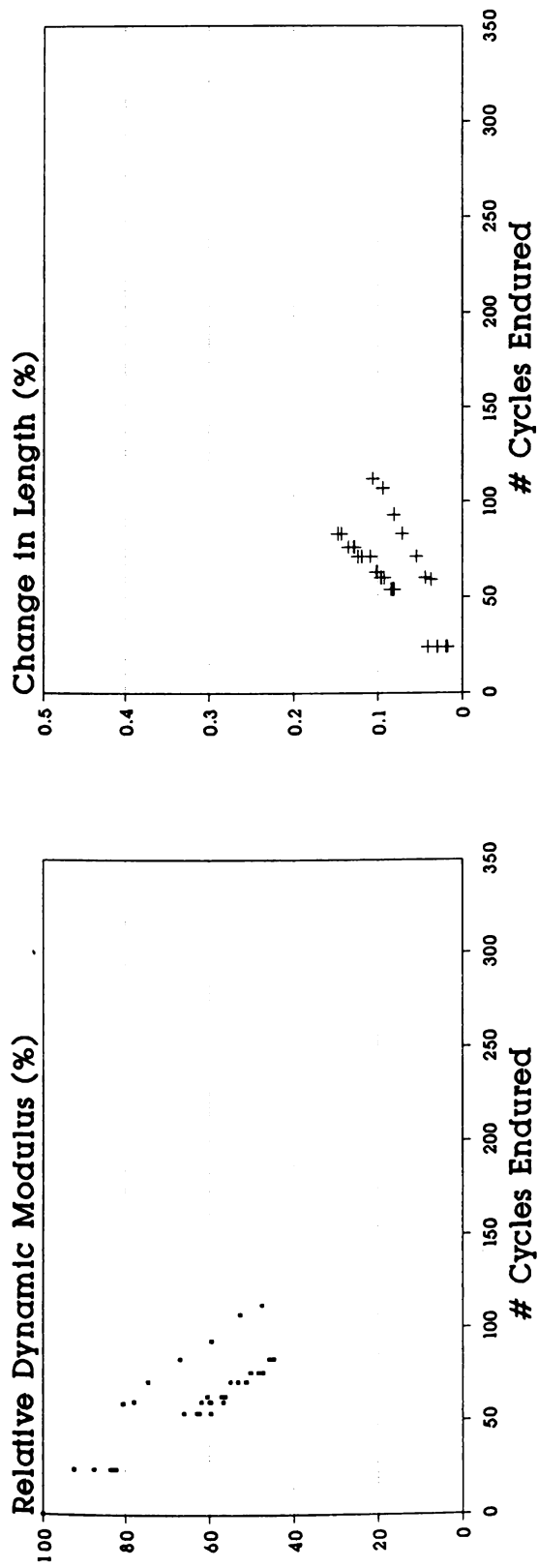
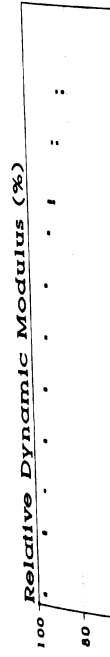
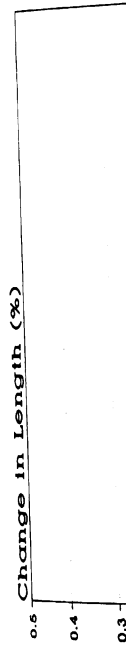


Figure C.30. RDM, change in length, and weight versus freeze-thaw cycles endured for PCC with WR, $W/C=0.45$, and 56 day curing period.



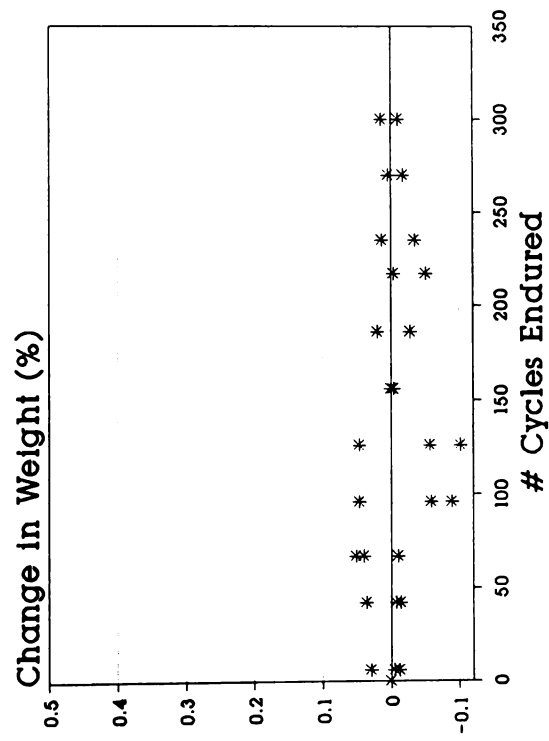
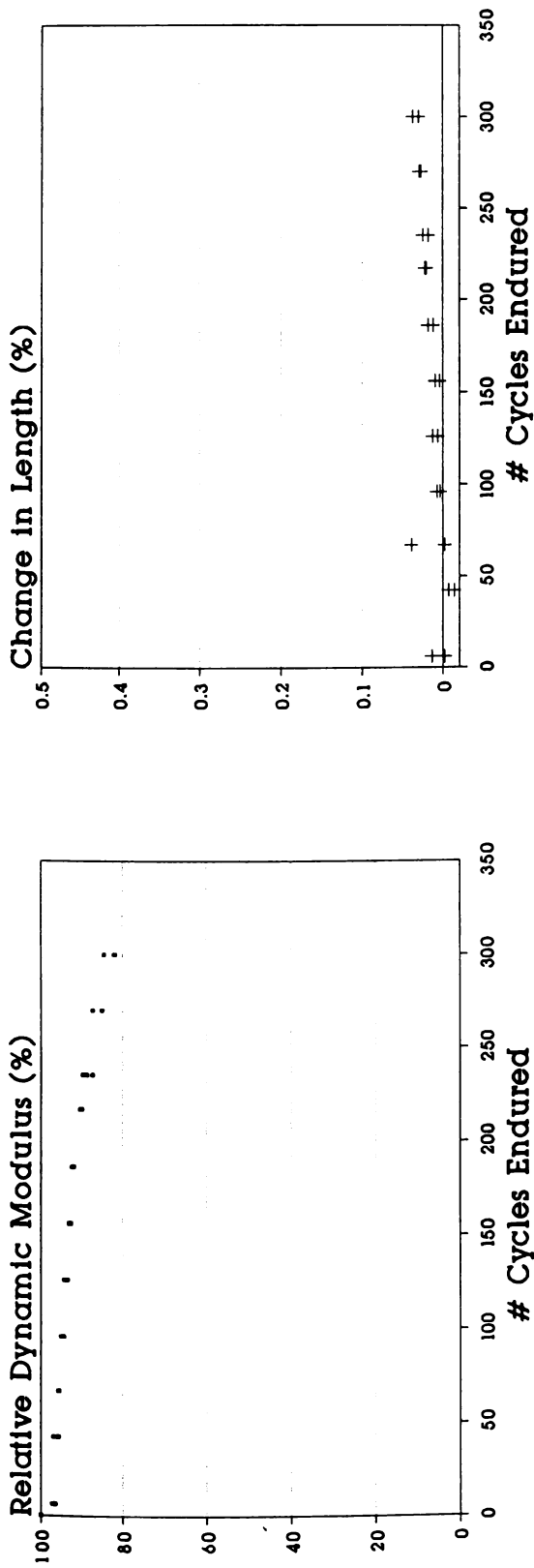
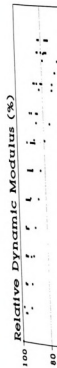


Figure C.31. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.40, 56 day curing period, and 15% C1 F FA.



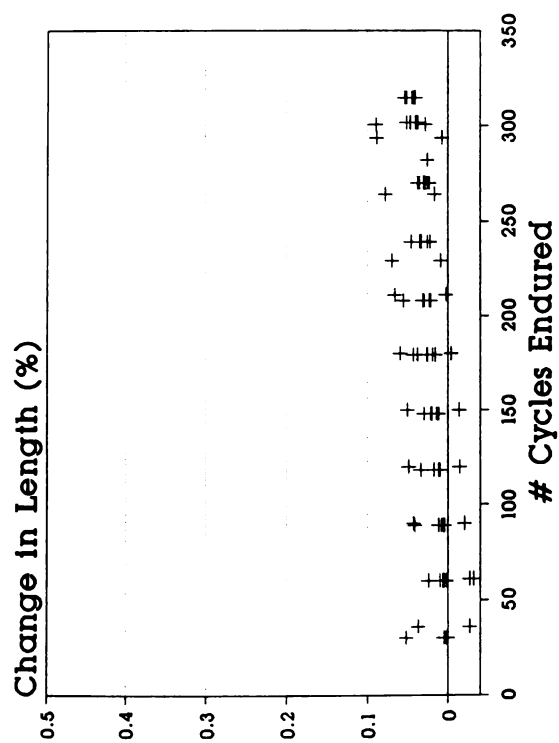
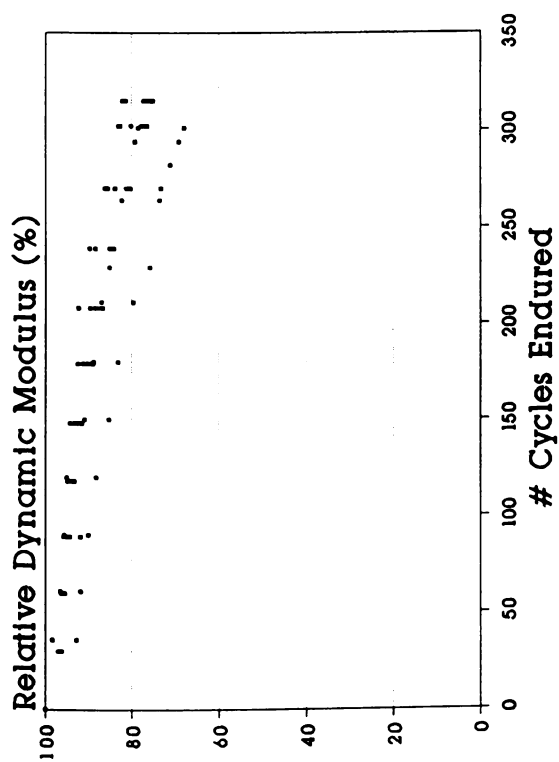
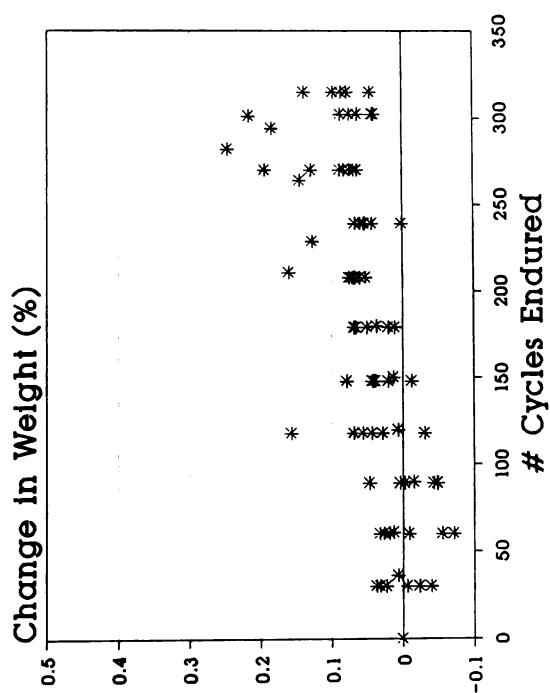
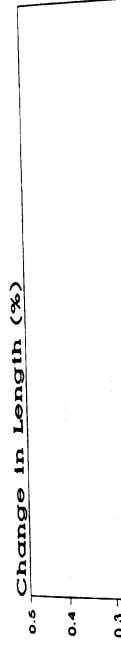
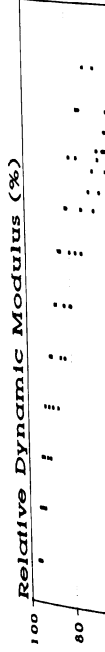


Figure C.32. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.45, 56 day curing period, and 15% Cl F FA.





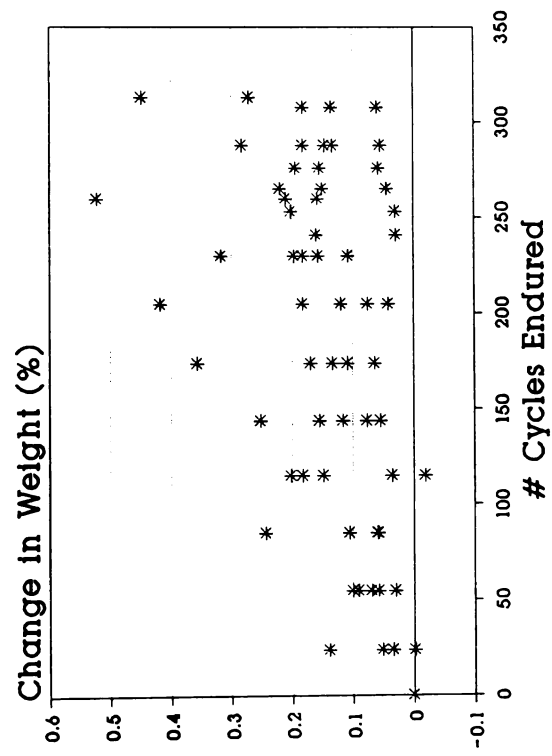
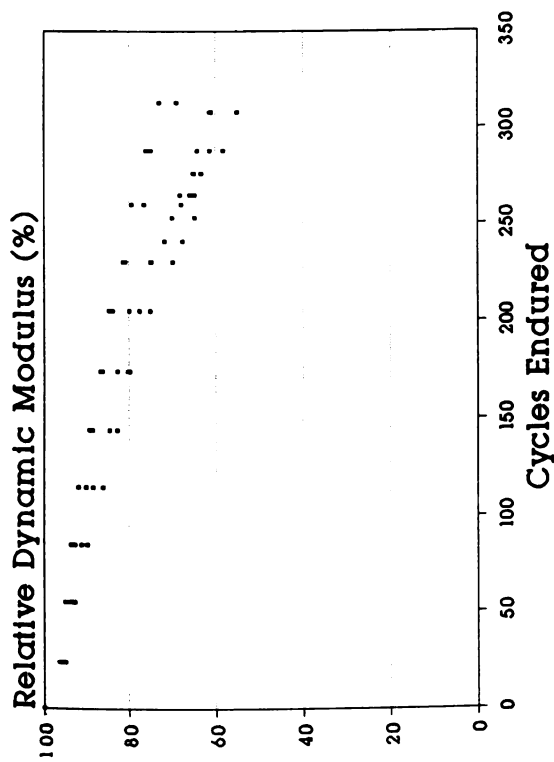
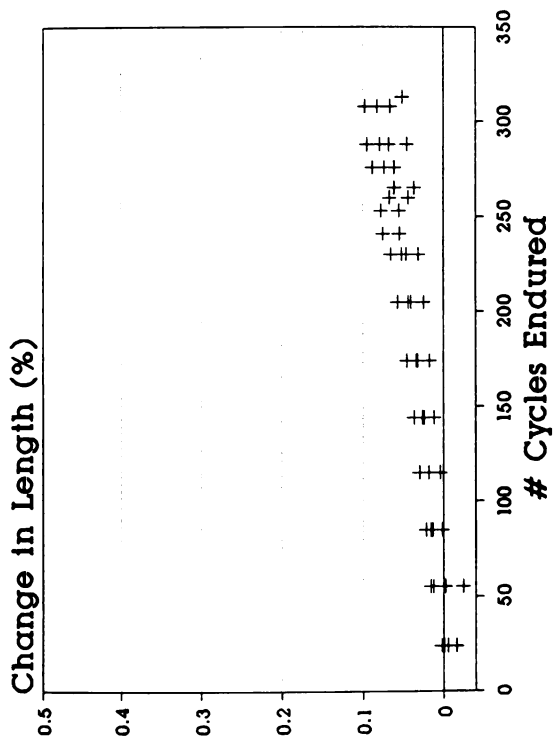
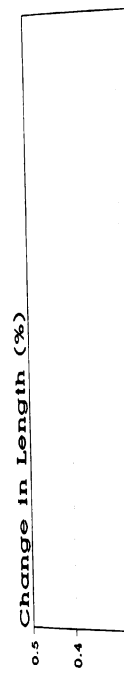
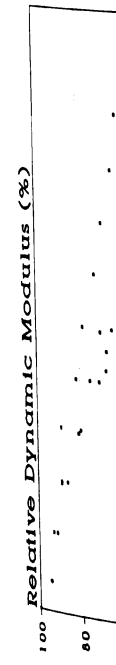


Figure C.33. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.40, 28 day curing period, and 30% Cl F FA.



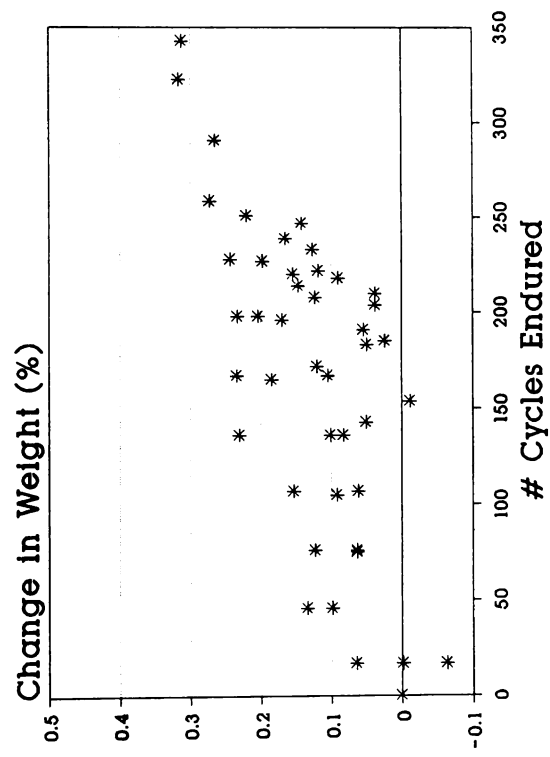
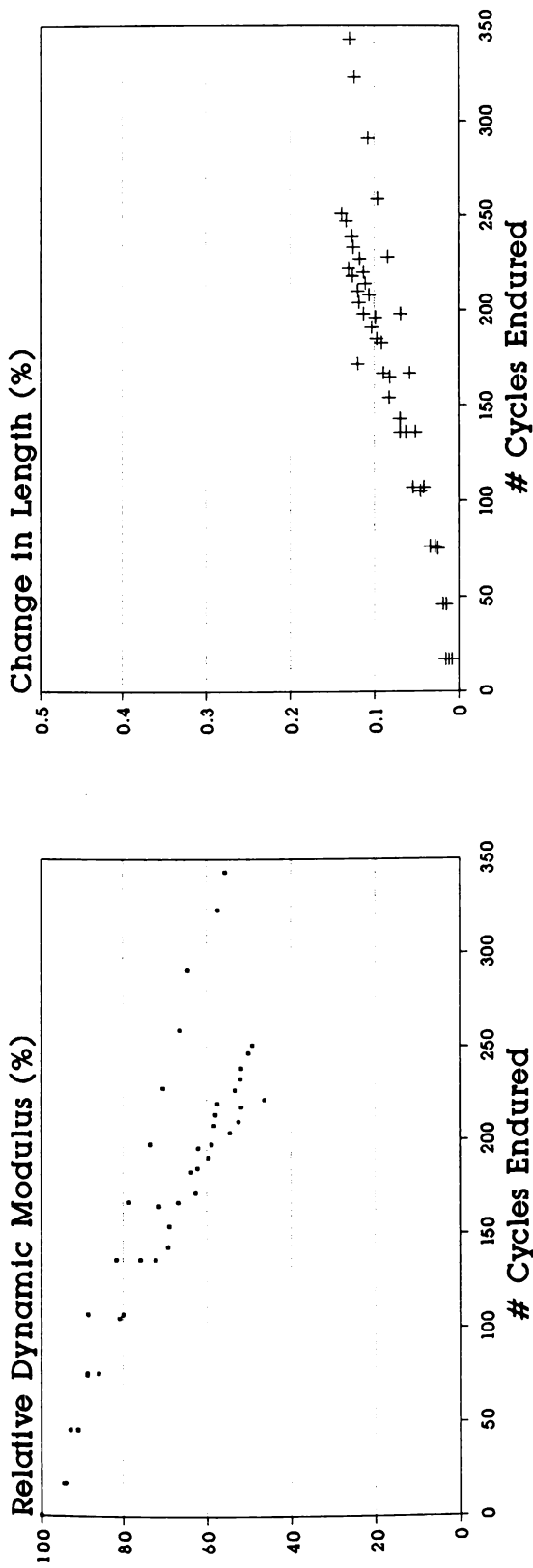
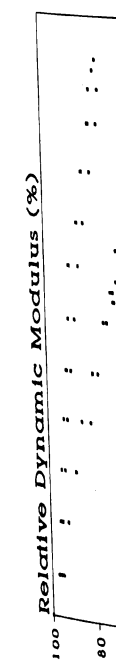
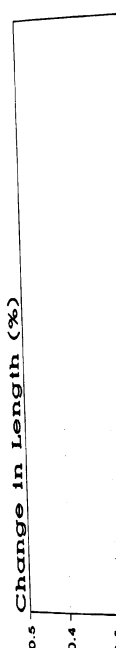


Figure C.34. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C=0+P.40, 56 day curing period, and 30% Cl F FA.



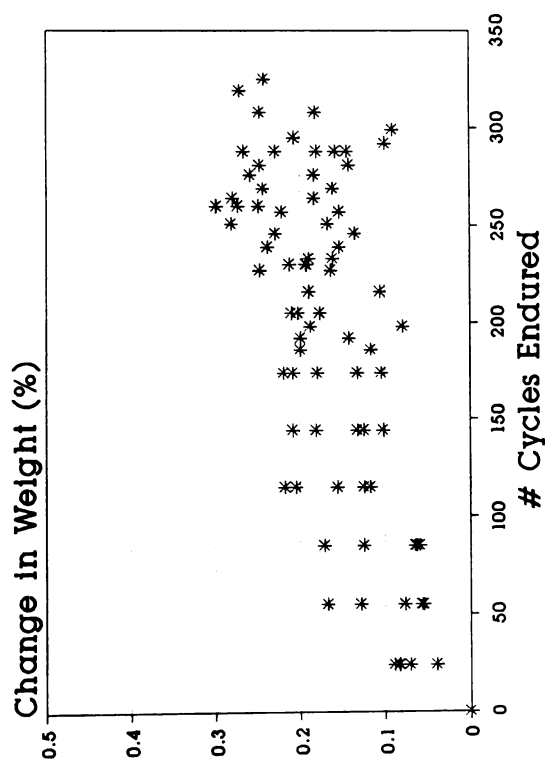
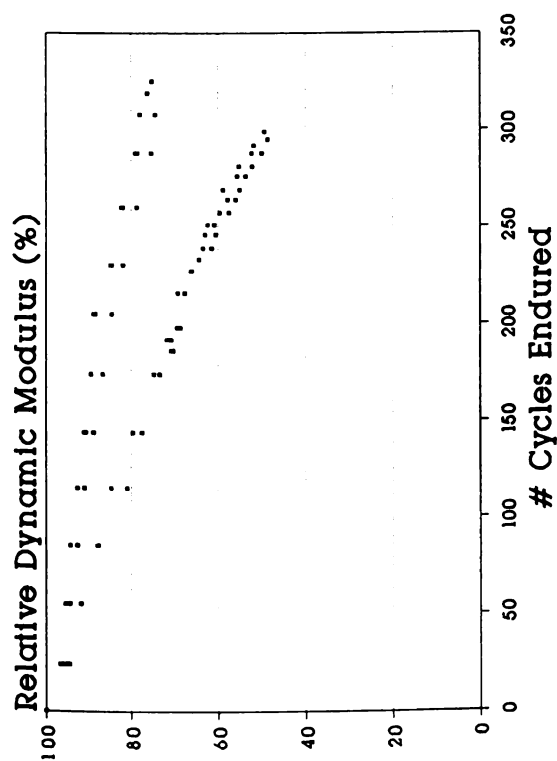
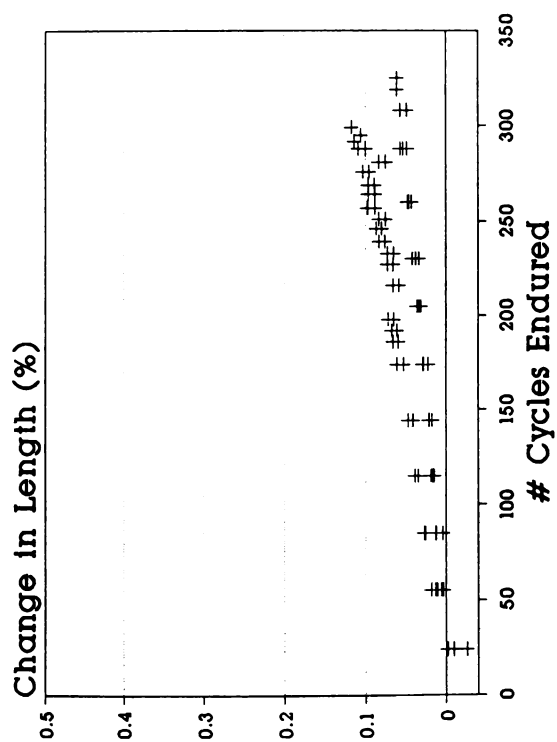
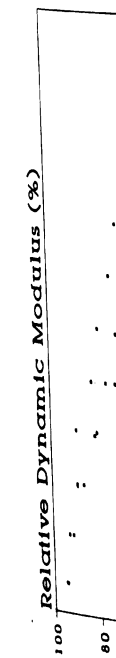
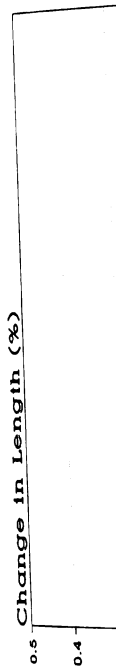


Figure C.35. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.45 28 day curing period, and 30% C1 F FA.



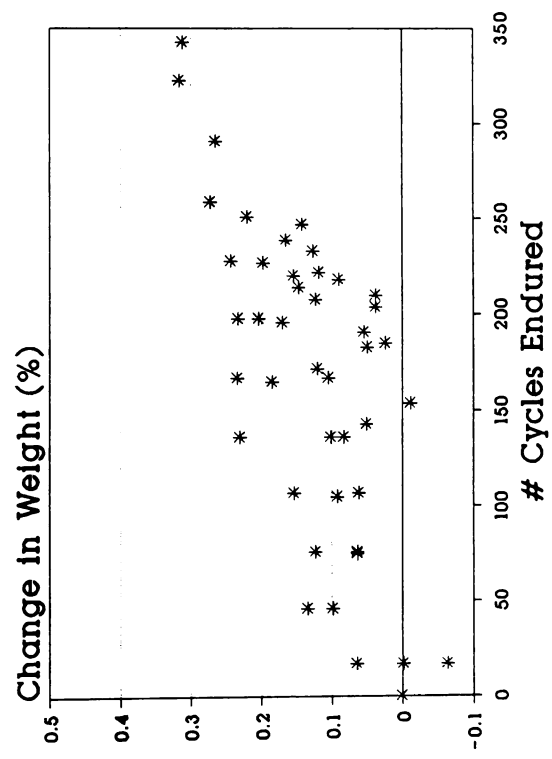
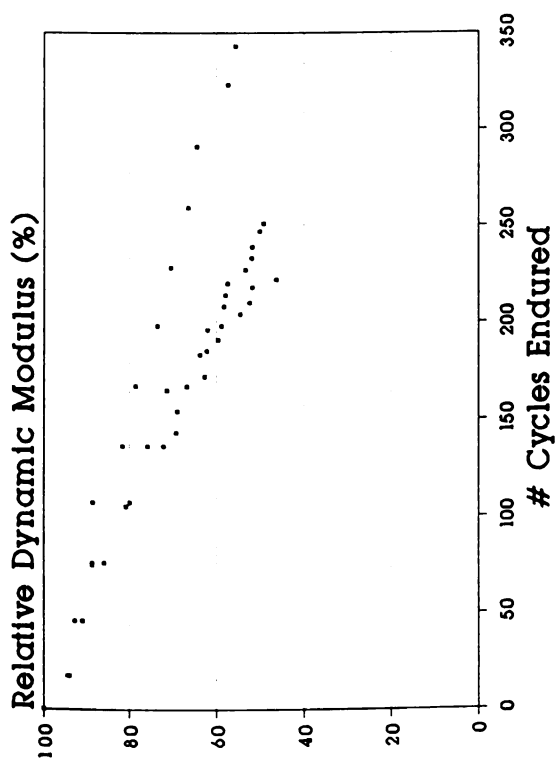
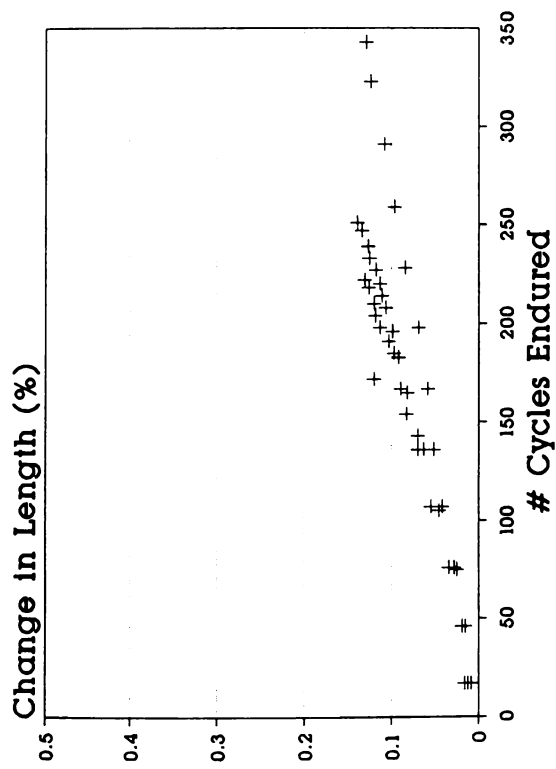
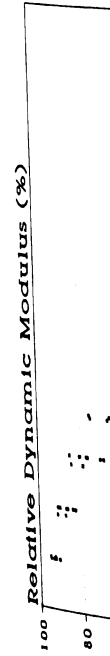
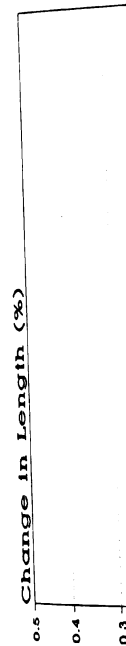


Figure C.36. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.45 56 day curing period, and 30% C1 F FA.



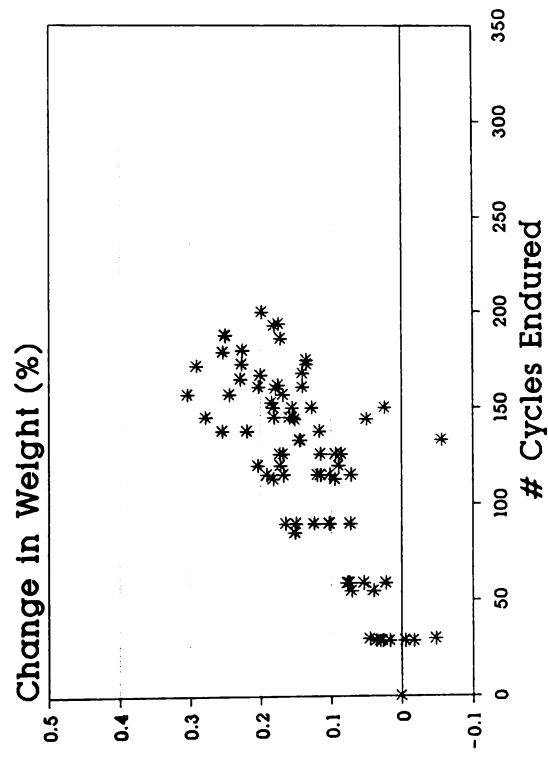
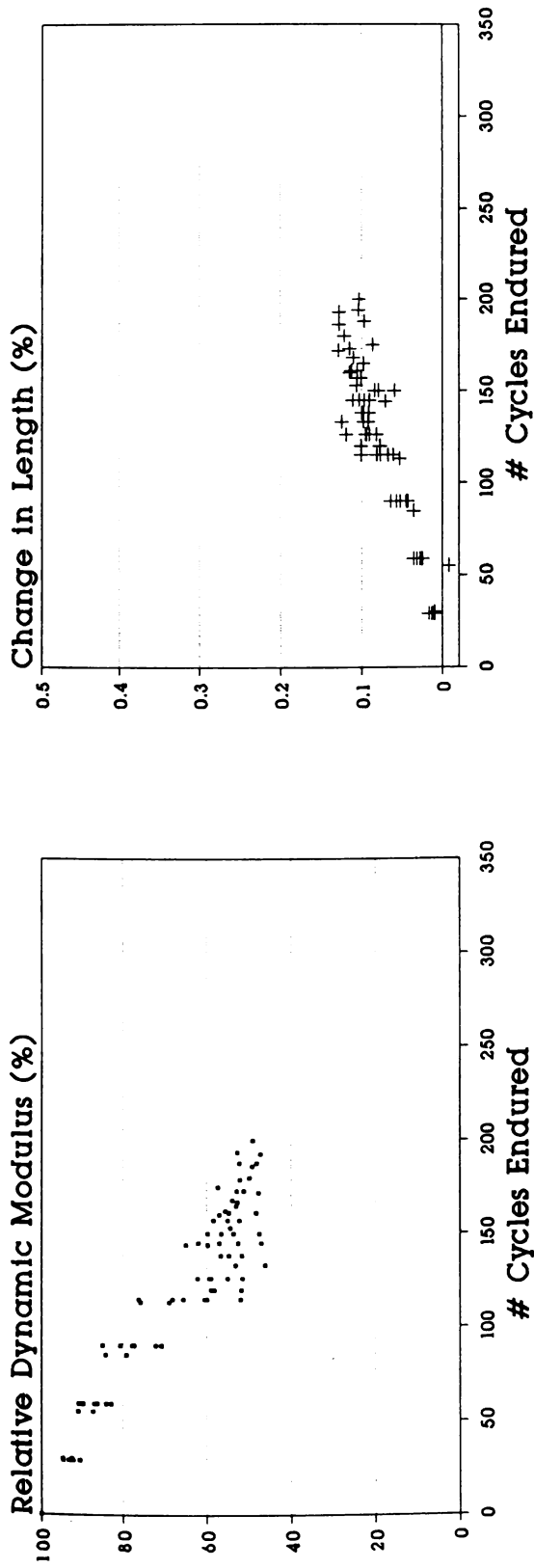
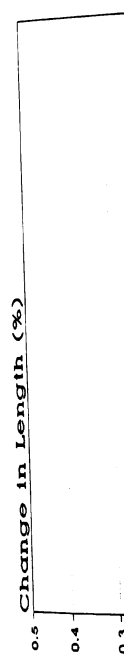


Figure C.37. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.40, 56 day curing period, and 15% C1 C FA.



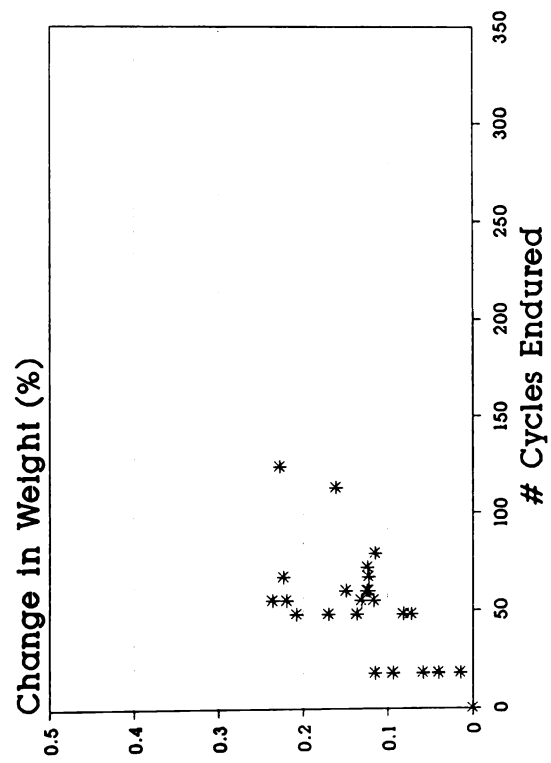
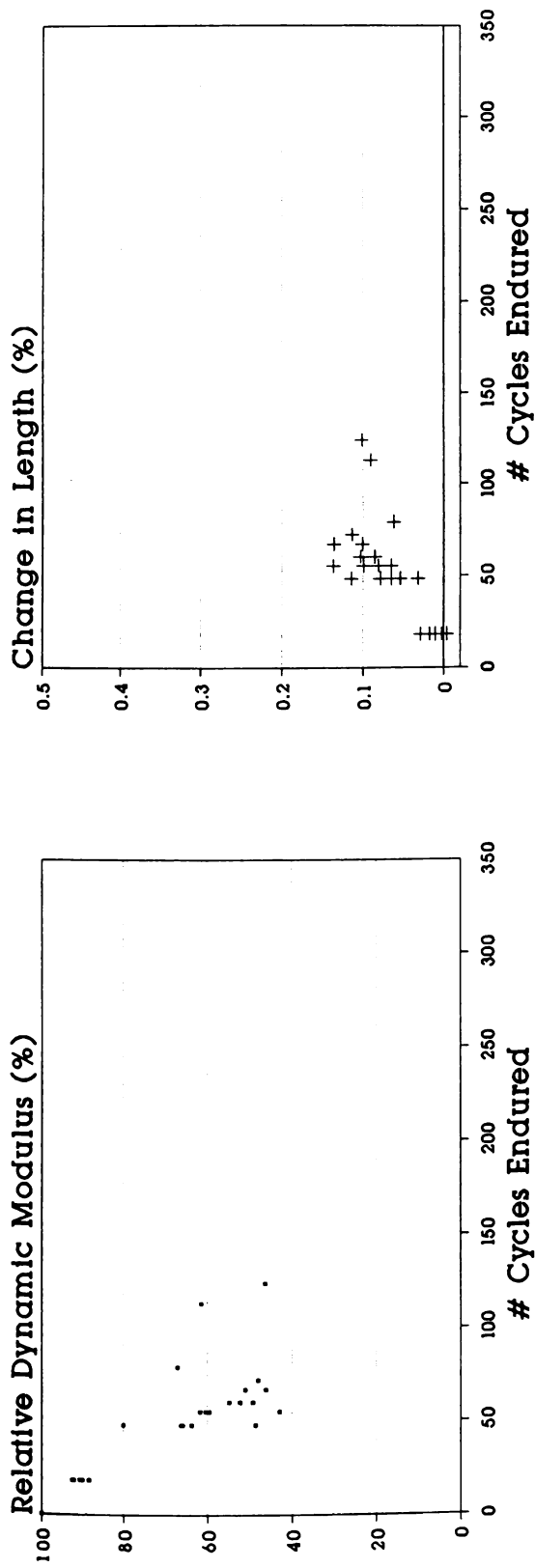
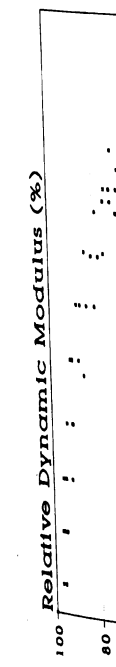
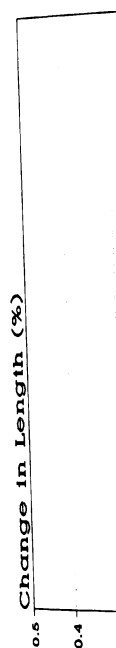


Figure C.38. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.45, 56 day curing period, and 15% C1 C FA.



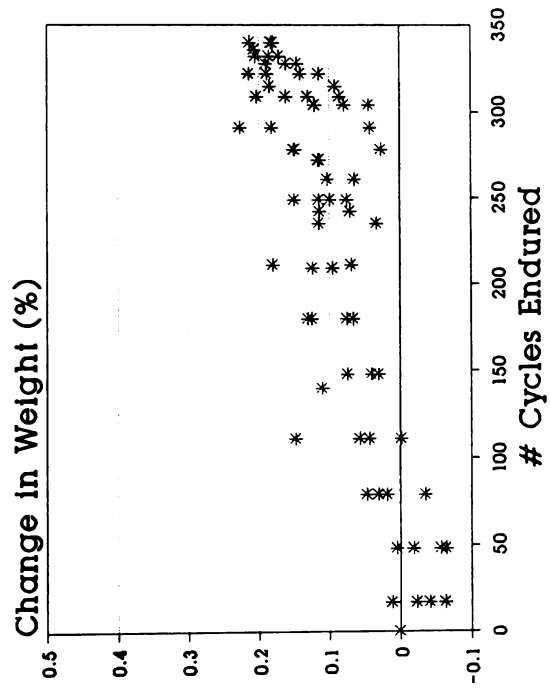
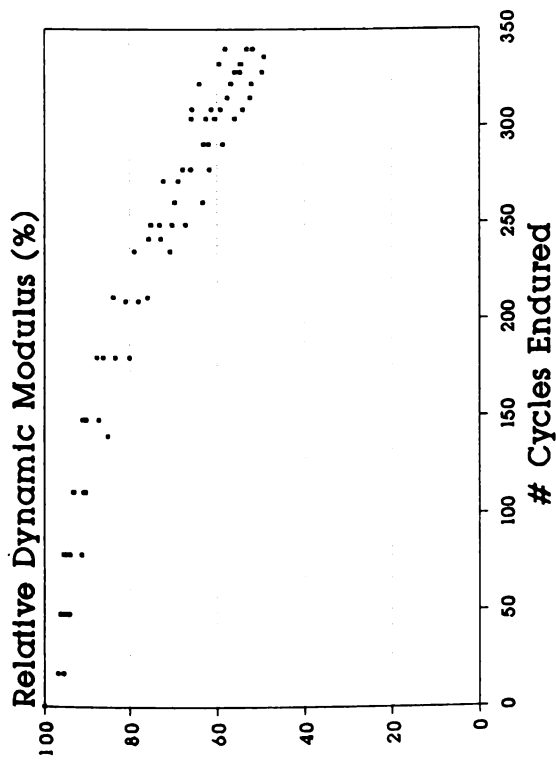
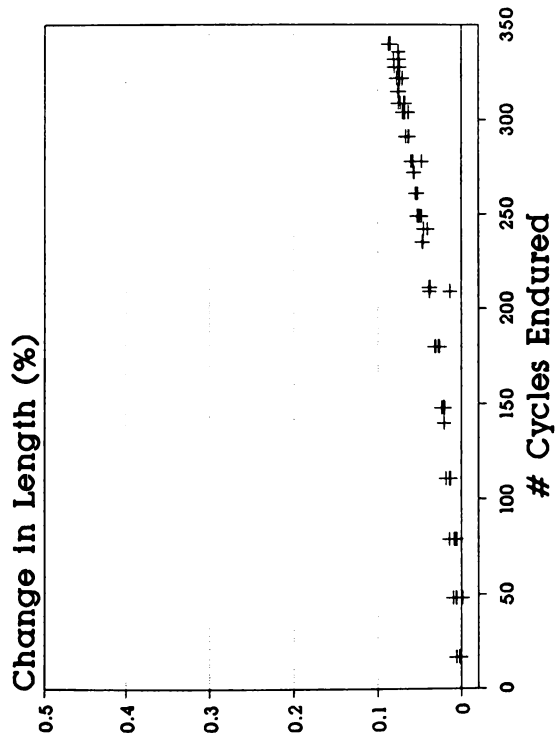


Figure C.39. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.40, 28 day curing period, and 30% C1 C FA.

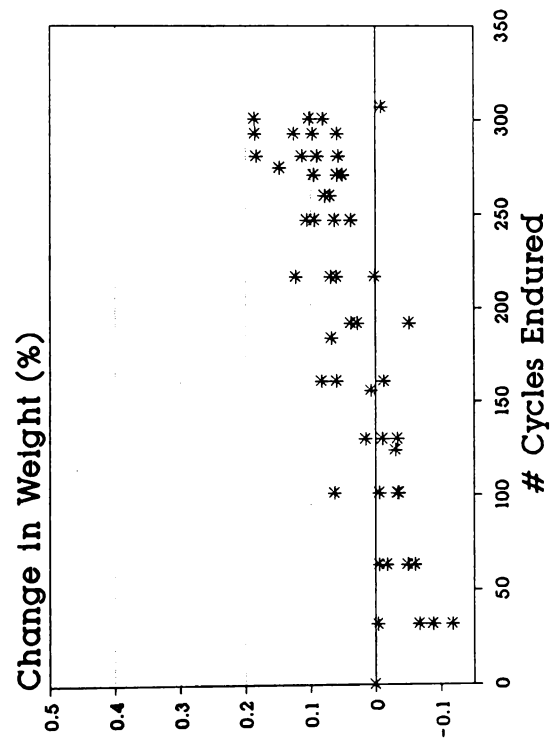
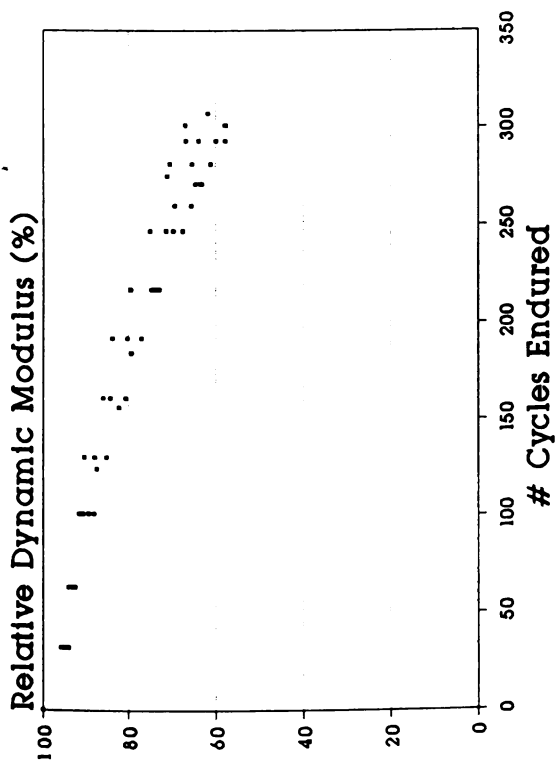
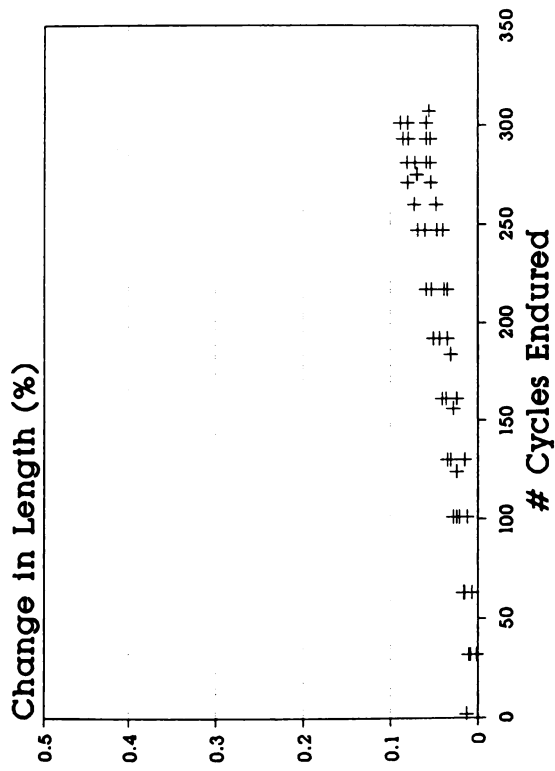


Figure C.40: RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.40, 56 day curing period, and 30% C1 C FA.

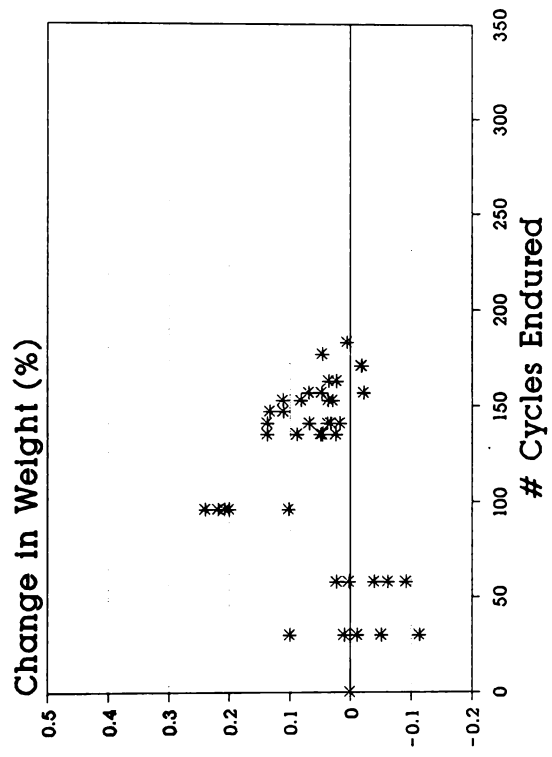
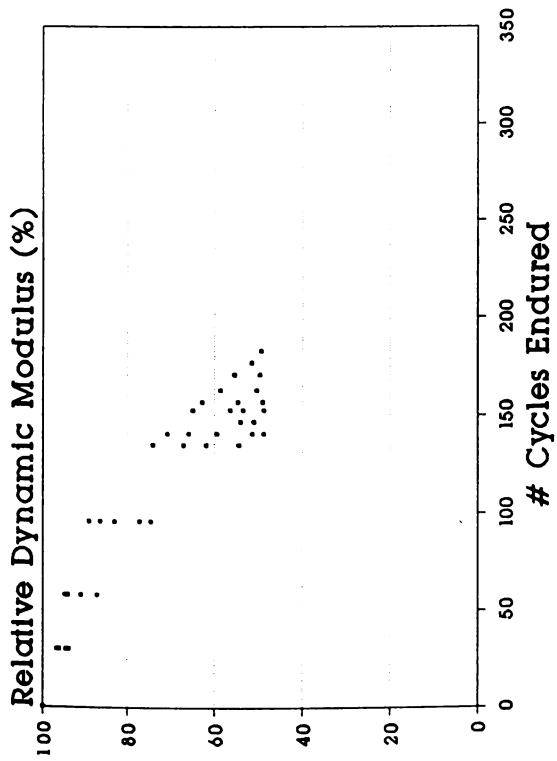
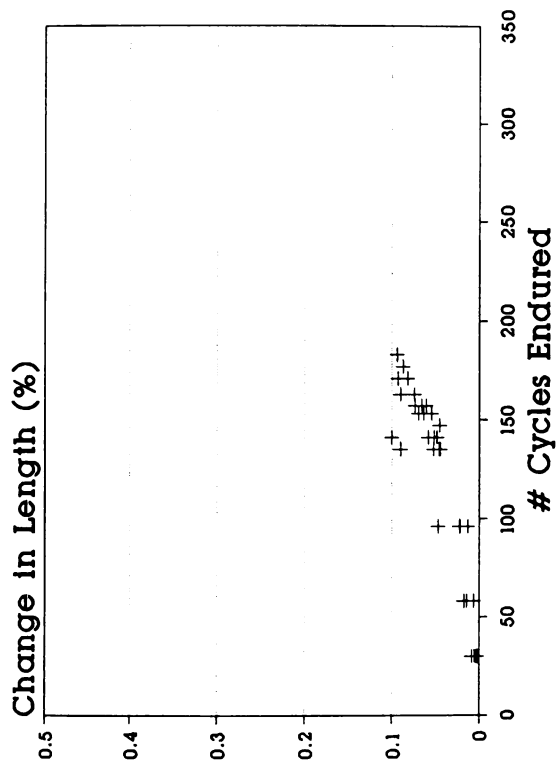


Figure C.41. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.45, 28 day curing period, and 30% C1 C FA.

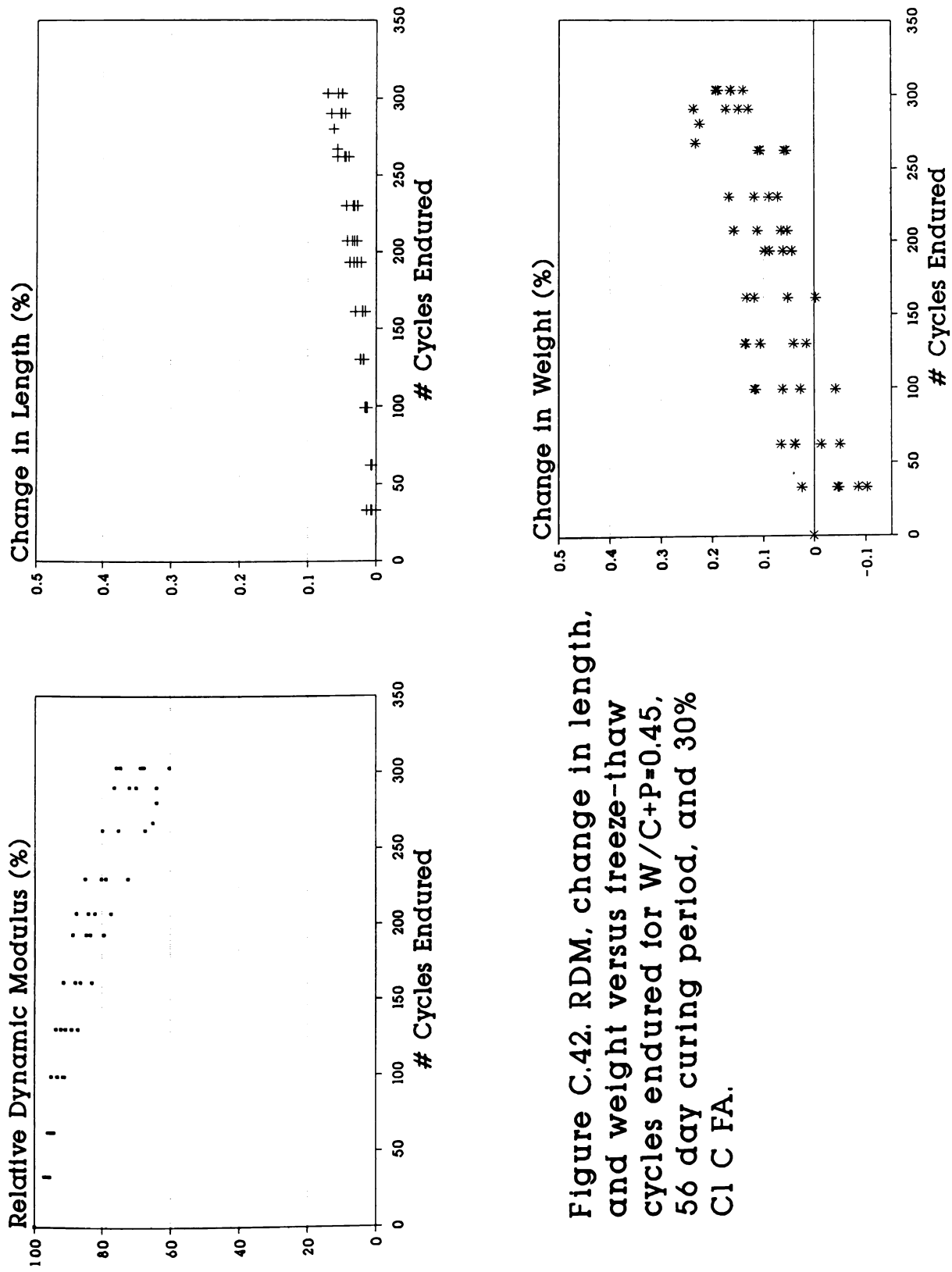


Figure C.42. RDM, change in length, and weight versus freeze-thaw cycles endured for W/C+P=0.45, 56 day curing period, and 30% C1 C FA.

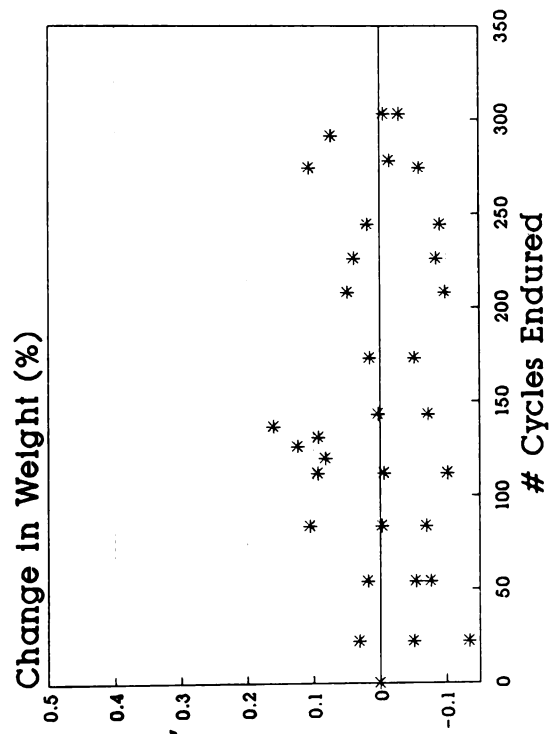
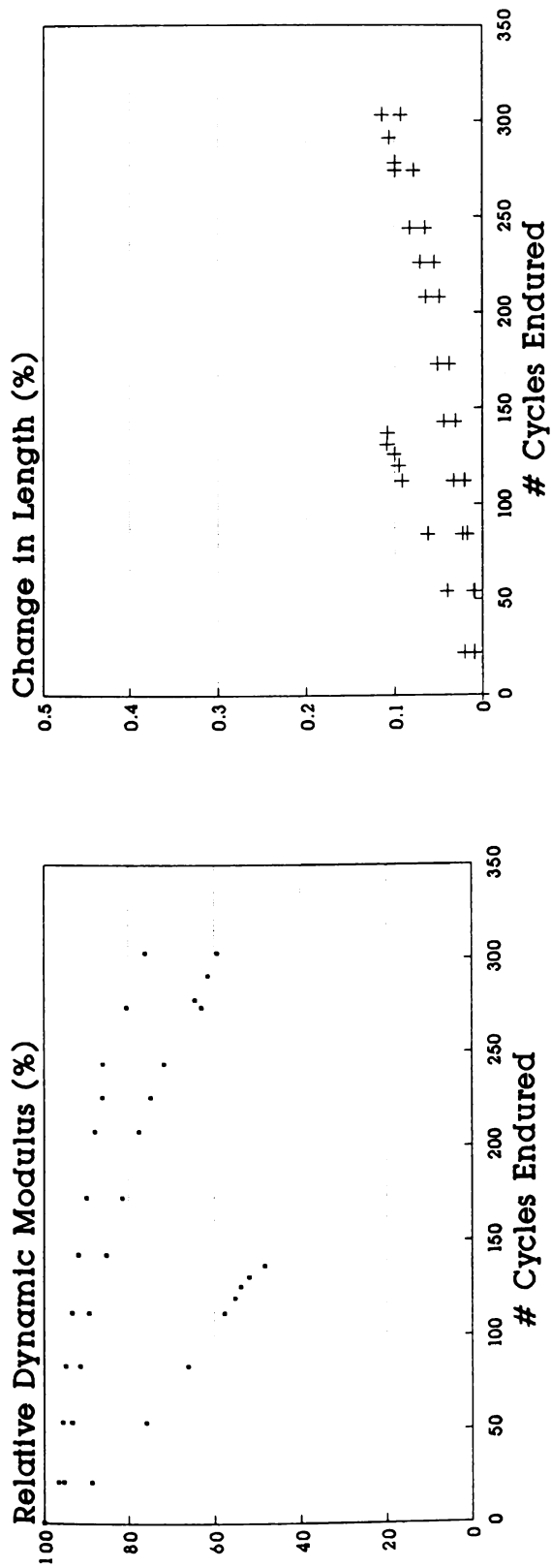


Figure C.43. RDM, change in length, and weight versus no. of freeze-thaw cycles endured with $W/C+P=0.40$, 28 day curing period, and 8% silica fume.

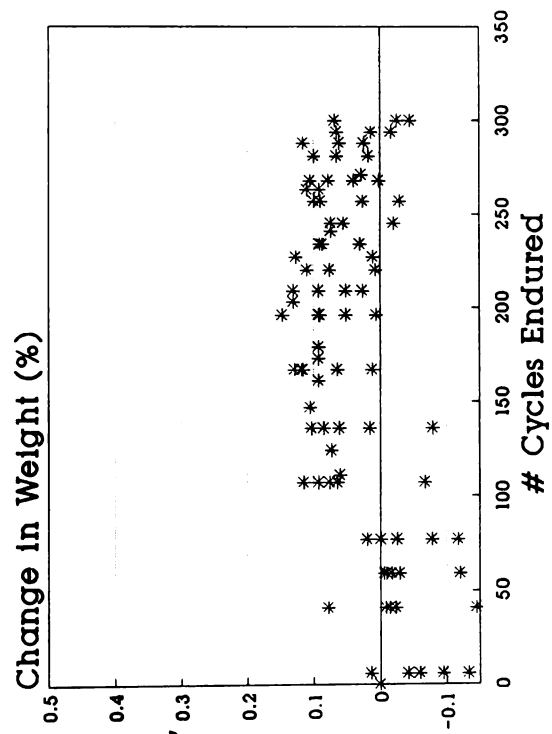
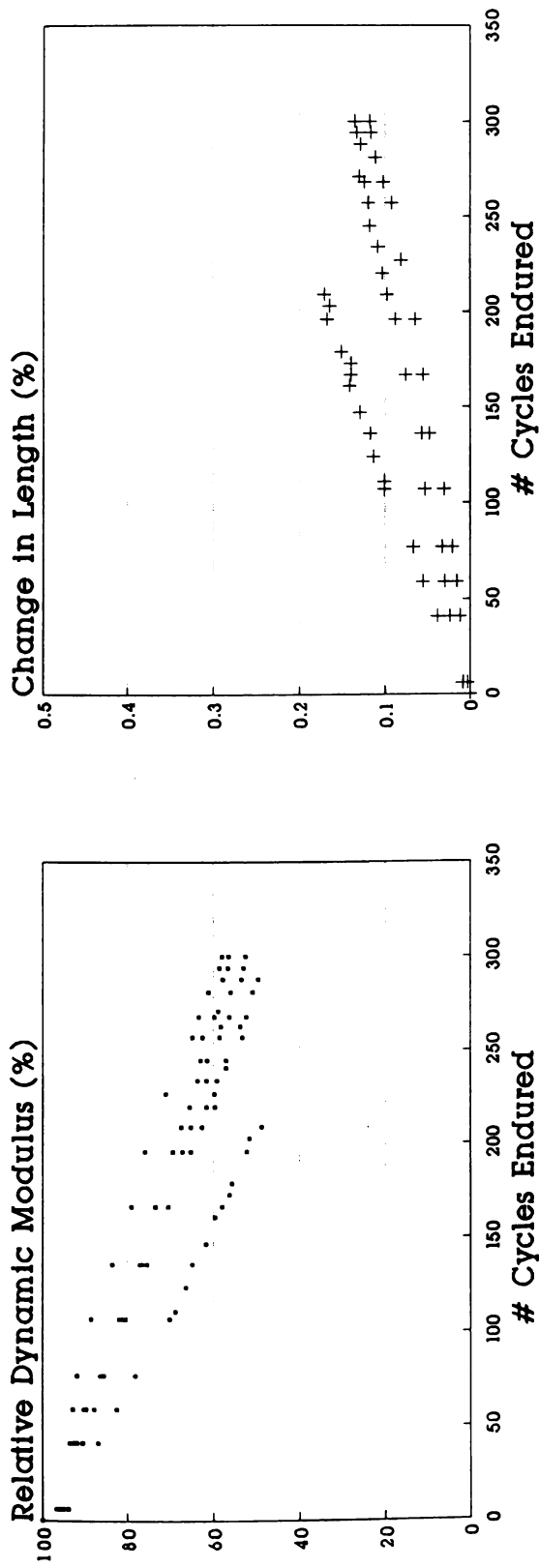


Figure C.44. RDM, change in length, and weight versus no. of freeze-thaw cycles endured with $W/C+P=0.40$, 56 day curing period, and 8% silica fume.

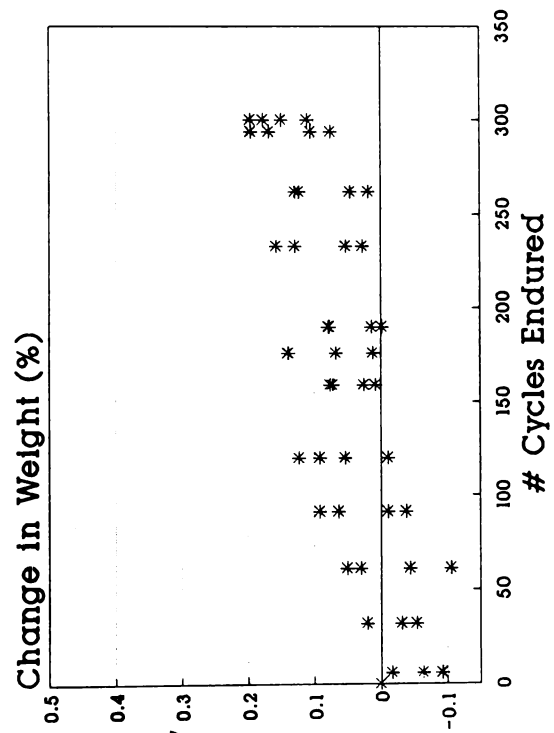
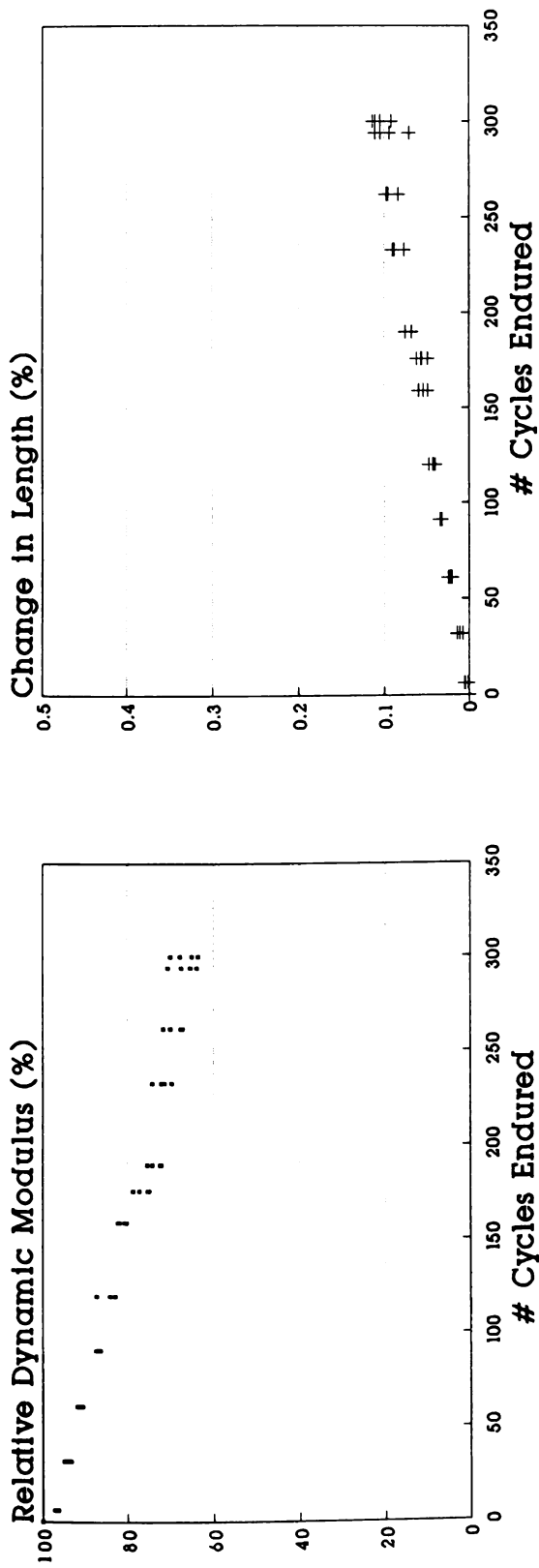


Figure C.45. RDM, change in length, and weight versus no. of freeze-thaw cycles endured with $W/C+P=0.45$, 28 day curing period, and 8% silica fume.

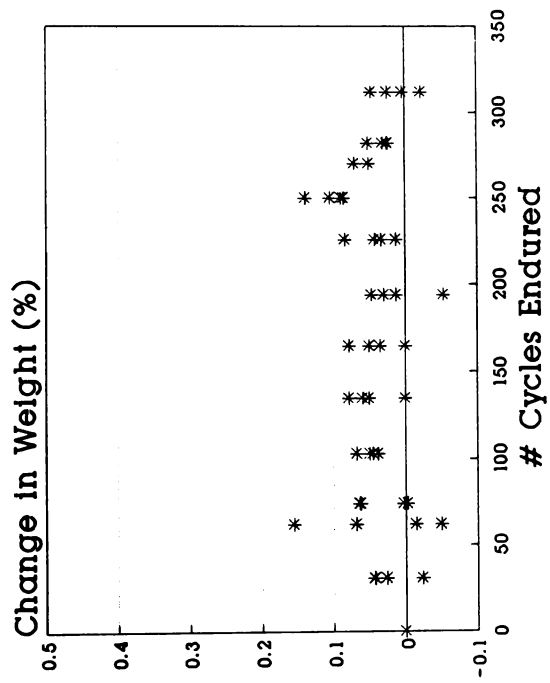
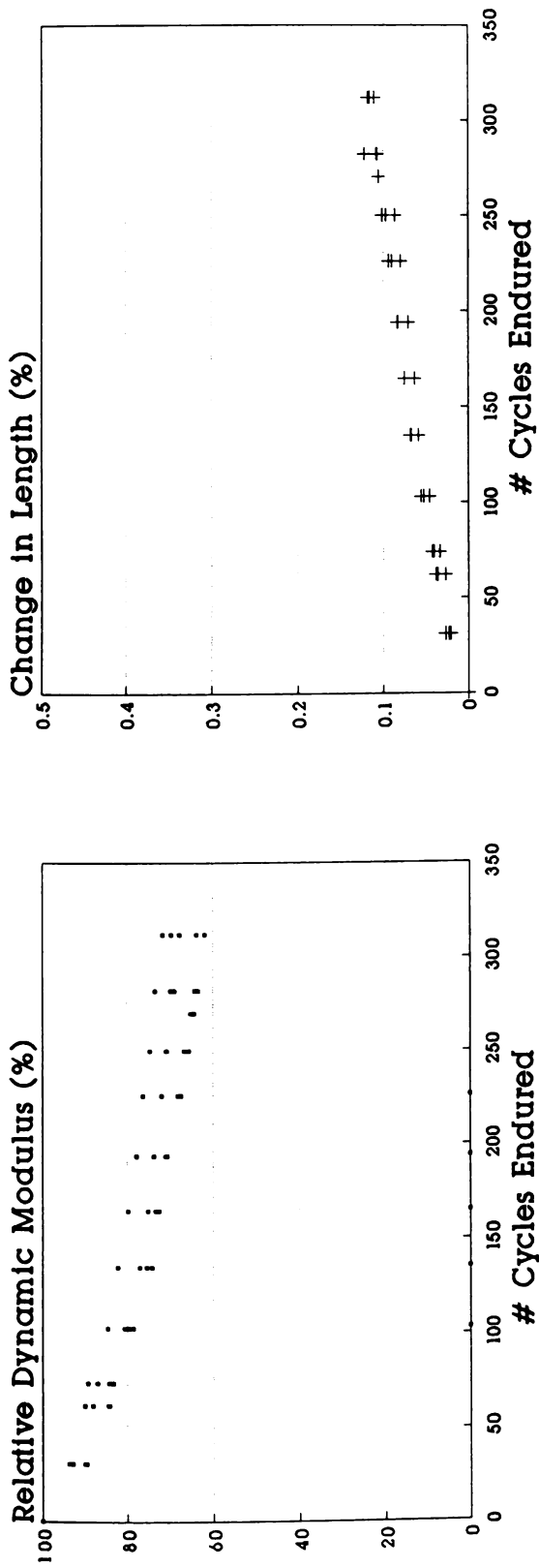


Figure C.46. RDM, change in length, and weight versus no. of freeze-thaw cycles endured with W/C+P=0.45, 56 day curing period, and 8% silica fume.

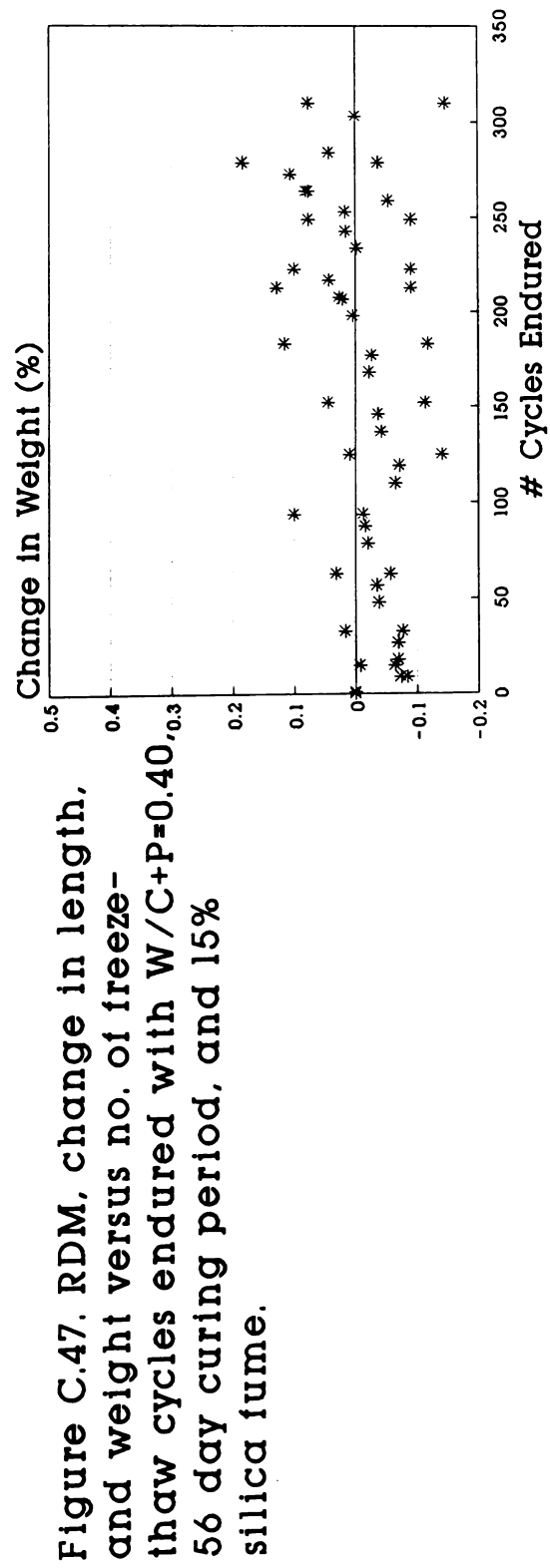
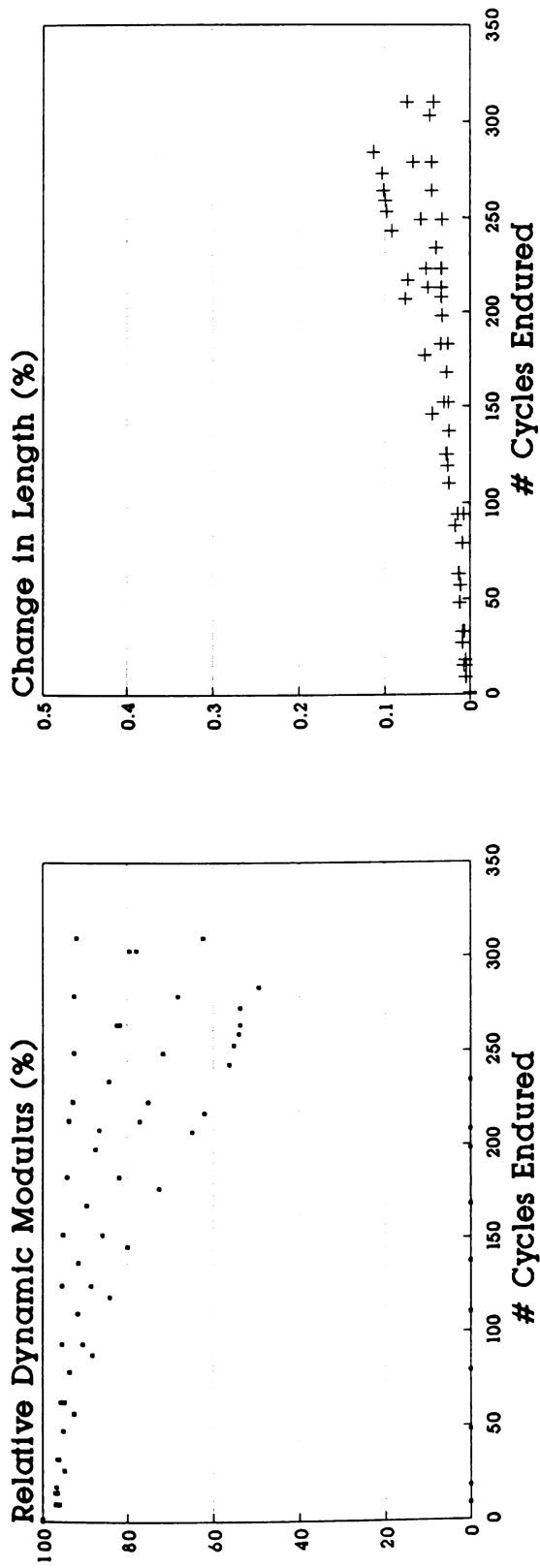


Figure C.47. RDM, change in length, and weight versus no. of freeze-thaw cycles endured with $W/C+P=0.40$, 56 day curing period, and 15% silica fume.

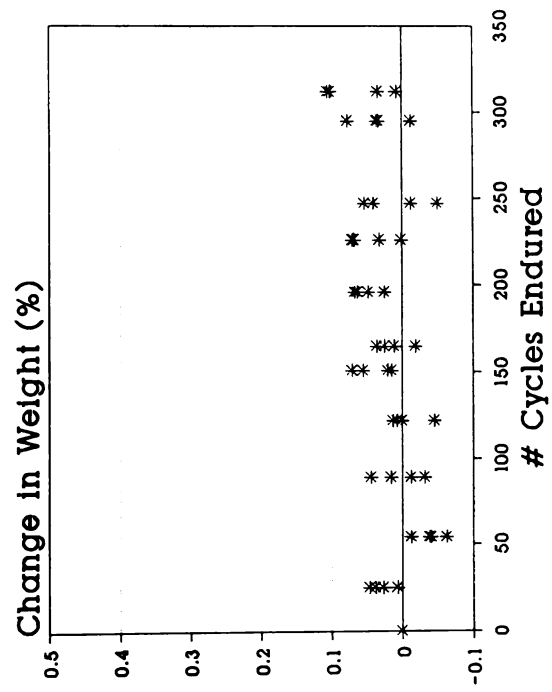
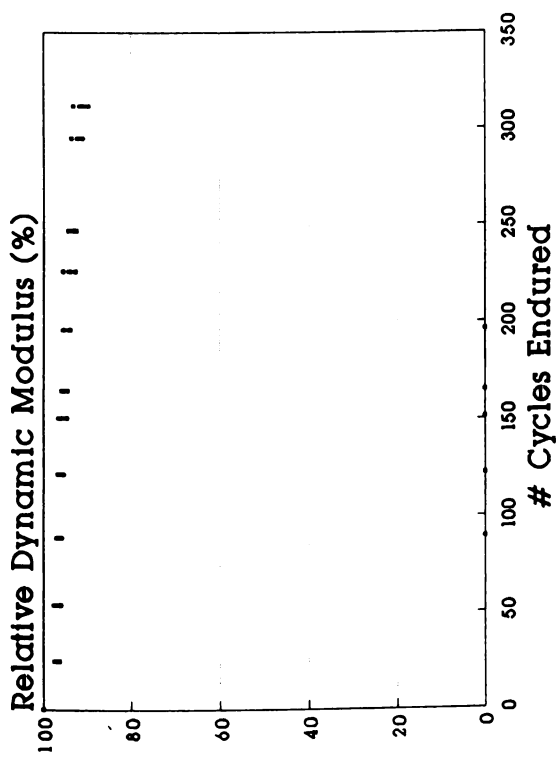
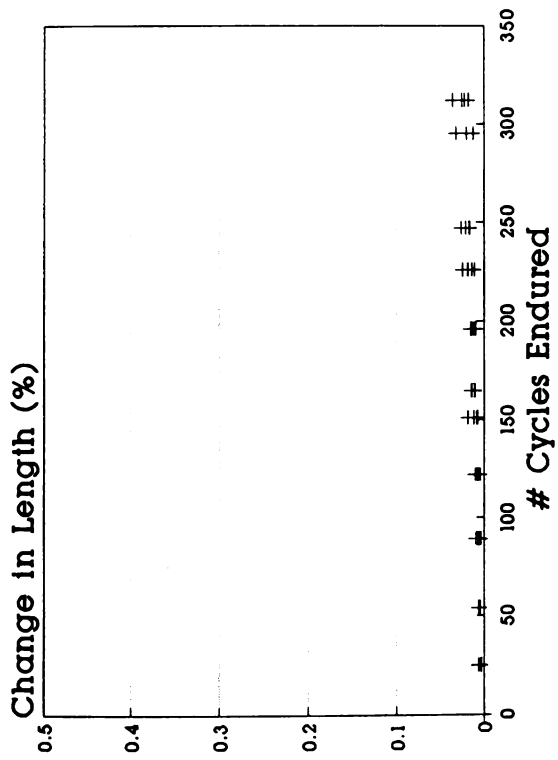


Figure C.48. RDM, change in length, and weight versus no. of freeze-thaw cycles endured with W/C+P=0.45, 56 day curing period, and 15% silica fume.



APPENDIX D
(Statistical Calculations)



Table D.1. Statistics, DF versus AC and W/C for Matrix A.

*** CELL MEANS ***						
	DF BY AC WC	DURABILITY FACTOR AIR CONTENT WATER-CEMENT RATIO				
TOTAL POPULATION						
	61.00 (73)					
AC						
	1	2	3			
	18.72 (25)	77.72 (25)	88.78 (23)			
WC						
	1	2	3			
	49.55 (20)	73.81 (21)	59.75 (32)			
	WC					
		1	2	3		
AC						
	1	26.44 (9)	27.80 (5)	8.27 (11)		
	2	68.45 (11)	79.20 (5)	88.22 (9)		
	3	.00 (0)	92.27 (11)	85.58 (12)		
*** ANALYSIS OF VARIANCE ***						
	DF BY AC WC	DURABILITY FACTOR AIR CONTENT WATER-CEMENT RATIO				
Source of Variation		Sum of Squares	DF	Mean Square	F	Signif of F
Main Effects		70040.457	4	17510.114	697.663	.000
AC		63922.645	2	31961.323	1273.449	.000
WC		608.450	2	304.225	12.121	.000
2-way Interactions		3746.157	3	1248.719	49.753	.000
AC WC		3746.157	3	1248.719	49.753	.000
Explained		73786.615	7	10540.945	419.987	.000
Residual		1631.385	65	25.098		
Total		75418.000	72	1047.472		
Correlations:						
	AC	WC	DF			
AC	1.0000	.2109	.8919**			
WC	.2109	1.0000	.0973			
DF	.8919**	.0973	1.0000			

Table D.2. Statistics, C-str with AC and W/C for Matrix A.

*** CELL MEANS ***						
	CSTR BY AC WC	COMPRESSIVE STRENGTH AIR CONTENT WATER-CEMENT RATIO				
TOTAL POPULATION						
	37194.70 (30)					
AC	1	2	3			
	39403.83 (12)	39860.00 (10)	30549.38 (8)			
WC	1	2	3			
	42152.67 (6)	39547.15 (13)	31710.18 (11)			
	WC	1	2	3		
AC	1	41899.25 (4)	40889.25 (4)	35423.00 (4)		
	2	42659.50 (2)	41881.60 (5)	34624.33 (3)		
	3	.00 (0)	35287.00 (4)	25811.75 (4)		
*** ANALYSIS OF VARIANCE ***						
	CSTR BY AC WC	COMPRESSIVE STRENGTH AIR CONTENT WATER-CEMENT RATIO				
Source of Variation		Sum of Squares	DF	Mean Square	F	Signif of F
Main Effects		861319138.502	4	215329784.63	32.389	.000
AC		311008692.864	2	155504346.43	23.390	.000
WC		378434901.744	2	189217450.87	28.461	.000
2-way Interactions		16593577.181	3	5531192.394	.832	.491
AC WC		16593577.181	3	5531192.394	.832	.491
Explained		877912715.683	7	125416102.24	18.865	.000
Residual		146260636.617	22	6648210.755		
Total		1024173352.30	29	35316322.493		
Correlations: AC WC CSTR						
AC	1.0000	.2631	-.5643**			
WC	.2631	1.0000	-.7000**			
CSTR	-.5643**	-.7000**	1.0000			



Table D.3. Effect of fly ash, WR/HRWR, AEA and W/C on frost resistance.

*** CELL MEANS ***			
		DF	DURABILITY FACTOR
		BY FLYASH	TYPE OF FLY ASH; CL F AND C
		WR	WATER REDUCER, AND HIGH RANGE WATER REDUCER
		AEA	TYPE OF AEA
		WC	WATER-TO-CEMENTITIOUS RATIO
AEA	=	1	
WC	=	1	
	WR		
		1	2
FLYASH			
	1	94.00	14.40
		(6)	(5)
	2	29.33	12.40
		(6)	(5)
AEA	=	2	
WC	=	1	
	WR		
		1	2
FLYASH			
	1	36.40	42.80
		(5)	(5)
	2	50.40	55.80
		(5)	(5)
AEA	=	1	
WC	=	2	
	WR		
		1	2
FLYASH			
	1	88.60	39.00
		(5)	(5)
	2	15.00	35.40
		(5)	(5)
AEA	=	2	
WC	=	2	
	WR		
		1	2
FLYASH			
	1	77.60	23.00
		(5)	(5)
	2	69.50	36.80
		(2)	(5)

Table D.3. (Cont'd).

*** ANALYSIS OF VARIANCE ***							
BY		DF	DURABILITY FACTOR				
		FLYASH	TYPE OF FLY ASH; CL F AND C				
		WR	WATER REDUCER, AND HIGH RANGE WATER REDU				
		AEA	TYPE OF AEA				
		WC	WATER-TO-CEMENTITIOUS RATIO				
Source of Variation			Sum of Squares	DF	Mean Square	F	Signif of F
Main Effects			18472.560	4	4618.140	62.026	.000
FLYASH			5178.134	1	5178.134	69.548	.000
WR			11750.983	1	11750.983	157.828	.000
AEA			793.835	1	793.835	10.662	.002
WC			399.866	1	399.866	5.371	.024
2-way Interactions			20208.175	6	3368.029	45.236	.000
FLYASH WR			8713.380	1	8713.380	117.030	.000
FLYASH AEA			8139.437	1	8139.437	109.321	.000
FLYASH WC			574.188	1	574.188	7.712	.007
WR AEA			1382.464	1	1382.464	18.568	.000
WR WC			60.410	1	60.410	.811	.371
AEA WC			91.399	1	91.399	1.228	.272
3-way Interactions			12143.775	4	3035.944	40.776	.000
FLYASH WR AEA			3790.661	1	3790.661	50.912	.000
FLYASH WR WC			240.499	1	240.499	3.230	.077
FLYASH AEA WC			27.582	1	27.582	.370	.545
WR AEA WC			8263.481	1	8263.481	110.987	.000
4-way Interactions			70.579	1	70.579	.948	.334
FLYASH WR AEA WC			70.579	1	70.579	.948	.334
Explained			50895.088	15	3393.006	45.572	.000
Residual			4690.633	63	74.454		
Total			55585.722	78	712.637		

Table D.4. Effect of GGBF slag (with and without WR) on frost resistance.

*** CELL MEANS ***			
	DF BY WR WC	DURABILITY FACTOR WATER REDUCER WATER-TO-CEMENTITIOUS RATIO	
TOTAL POPULATION			
	19.45 (20)		
WR	1 24.90 (10)	2 14.00 (10)	
WC	1 17.10 (10)	2 21.80 (10)	
	WC		
		1	2
WR	1 2	19.40 14.80 (5) (5)	30.40 13.20 (5) (5)

*** ANALYSIS OF VARIANCE ***					
	DF BY WR WC	DURABILITY FACTOR WATER REDUCER WATER-TO-CEMENTITIOUS RATIO			
Source of Variation		Sum of Squares	DF	Mean Square	Signif of F
Main Effects		704.500	2	352.250	34.366
WR		594.050	1	594.050	57.956
WC		110.450	1	110.450	10.776
2-way Interactions		198.450	1	198.450	19.361
WR WC		198.450	1	198.450	19.361
Explained		902.950	3	300.983	29.364
Residual		164.000	16	10.250	
Total		1066.950	19	56.155	

Table D.5. Effect of amount of class F fly ash, WC and CT on frost resistance.

*** CELL MEANS ***		
	DF BY AMOUNT WC CT	DURABILITY FACTOR AMOUNT OF CLASS F FLY ASH WATER-TO-CEMENTITIOUS RATIO CURING TIME
TOTAL POPULATION		
56.29		
(58)		
AMOUNT		
1	2	3
30.05	86.37	53.84
(20)	(19)	(19)
WC		
1	2	
59.27	53.88	
(26)	(32)	
CT		
1	2	
67.73	44.04	
(30)	(28)	
WC		
	1	2
AMOUNT		
1	36.00	24.10
	(10)	(10)
2	90.00	83.73
	(8)	(11)
3	57.63	51.09
	(8)	(11)
CT		
	1	2
AMOUNT		
1	45.80	14.30
	(10)	(10)
2	91.50	80.67
	(10)	(9)
3	65.90	40.44
	(10)	(9)
CT		
	1	2
WC		
1	72.00	41.91
	(15)	(11)
2	63.47	45.41
	(15)	(17)
CT	= 1	
WC		
	1	2
AMOUNT		
1	56.40	35.20
	(5)	(5)
2	94.40	88.60
	(5)	(5)
3	65.20	66.60
	(5)	(5)
CT	= 2	
WC		
	1	2
AMOUNT		
1	15.60	13.00
	(5)	(5)
2	82.67	79.67
	(3)	(6)
3	45.00	38.17
	(3)	(6)

Table D.5. (cont'd)

*** ANALYSIS OF VARIANCE ***							
BY		DF	DURABILITY FACTOR				
		AMOUNT	AMOUNT OF CLASS F FLY ASH				
		WC	WATER-TO-CEMENTITIOUS RATIO				
		CT	CURING TIME				
Source of Variation			Sum of Squares	DF	Mean Square	F	Signif of F
Main Effects			39058.051	4	9764.513	165.230	.000
AMOUNT			30808.566	2	15404.283	260.664	.000
WC			487.506	1	487.506	8.249	.006
CT			6994.165	1	6994.165	118.352	.000
2-way Interactions			1512.383	5	302.477	5.118	.001
AMOUNT WC			258.267	2	129.134	2.185	.124
AMOUNT CT			1100.819	2	550.409	9.314	.000
WC CT			85.330	1	85.330	1.444	.236
3-way Interactions			431.150	2	215.575	3.648	.034
AMOUNT WC CT			431.150	2	215.575	3.648	.034
Explained			41001.584	11	3727.417	63.074	.000
Residual			2718.433	46	59.096		
Total			43720.017	57	767.018		

Table D.6. Effect of amount of Cl C fly ash, WC and CT on frost resistance.

*** CELL MEANS ***			
DF BY AMOUNT		DURABILITY FACTOR	
WC		AMOUNT OF CLASS C FLY ASH	
CT		WATER-TO-CEMENTITIOUS RATIO	
CURING TIME			
TOTAL POPULATION			
34.85			
(62)			
AMOUNT			
1	2	3	
30.05	20.59	55.35	
(20)	(22)	(20)	
WC			
1	2		
43.38	25.77		
(32)	(30)		
CT			
1	2		
34.10	35.61		
(31)	(31)		
WC			
	1	2	
AMOUNT			
1	45.80	14.30	
	(10)	(10)	
2	26.17	13.90	
	(12)	(10)	
3	61.60	49.10	
	(10)	(10)	
CT			
	1	2	
AMOUNT			
1	36.00	24.10	
	(10)	(10)	
2	22.36	18.82	
	(11)	(11)	
3	45.10	65.60	
	(10)	(10)	
CT			
	1	2	
WC			
1	47.75	39.00	
	(16)	(16)	
2	19.53	32.00	
	(15)	(15)	
CT			
=	1		
WC			
	1	2	
AMOUNT			
1	56.40	15.60	
	(5)	(5)	
2	28.50	15.00	
	(6)	(5)	
3	62.20	28.00	
	(5)	(5)	
CT			
=	2		
WC			
	1	2	
AMOUNT			
1	35.20	13.00	
	(5)	(5)	
2	23.83	12.80	
	(6)	(5)	
3	61.00	70.20	
	(5)	(5)	

Table D.6. (cont'd)

*** ANALYSIS OF VARIANCE ***

BY	DURABILITY FACTOR		Sum of Squares	DF	Mean Square	F	Signif of F
	DF	AMOUNT					
	WC	AMOUNT OF CLASS C FLY ASH					
	CT	WATER-TO-CEMENTITIOUS RATIO					
		CURING TIME					
Source of Variation							
Main Effects			18700.887	4	4675.222	157.954	.000
AMOUNT			13864.431	2	6932.216	234.207	.000
WC			5326.383	1	5326.383	179.953	.000
CT			35.629	1	35.629	1.204	.278
2-way Interactions			5772.104	5	1154.421	39.002	.000
AMOUNT WC			1236.869	2	618.434	20.894	.000
AMOUNT CT			2792.731	2	1396.366	47.177	.000
WC CT			1692.428	1	1692.428	57.179	.000
3-way Interactions			1102.769	2	551.384	18.629	.000
AMOUNT WC CT			1102.769	2	551.384	18.629	.000
Explained			25575.760	11	2325.069	78.553	.000
Residual			1479.933	50	29.599		
Total			27055.694	61	443.536		

Table D.7. Effect of CSF with HRWR on frost resistance.

*** CELL MEANS ***		
	DF BY AMOUNT WC CURE	DURABILITY FACTOR AMOUNT OF SILICA FUME WATER-TO-CEMENTITIOUS RATIO CURING PERIOD
TOTAL POPULATION		
58.83 (69)		
AMOUNT		
1 2 3		
40.83 57.75 86.00		
(29) (20) (20)		
WC		
1 2		
52.09 65.00		
(33) (36)		
CURE		
1 2		
54.71 62.83		
(34) (35)		
WC		
1 2		
AMOUNT		
1 34.00 46.38		
(13) (16)		
2 48.10 67.40		
(10) (10)		
3 79.60 92.40		
(10) (10)		
CURE		
1 2		
AMOUNT		
1 26.93 53.80		
(14) (15)		
2 58.20 57.30		
(10) (10)		
3 90.10 81.90		
(10) (10)		
CURE		
1 2		
WC		
1 48.42 57.07		
(19) (14)		
2 62.67 66.67		
(15) (21)		
CURE = 1		
WC		
1 2		
AMOUNT		
1 26.44 27.80		
(9) (5)		
2 49.00 67.40		
(5) (5)		
3 87.40 92.80		
(5) (5)		
CURE = 2		
WC		
1 2		
AMOUNT		
1 51.00 54.82		
(4) (11)		
2 47.20 67.40		
(5) (5)		
3 71.80 92.00		
(5) (5)		

Table D.7. (cont'd)

*** ANALYSIS OF VARIANCE ***					
BY		DF	DURABILITY FACTOR		
		AMOUNT	AMOUNT OF SILICA FUME		
		WC	WATER-TO-CEMENTITIOUS RATIO		
		CURE	CURING PERIOD		
Source of Variation		Sum of Squares	DF	Mean Square	Signif of F
Main Effects		28517.931	4	7129.483	72.637
AMOUNT		24996.312	2	12498.156	127.335
WC		3042.757	1	3042.757	31.000
CURE		713.902	1	713.902	7.273
2-way Interactions		4107.309	5	821.462	8.369
AMOUNT WC		786.907	2	393.453	4.009
AMOUNT CURE		3603.159	2	1801.580	18.355
WC CURE		149.136	1	149.136	1.519
3-way Interactions		138.015	2	69.007	.703
AMOUNT WC CURE		138.015	2	69.007	.703
Explained		32763.254	11	2978.478	30.346
Residual		5594.659	57	98.152	
Total		38357.913	68	564.087	

APPENDIX E

(Development of Relationship between AVS, WPS, and Performance Characteristics)

Table E.1. Regression analysis of AVS, WPS, and performance characteristics.

Ser.	FAC	HTA	HEA	SFTA	SFEA	C-STR	PERM	FM	DF	FTC	RSq./ARSq.
1			X	X	X	X	X		X		0.192/0.102
2			X	X	X	X	X			X	0.092/-0.009
3	X						X			X	0.135/0.075
4	X		X	X	X	X				X	0.397/0.338
5	X		X	X	X	X			X		0.435/0.381
6	X		X	X	X	X	X		X		0.274/0.196
7	X		X	X	X	X		X	X		0.906/0.719
8	X				X	X		X	X		0.822/0.751
9			X	X	X	X		X	X		0.906/0.813
10			X	X	X	X			X		0.198/0.148
11			X					X	X		0.743/0.640
12					X	X		X	X		0.645/0.468

Table E.1. (Cont'd).

Ser.	FAC	HTA	HEA	SFTA	SFEA	CSTR	PERM	FM	DF	FTC	RSq./ARSq.
13	X			X					X		0.345/0.306
14	X					X			X		0.374/0.335
15	X								X		0.246/0.224
16				X					X		0.176/0.152
17						X			X		0.069/0.042
18								X	X		0.416/0.318
19		X			X	X		X	X		0.918/0.808
20					X	X		X	X		0.858/0.751
21	X			X		X		X		X	0.826/0.593
22				X		X		X		X	0.818/0.682
23	Logx			X		X		X	Logx		0.803/0.409
24	1/x			X		X		X	Logx		0.811/0.432

Table E.1. (Cont'd).

Ser.	FAC	HTA	HEA	SFTA	SFEA	CSTR	PERM	FM	DF	FTC	RSq./ARSq.
25	X			X		X		X	Logx		0.793/0.393
26	1/Logx			X		X		X	Logx		0.812/0.436
27	Log(1/x)			X		X		X	Logx		0.803/0.409
28				X		X		X	Logx		0.790/0.580
29	Sqtx			X		X		X	Logx		0.800/0.400
30	1/x			X		Logx		X	Logx		0.811/0.432
31	1/x				X	Logx		X	Logx		0.721/0.163
32	X				X	Logx		X	Logx		0.723/0.170
33	X				X	X		X	Logx		0.724/0.171
34	X				X			X	Logx		0.636/0.363
35	X			X		X		X	Logx		0.798/0.393
36	X			X				X	Logx		0.750/0.563

Table E.2. Development of regression equation between AVS, WPS, and Freeze-Thaw performance characteristics for mixes tested.

Ser	X-Axis	Y-Axis	Z-Axis	R ²	AR ²	Equation
1	SFTA	C-STR	DF	0.198	0.148	57.814-88.539SFTA+0.385E-3C-STR
2	SFTA	FM	DF	0.743	0.640	225.041-238.714SFTA-147.219FM
3	FM	C-STR	DF	0.645	0.468	312.052-445.497FM+0.462E-3C-STR

300

Combined Equation: $DF = 281.470325 - 214.351716SFTA - 270.511236FM + 1.9577E-4C-STR$

$R^2 = 0.90642$, $AR^2 = 0.81284$

SE = 13.21783

Boundries of the Equation:	SSTA (mm)	= 0.186	-	0.421
	FM (%)	= 0.55	-	0.71
	C-STR (KPa)	= 25580	-	42355



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