

PRELIMINARY REVIEW COPY

Technical Report Documentation Page

1. Report No. <u>PRELIMINARY REVIEW COPY</u>		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle RESISTANCE OF HIGH STRENGTH CONCRETE TO COLD WEATHER ENVIRONMENTS				5. Report Date July 1992	
				6. Performing Organization Code	
7. Author(s) James J. Ernzen and Ramon L. Carrasquillo				8. Performing Organization Report No. Research Report 481-7	
9. Performing Organization Name and Address Center for Transportation Research The University of Texas at Austin Austin, Texas 78712-1075				10. Work Unit No. (TRAIS)	
				11. Contract or Grant No. Research Study 3-5/9-87-481	
12. Sponsoring Agency Name and Address Texas Department of Transportation Transportation Planning Division P. O. Box 5051 Austin, Texas 78763-5051				13. Type of Report and Period Covered Interim	
				14. Sponsoring Agency Code	
15. Supplementary Notes Study conducted in cooperation with the U. S. Department of Transportation, Federal Highway Administration Research Study Title: "Durability and Performance of Concrete Containing Fly Ash"					
16. Abstract <p>This report describes an experimental laboratory evaluation program which was conducted on several high strength concrete mix designs in order to ascertain the effects of various air entrainment levels in the short and long-term performance of high strength concrete. The project included comparisons in slump, strengths, freeze-thaw cycling performance, chloride ion penetration, permeability, deicer scaling, and microscopical air void analyses.</p>					
17. Key Words high strength concrete, mix designs, air entrainment levels, performance, slump, strengths, freeze-thaw cycling, chloride ion penetration, permeability			18. Distribution Statement No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 326	22. Price

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**RESISTANCE OF HIGH STRENGTH CONCRETE TO
COLD WEATHER ENVIRONMENTS**

by

James J. Ernzen and Ramon L. Carrasquillo

Research Report No. 481-7

Research Project 3-5/9-87-481

"Durability and Performance of Concrete Containing Fly Ash"

PRELIMINARY REVIEW COPY

Conducted for

Texas Department of Transportation

**In Cooperation with the
U.S. Department of Transportation
Federal Highway Administration**

by

**CENTER FOR TRANSPORTATION RESEARCH
BUREAU OF ENGINEERING RESEARCH
THE UNIVERSITY OF TEXAS AT AUSTIN**

July 1992

NOT INTENDED FOR CONSTRUCTION,
PERMIT, OR BIDDING PURPOSES

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PREFACE

This report presents the details and results of a laboratory study on the durability of high strength concrete exposed to cold weather environmental conditions. The durability of concrete is determined by its ability to endure its physical and environmental surroundings without losing the functional properties and structural integrity of the original design. In cold weather climates, where freezing temperatures are common, the durability of concrete is governed by its ability to control internal and external sources of freezable water. High strength concrete has been proposed by some to be frost resistant by virtue of its low water/cement ratio and low permeability without the need for entrained air. Others have stated that the entrained air-void system parameters may be relaxed from their present standards for normal strength concrete.

ABSTRACT

This report describes an experimental laboratory evaluation program which was conducted on several high strength concrete mix designs in order to ascertain the effects of various air entrainment levels in the short and long-term performance of high strength concrete. The project included comparisons in slump, strengths, freeze-thaw cycling performance, chloride ion penetration, permeability, deicer scaling, an microscopical air void analyses.

SUMMARY

This study investigated the durability of high strength concrete at levels of 8, 10, and 12 ksi both with and without entrained air. Variables included air content, fly ash content, coarse aggregate type, cement and silica fume content, and type and length of curing. Testing performed included compressive strength, freeze-thaw resistance, rapid chloride ion permeability, deicer scaling resistance, chloride ion penetration, and microscopical air-void analysis. Testing indicates the need for entrained air in high strength concrete in order to render it freeze-thaw resistant.

IMPLEMENTATION

Results from this study indicated the following recommendations. Approximately three percent entrained air is required to produce freeze-thaw resistant high-strength concrete containing flyash, and four percent is necessary to produce frost resistance when the concrete contains silica fume. Extend moist curing as long as possible for improved durability.

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CHAPTER I

INTRODUCTION

1.1 General

The nation's transportation infrastructure has been the focus of much attention in recent years. Many of the concrete facilities which were constructed during the 1950's and 1960's are experiencing serious distress from exposure to the environment. Many of these structures have required substantial repair or replacement long before their design life was reached. Consequently the current decade has seen an increased interest in the durability of its structures. Engineers are more aware that concrete structures must be designed and built not only to achieve a specified strength but also to withstand the long term effects of exposure to the structure's chemical and physical environment.

As developments in technology enable the design of structures which can carry greater loads using smaller members, it is incumbent upon designers to ensure that structural elements be able to withstand the effects of the environment. This task has become increasingly complex in the last ten years as new products and construction techniques continuously enter the market. Mineral and chemical admixtures have made the chemistry of cement hydration much more complex. Furthermore, increasing use of pumping as a delivery method and spiralling labor costs encourage contractors to shorten form cycle times and associated curing. Thus it is critical that the engineer specify the right combination of materials which will ensure both durability and strength.

1.2 History

The durability of concrete exposed to cold weather is not a new topic to the concrete community. Researchers^{18,45,55} have been investigating the detrimental effect that subfreezing temperatures have on the water held in hardened concrete paste for more than 50 years. The development of air entrainment in the 1930s has to a large degree eliminated the problem of frost damage to concrete. Air entrainment (AE) was considered a revolutionary breakthrough in that it eliminated freeze-thaw damage to the hardened concrete, increased workability, improved scaling resistance, reduced permeability and lowered unit weight thus lowering dead load. The only drawback to using AE was the loss of compressive strength that accompanied replacing 5 to 6 percent of the concrete volume with air.

Much research^{17,29,30,76} was done to quantify the strength loss finding it to be in the range from 2 to 6 percent of the compressive strength for each percent of air entrained. Meanwhile researchers^{28,56} found that for most applications, the amount of entrained air required to provide the necessary frost resistance was 4 to 6 percent of the concrete by

volume. This can amount to a 30 percent loss of strength in order to obtain frost resistant concrete. Before 1980, this posed no serious problem for concrete producers because the added workability provided by the air bubbles enabled them to reduce the water/cement ratio thus offsetting some of the strength loss. Additional cement was then added until a durable concrete that met the strength was obtained.

The development and subsequent widespread use of high range water reducing admixtures or superplasticizers in the past 15 years has drastically changed many aspects of concrete practice. It has enabled producers to reach strengths that were previously not possible. Today 12,000 to 15,000 psi concrete is a common occurrence in many parts of the country. The dispersion of the cement particles and increased lubrication provided by the superplasticizer enables placement of concrete with water/cement ratios as low as 0.25^{20,80}. These low water/cement ratios have placed compressive strength on a collision course with durability. Most high strength concrete is made with very high cement contents (>750 lbs/cy) which usually results in unhydrated cement in the hardened concrete. If the producer adds entrained air to concrete whose water/cement ratio equals 0.25, he cannot regain the lost strength as before because adding more cement will only result in more unhydrated cement particles in the paste upon hardening.

Additionally, at these new strength levels, a 20 percent loss due to air entrainment can represent 2,000 to 4000 psi which translates to increased member dimensions to carry the same loads. This dilemma has caused some engineers and researchers to say that high strength concrete does not need air entrainment because of its higher tensile strength and lower water content. Because most of the early applications for high strength concrete have been in building columns which were clad and thus not subject to freezing weather, research on the frost durability of high strength concrete has lagged behind its use. The laboratory research and field data that do exist in the area has indicated mixed results on performance which has provided the justification for this research project.

1.3 Problem Statement

Concrete's resistance to freeze-thaw damage is a function of the air void system of the mortar, the characteristics of the coarse aggregate, and the moisture content of the concrete at the time of freezing. If concrete containing freezable water is subjected to a freezing environment, the water in the concrete will expand upon freezing and cause internal cracking. Sources of freezable water can be classified as either internal or external to the concrete. Internal sources of water, typically mixing water not consumed during hydration, are handled by the entrained air in the concrete. External water, such as that resulting from exposure to a marine environment, is controlled by the concrete's permeability.

Cold weather protection for normal strength concrete has traditionally centered on controlling freezable water through the use of entrained air with little consideration given to the concrete's permeability. This approach is undesirable when using high strength

concrete due to the inherent strength loss associated with the use of air entrainment. With its low water/cement ratio, high strength concrete contains less internal water and is much more impermeable to external water than normal strength concrete. The low water/cement ratio also produces a much finer internal pore system which imbibes an increasingly concentrated pore solution into smaller cavities. This more concentrated solution then freezes at a lower temperature thus effectively increasing the concrete's resistance to freezing. The question to be addressed by this research is can low water/cement ratio, low permeability, high strength concrete be produced that controls both internal and external water and exhibit frost resistance without entrained air?

1.4 Research Objective

The main objective of this study is to investigate the cold weather durability performance of high strength concrete made with locally available raw materials and to then provide guidelines for the use of this concrete in areas where exposure to freezing temperatures is expected. The study was divided into two tasks:

1. determine the effect of the amount of air entrainment, mineral admixtures, and curing conditions on the durability performance of high strength concrete and,
2. investigate the relationship between entrained air content, permeability, and air void system to determine the controlling mechanism for providing durable high strength concrete.

1.5 Research Plan

The research study concentrated on five areas:

1. Freeze-thaw resistance
2. Permeability
3. Deicer scaling performance
4. Chloride penetration testing
5. Air void system analysis.

Approximately 60 mixes totaling nearly 2000 specimens were cast over a period of two years. Test variables included air contents of 0, 3, and 6 percent, and use of ASTM Class C fly ash at cement replacement levels of 0, 27, and 33 percent. The water/cement ratio was varied from 0.26 to 0.30 by weight to produce concrete with 91 day strengths in the range of 8,000 psi to 12,000 psi. Specimens were tested for durability at 7 and 91 days of age under both moist and air curing. All tests were duplicated using both a high and low absorptive coarse aggregate to determine the effect of aggregate selection on the durability performance. A limited number of mixes containing silica fume added at levels of 7 and

10 percent by weight of cement were also tested and their performance compared to the fly ash mixes.

The entire project was conducted in cooperation with the Materials and Test Division of the Texas State Department of Highways and Public Transportation, the Federal Highway Administration, and private industry. The Materials and Test Division in particular provided valuable information, materials, and testing assistance and expertise throughout the research project.

1.6 Format

The format for this document consists of a summary in Chapter 2 of the basic mechanism of freeze-thaw damage in concrete as it is understood today. Chapter 3 reviews the research that has been conducted on the durability of high strength concrete focusing specifically on freeze-thaw performance, permeability, and air void parameters. A description of the materials, casting and testing procedures that were used throughout the study is presented in Chapter 4. Chapters 5 and 6 present and discuss the results of the permeability, deicer scaling, and chloride ion penetration testing. Chapter 7 reports the results of the petrographic analysis conducted on selected mixes. Chapter 8 reports and discusses the results of the freeze-thaw testing. The final chapter summarizes the study and concludes with recommendations and guidelines for producing durable high strength concrete in freezing environments.

CHAPTER II

REVIEW OF THE FREEZE-THAW DAMAGE MECHANISM

2.1 Introduction

The mechanism involving deterioration of concrete due to freezing of the water held within it has been studied at great length. Much of the early work was done in the 1940s and 1950s most notably by Powers and Brownyard^{22,54}. While in more recent years the work of Malhotra³⁹, Mather⁴⁰, and Whiting⁷¹ continue to explore this as yet not totally understood phenomenon. This chapter represents a synopsis of relevant material from these and other sources in an attempt to explain the physical and chemical processes which take place when concrete is exposed to freezing temperatures. The chapter will cover the microstructure involved in the hydration process and the resulting porosity and the form which water takes within the concrete. The role of air entrainment, an adequate air void system, and permeability in providing durability protection to the concrete is also discussed.

2.2 Microstructure of Hydrated Cement Paste

There are five major crystalline compounds which make up portland cement. Written in abbreviated chemical notation they are: tricalcium silicate, C_3S ; dicalcium silicate, C_2S ; tricalcium aluminate, C_3A ; tetracalcium aluminoferrite, C_4AF ; and gypsum, CSH_2 . Upon mixing with water, these compounds ionize and precipitate three main solid phases. The most critical component is the hydrated form of the two calcium silicate compounds called calcium silicate hydrate, abbreviated C-S-H. This highly amorphous product is the binding glue which holds portland cement together and determines most of its properties. The second largest compound formed in the hydration process is calcium hydroxide, $Ca(OH)_2$. $Ca(OH)_2$ is a well defined crystalline substance which makes up between 20 and 25 percent of the hydrated paste volume. The last hydrate is made up of calcium sulfoaluminate compounds which make up 15 to 20 percent of the paste. Although critical in terms of sulfate attack and deterioration, these sulfate compounds play only a minor role in the structure-property relationship of hydrated cement paste with respect to frost resistance and are not considered in this study.

C-S-H is a poorly defined compound whose stoichiometry will vary considerably depending on such things as age, temperature, and curing conditions. It develops into extremely small, irregular particles that can barely be distinguished using an electron microscope. They are characterized as very thin sheets or layers that are crumpled or rolled as foils^{11,58}. Due to the extremely small size, these particles have enormous surface areas which have been estimated at 100 to 700 m^2/g ²³ depending upon the measurement technique used. The strength of the material is derived from Van der Waals' forces between the very large surface areas at an average spacing estimated at 5 to 25 \AA . Calcium hydroxide has a definite chemical make up, $Ca(OH)_2$, which tends to form in large crystals with a distinctive

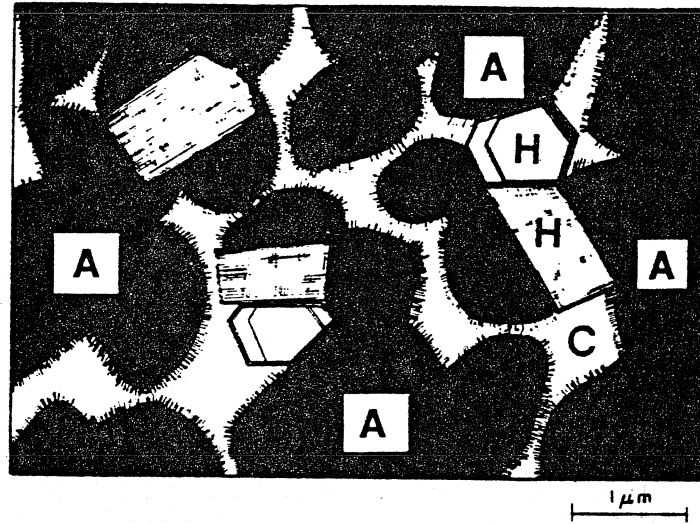
hexagonal prism morphology. Due to their much larger size, and thus lower surface area, the Van der Waals' forces which bind them are much weaker than that of the C-S-H so they contribute little to the strength of the hydrated paste. They do play an important role in later stages of hydration when pozzolanic materials are used as admixtures.

2.3 Porosity

In addition to the solid phases described above, hydrated concrete paste contains several types and sizes of voids throughout its structure which have an important effect on its engineering properties especially resistance to freezing. The solid C-S-H phase is not completely solid but a gel like substance of very fine particles with even finer spaces in between. These spaces are referred to as gel pores in older research and as interlayer space in more recent work. Powers⁵⁴ estimated the actual porosity of the hydrate gel to be 28% of the gel volume but concluded that the void sizes were too small to seriously affect the material's strength.

When individual cement particles hydrate, the resulting volume of the C-S-H gel is approximately twice the volume of the constituent cement and water. The calcium silicate reaction is not an expansive one in that the hydration products only fill the space previously occupied by the cement and water. As hydration continues, the gel fills more and more of the space previously occupied by the mix water which is either consumed in hydration or evaporates over time. Since more water is needed for concrete workability than is required for hydration, the products of hydration seldom completely occupy the water filled space in the fresh concrete. Consequently, after the concrete has hardened, there are spaces between the hydrated cement grains left by the evaporated mix water which are called capillary voids or pores. Any part of the paste that is not filled with solid hydration products is part of the capillary porosity of the paste. These voids are much larger than the gel pores and have a large effect on the mechanical properties of the material. Figure 2.1 shows a model of the principal solid phases and voids found in a typical hydrated cement paste.

Two important factors which characterize concrete porosity are the size and distribution of the pores. Gel porosity is relatively fixed in any hydrated paste varying slightly with the type and fineness of cement and temperature of curing. The capillary porosity is entirely dependent upon the initial water/cement ratio since this determines the amount of space needed to be filled by hydration products. Although the size spectrum of the pores is a continuous one with no definitive cutoff between them, gel pores are typically considered to be between 0.5 and 10 nm while capillary voids can be as large as 5 microns. Figure 2.2 shows the dimensional range of the solids and pores in a typical hydrated cement paste. Thus two fully hydrated samples of cement paste having equal amounts of cement and water/cement ratios of 0.5 and 0.7 will have the same amount of gel porosity. The 0.70 water/cement ratio sample will have much higher capillary porosity due to the additional water used for mixing. This increased capillary porosity will manifest itself in lower strength and higher permeability.



A represents aggregation of poorly crystalline C-S-H particles which have at least one colloidal dimension. Interparticle spacing within the aggregation is 0.5 to 3.0 nm. H represents hexagonal crystalline products such as CH , $\text{C}_4\text{ASH}_{18}$, and C_4AH_{19} . They form large crystals typically $1 \mu\text{m}$ wide. C represents capillary cavities or voids which exist when the spaces originally occupied with water do not get completely filled with the hydration products. The size of the capillary voids ranges from 10 nm to $1 \mu\text{m}$ but are $< 100 \text{ nm}$ in well hydrated low water/cement ratio pastes.

Figure 2.1 Model of a well-hydrated cement paste⁴².

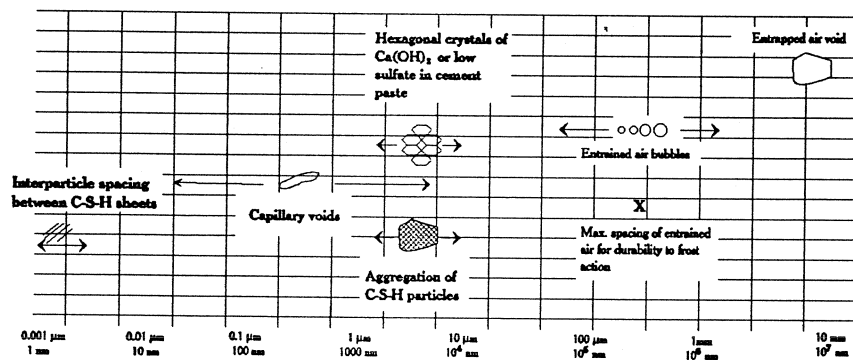


Figure 2.2 Dimensional Range of Solids and Pores in Hydrated cement Paste⁴².

2.4 Water in Hydrated Cement Paste

It is commonly accepted that water can exist in hardened cement paste in one of three forms. The forms are

1. hydration water,
2. gel water, and
3. capillary water.

The form in which the water exists in the hydrated cement paste determines the water's physical properties and this has a great effect on the durability of the paste. Powers⁵⁴ referred to the hydration water as that which is chemically combined with the cement and as such had lost its identity as water. Most hydration water can only be extracted from the paste by heating the sample to ignition (ie. 1000 °C). Gel water is defined as that which is held by physical adsorptive forces to the walls of the tiny gel pores which are formed during the cement hydration process. Mehta⁴² estimates that up to 6 molecular layers (15 Å) of water can be physically held by hydrogen bonding to the pore walls. Most of this water can be removed by drying the paste at low relative humidity. When this water is removed, shrinkage of the paste takes place. Capillary water forms in large capillary spaces between hydrated cement grains in the hardened paste. Its physical properties are considered to be that of bulk water because it is free from the influence of the adsorption forces of the solid surfaces of the gel. Loss of capillary water takes place without shrinkage and occurs spontaneously whenever the humidity is reduced below the equilibrium level within the paste.

Powers⁵⁴ further divided the water into thermodynamic classes called evaporable and non-evaporable based upon the relative ease or difficulty with which the water could be removed from the paste. Non-evaporable water is defined as that retained in the cement after desiccation to constant weight over a particular desiccant at 23°C. This amount retained is then determined by heating the sample to 1000°C and reweighing. Evaporable water is considered to be all the water in the concrete that is not non-evaporable. Although not entirely accurate, non-evaporable water for the most part equals the amount of water in the paste that is chemically combined while the evaporable water is found primarily in the capillary and gel pores. Table 2.1, from Mindess and Young⁴⁶, shows the spectrum of pore sizes in concrete and the role of water in those pores.

2.5 Mechanism of Frost Damage

Numerous theories exist which attempt to explain the cause of frost damage in concrete. Early attempts were based upon the 9% expansion of water as it changes state. It was known that if a closed vessel was more than 91% filled with water, it would be subjected to stresses upon freezing of the water. As a result, it was assumed that if concrete was more than 91% saturated, freezing would cause damage to the internal structure of the

material. Powers, an avid supporter of this early theory, proposed an alternate theory in 1945⁵⁵ stating that most concrete has in fact more than 10 percent voids and theoretically should be able to withstand the effects of the increased volume upon freezing. He also found that when freezing tests were done on specimens in which the evaporable water had been removed and replaced with a liquid that contracts upon freezing such as benzene, damage to the concrete still occurred.

Powers further stated that due to the presence of dissolved alkalis in the water and the physical forces exerted on it by the gel, the water content of a saturated cement paste has no single freezing point but a range a values. Upon initial freezing, the unfrozen water adjacent to the freezing site is expelled by the expansion. This forced flow of water through the capillaries is the actual cause of damage. Based upon this, Powers hypothesized that the resistance to the flow of water in concrete is proportional to the concrete's permeability and the length of flow path. He reasoned that there must be a critical path length beyond which the pressure would exceed the strength of the material. Powers performed experiments using different cooling rates and concretes and found the critical path length for most concrete to be on the order of 0.01 inch. Further refinement of this work has provided the now familiar maximum critical spacing factor value of 0.008 inches.

Pore Designation	Range of Diameters	Pore Description	Role of Water	Paste Properties Affected
Capillary Pores	0.5 - 10 um	large capillaries	Behaves as bulk water	Strength and Permeability
	10 - 50 um	medium capillaries	Moderate surface tension forces generated	Strength and permeability, shrinkage at high humidity
Gel Pores	2.5 - 10 nm	small (gel) capillaries	Strong surface tension forces generated	Shrinkage to 50% RH
	0.5 - 2.5 nm	Micropores	Water strongly adsorbed; no menisci formed	Shrinkage and creep
	<0.5 nm	Interlayer micropores	Structural water involved in bonding	Shrinkage and creep

An alternative theory was proposed by Collins¹⁶ which credited the origination of stress not to hydraulic pressure but to the segregation of ice into lenses similar to the

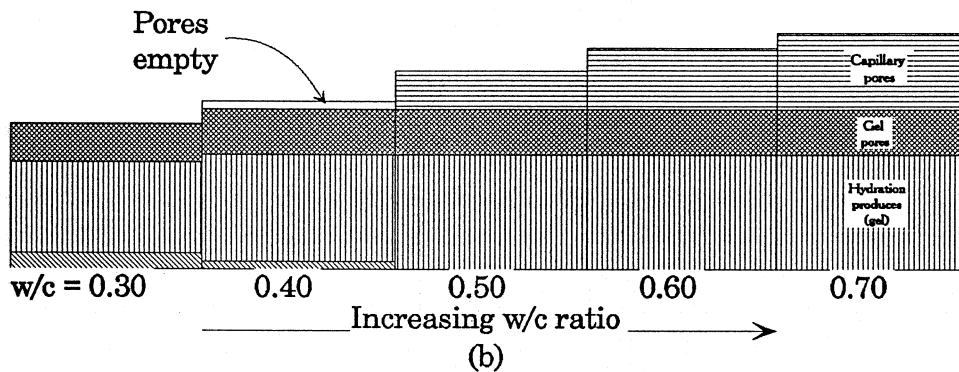
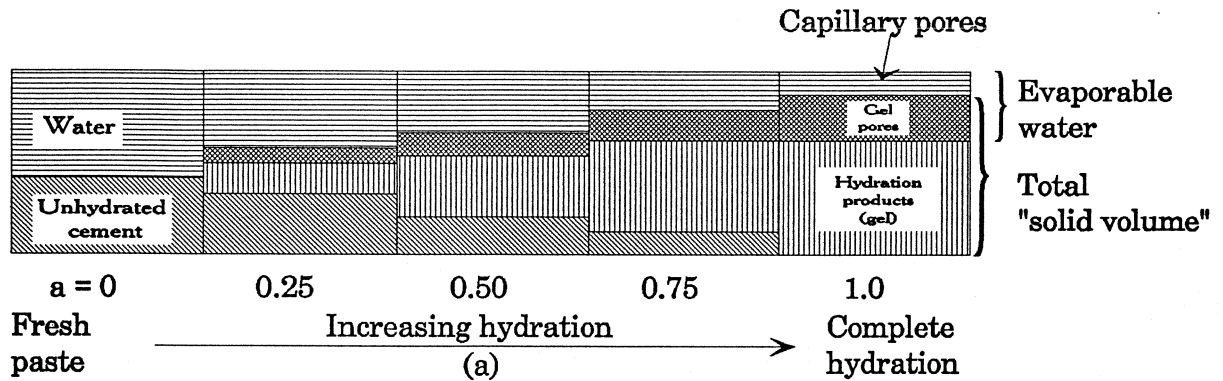
phenomenon which occurs during frost heaving in soils. According to this theory, the unfrozen water actually flows toward the freezing sites instead of away from them and is driven by thermodynamic equilibrium between the ice and the water. Later studies by Powers and Brownyard⁵⁴ and Dunn²¹ reaffirmed that the pressure theory proposed earlier was incorrect but disagreed on the direction of water movement.

Helmuth²⁴ found that non-air entrained concrete subjected to cooling often continued to dilate long after the temperature was held constant. Helmuth also found that volume changes observed in paste samples undergoing temperature changes could not be explained by thermal expansion and contraction alone. Based upon these results, he suggested a thermodynamic water flow into or out of the C-S-H gel as the driving force behind the observed behavior. Another possible cause of damage is water flow due to osmotic pressure within the paste. It is well known that concrete pore solution is not pure water but contains many dissolved alkalis. As freezing starts, the solution concentration immediately adjacent to the ice increases and this gives rise to osmotic water flow toward the ice as the solution attempts to reach equilibrium within itself.

As can be seen, the physical process by which concrete is actually damaged by frost effects is not totally understood and probably is the result of several mechanisms. The root cause may be the development of hydraulic or osmotic pressure, desorption of water from the C-S-H, segregation of ice into lenses, or perhaps a combination of all of these depending upon the circumstances involved. The common agent in each mechanism, however, is the movement of water within the paste which creates increasing pressure on the capillary walls with the distance it is forced to move. If this is true, then regardless of mechanism a concrete's frost resistance depends upon the amount of freezable water in the paste, the degree of saturation, the rate of freezing, and the concrete's permeability.

2.5.1 Amount of Freezable Water. Through extensive testing, researchers⁴⁶ have determined that 0.24 grams of water is consumed during hydration by each gram of cement. Further, 0.18 grams of water is adsorbed to the walls of the gel pores of the created C-S-H (ie. becomes gel water) when each gram of cement hydrates. From this information, given the original water/cement ratio and the degree of hydration, it is possible to determine just how much capillary or freezable water exists in a concrete mix. Figure 2.3a illustrates the changes in porosity that occur in concrete as the percent hydration moves from 0 to 100 percent. As hydration proceeds, hydration products and gel porosity continue to grow in volume at the expense of capillary space. Powers⁵⁴ calculated that given a well cured sample with a by weight water/cement ratio of less than 0.35, no water should remain in the capillaries after complete hydration. This is illustrated qualitatively in Figure 2.3b. Theoretically if no freezable water exists, that is if all remaining water resides either as gel water or combined as hydration products, then freeze-thaw damage cannot occur.

2.5.1.1 Effect of Surface Forces. The water which fills the pores of hardened concrete does not behave like water in its bulk form. The gel water exists as water chemically but it behaves differently due to the physical effects of its surroundings. The



- (a) Hydration percentage at constant $w/c = 0.50$.
 (b) Changing w/c and hydration percentage = 1.0

Figure 2.3 Porosity Relationships in Concrete⁴⁶

physical attraction for the water by the surrounding paste affects the intermolecular forces existing in the water. This can best be described by considering a column of water in a narrow glass cylinder as shown in Figure 2.4. Due to adhesion of the water to the sides of the glass cylinder and the surface tension forces trying to straighten out the meniscus, the water at the surface of the column is under tension. Because of this force, the water in the column will have stronger intermolecular forces, and lower vapor pressure than bulk water. As the cylinder narrows, the curvature of the meniscus increases. This causes greater tension in the water, and this lowers the vapor pressure. For this reason, only the water held in the larger capillaries of the cement paste freezes at the normal freezing point. The remaining water freezes at continuously lower temperatures due to its lower vapor pressure which is driven by its positioning in smaller and smaller pores in the paste. This is why continued hydration is beneficial because it turns capillary space containing water that is

relatively freezable, into calcium silicate hydrate in which the water does not freeze until the temperature drops much lower.

2.5.1.2 Effect of Dissolved Salts.

Another factor affecting the response of water in hardened concrete to freezing temperatures is the effect of dissolved salts in the concrete pore water. It is well known that a nonvolatile solute will elevate the boiling point and depress the freezing point of any solvent. This phenomenon is also related to vapor pressure. Because the solute disperses throughout the solution, it takes up space near the surface of the liquid that would normally be occupied by solvent molecules and this results in fewer

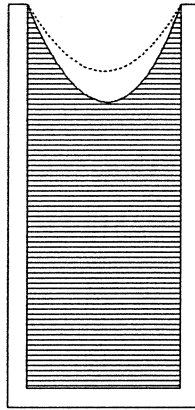


Figure 2.4 Effect of Adhesion and Surface Tension on Water held in a Narrow Cavity.⁵⁴

of the solvent molecules escaping into the air above the solution, hence lowering the vapor pressure. The pore solution of hardened concrete contains several dissolved salts predominately hydroxides of calcium, sodium and potassium. The calcium hydroxide $\text{Ca}(\text{OH})_2$ is a byproduct of the hydration reactions but is not readily soluble so it is typically ignored. However, NaOH and KOH come to the pore water from the cement itself and readily enter into solution upon mixing with water. While these alkalies are best known for their role in raising the pH of the pore solution and thus protecting the reinforcing steel from corrosion, they also play a role in the frost behavior of the concrete. As the temperature lowers, the water in the largest capillaries freezes first and the solute migrates to the remaining unfrozen pore water increasing its concentration. This lowers the vapor pressure of the solution which lowers the freezing point of this water in the concrete, thus increasing frost resistance.

2.5.2 Degree of Saturation. This is an extremely critical point that is often overlooked in concrete. If the concrete is partially dry when it is subjected to the freezing environment, it will not suffer damage. This is because the capillaries are partially empty of water and are thus free to accept water which diffuses from the water filled cavities when they freeze. Whiteside and Sweet⁷⁰ confirmed this in 1950 through a series of experiments in which they calculated the percent of saturation in concrete samples by measuring the increase in unit weight after submerging the samples. They found that samples over 91% saturated were consistently damaged by freeze thaw cycles. If the saturation level was kept below 87% however, no damage occurred. As would be expected, the samples saturated in the range of 88-90% showed variable results. Figure 2.5 shows the results of this work.

The effect of sample saturation also becomes apparent when comparing freeze-thaw testing methods. Under current ASTM Standard C 666 "Resistance of Concrete to Rapid Freezing and Thawing", two procedures for freeze-thaw testing of concrete are allowed.

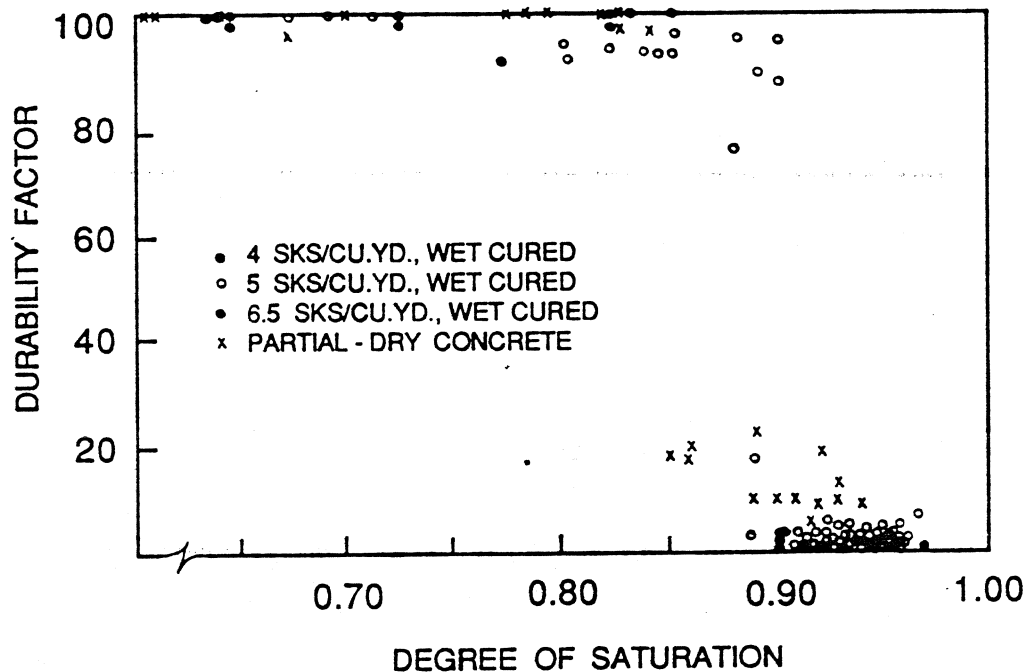


Figure 2.5 Plot of Degree of Saturation vs. Durability⁷⁰

Procedure A specifies the sample be surrounded by water during freezing while Procedure B allows freezing in air. Under both procedures thawing occurs under submerged conditions. Researchers have found that identical samples tested under both methods always perform significantly better under Procedure B due to the fact that the sample retains a lower saturation level. Thus it is only necessary to protect concrete that will be frozen in a near saturated condition.

2.5.3 Rate of Freezing. In general, the pressure that is generated within a concrete sample subject to freezing temperatures will be directly related to the rate of movement of water within the paste as the unfrozen water either migrates away from, or to the freezing sites. As a result, the faster the freezing rate, the more damage the test specimen will exhibit. This fact has been a source of much concern among researchers who argue that the most common test currently used to grade a concrete as freeze-thaw resistant (ASTM C 666) specifies a freezing rate several times faster than that seen in nature and thus should not be used to judge a concrete as non-durable. The size of the specimen also affects freezing rate as tests have shown that freezing rate slows considerably as the temperature progresses deeper into the concrete.

2.5.4 Permeability. The permeability of concrete is a physical property related to the ability of fluids, gases, or ions to penetrate the hardened paste. There are three methods by which substances are transported in concrete.

1. capillary attraction
2. vapor transmission
3. ionic diffusion

Capillary attraction is the method by which a fluid such as water is moved through the concrete and is the method of primary importance when studying the effect of permeability on frost damage in concrete. Vapor transmission is the method by which gases move through concrete however this method is not considered relevant to this study. The principle of ionic diffusion is of interest due to its application to road and bridge salt scaling and is reviewed further in Chapter 6.

The flow of water through concrete obeys D'Arcy's Law shown below:

$$Q = K_p dp/ds$$

Q	=	Flow rate
K_p	=	Permeability coefficient of the cement paste
dp/ds	=	Pressure gradient within the specimen

The permeability coefficient K_p is not constant but a function of both the water/cement ratio and the age of the paste. It is strongly dependent upon the capillary porosity. Tables 2.2 and 2.3 taken from Mindess and Young⁴⁶ illustrates how K_p varies both with age and water/cement ratio. The importance of a low water/cement ratio and proper curing is obvious from these tables. As hydration continues, the concrete's capillary porosity is reduced and its gel porosity increases with the increase in C-S-H. The water cannot penetrate the gel pores nearly as easily as the capillaries and thus the result is a decrease in K_p and in concrete permeability.

From a general durability viewpoint, low permeability is always desirable. When considering freeze-thaw resistance alone however, low permeability can be a liability as well. A matrix with a low value of K_p will be very impermeable to outside water sources saturating the concrete. This saturation is essential to the occurrence of freeze-thaw damage so in this sense low permeability is a very positive feature. A negative aspect however is the fact that the decrease in capillary size that accompanies lower permeability will result in higher pressures being applied to the paste when water within the concrete freezes. This relationship between the water/cement ratio, the curing conditions, the amount of freezable water, and the concrete's permeability is one of the key relationships explored in the study described herein.

Table 2.2 Effect of Age of Cement Paste on its Permeability Coefficient ($w/c = 0.51$)

Age (days)	K_p (m/s)	
Fresh paste	1.00E-05	Independent of w/c
1	1.00E-08	capillary pores interconnected
3	1.00E-09	
4	1.00E-10	
7	1.00E-11	
14	1.00E-12	
28	1.00E-13	
100	1.00E-16	capillary pores discontinuous
240	1.00E-18	

Table 2.3 Curing Time Required to Produce a Discontinuous System of Capillaries (moist curing).

W/C Ratio	Curing Time (days)
0.40	3
0.45	7
0.50	28
0.60	180
0.70	365
>0.70	not possible

2.6 Role of Air Entrainment

All concrete incorporates an amount of air in the fresh state due to the mixing and kneading action of the mixing blades as they blend the constituents. These air bubbles are usually called entrapped air bubbles and they tend to coalesce during placement and if large and buoyant enough, float out of the concrete. The role of the air entraining agent is to

stabilize the bubbles created in a size range between .002 and .05 inches (50 μ m to 1.27 mm) in diameter. The ionic charges possessed by each air entraining molecule tend to repel like charged neighbors and this keeps the air bubbles from coalescing and floating out of the concrete.

2.6.1 Air Void Parameters. As indicated in previous sections, the role of air entrainment in hardened concrete is to act as a reservoir to receive unfrozen water as it flows either to or from the freezing sites in the concrete through the capillary pore system. In order to accomplish this task successfully, researchers^{45,56,59} have found that the entrained air system must meet certain criteria with respect to volume, size, and distribution. Microscopic examination of hardened concrete which has performed well in freezing and thawing tests typically show that the air bubbles are very close together with no place in the paste more than 0.008 inches (0.2 mm) from a bubble. The bubbles need to be small so that they do not become too buoyant and float out of the concrete during placement and consolidation. If the bubbles are spaced too far apart, the resulting pressure from the movement of the water from the capillary to the air bubble will rupture the paste. Finally the bubbles must be adequately distributed throughout the concrete in order to insure frost protection.

Evaluation of a concrete air void system is done according to ASTM C 457 "Standard Practice for Microscopical Determination of Air-Void Content and Parameters of the Air-Void System in Hardened Concrete". In this test, a minimum of 100 linear inches of concrete surface is examined and the number, size, and distances between air voids are measured and recorded. An air void system is graded adequate based upon three parameters: the spacing factor (L Bar), the specific surface (alpha), and the number of voids per linear inch. L Bar is the average maximum distance between any point in the paste to the nearest air void and is recommended to be less than 0.008 inches. The specific surface alpha is the ratio of the surface area of the bubbles over the volume of air they enclose and the recommended range is 400-600 in²/in³. Given two mixes with the same air content, a higher value of alpha indicates a larger number of smaller bubbles while a small value of alpha indicates a smaller number of larger bubbles. A larger value of specific surface will always result in a smaller spacing factor given equal air contents. The third factor, average number of voids per linear inch, assures an equal distribution of the bubbles throughout the paste. The required value for a proper air void system is at least 1.5 times the value of the entrained air volume in percent.

So while it is critical for an air-void system to attain these three related parameters, a problem arises in that until very recently, none of these could be measured in the fresh state. For this reason they have been correlated to the necessary volume of total air required as a percentage of the concrete volume since this can easily be measured in the fresh state before the concrete is placed in the forms. The required volume of air will range from 4 to 8 percent depending upon the size of the coarse aggregate used. Aggregate size is typically associated with the amount of mortar required to achieve adequate concrete properties. The new method developed to measure air-void system parameters in fresh

concrete uses fiber optics and, if accepted, may eventually eliminate the need to specify air content by volume.

2.7 Applicability to High Strength Concrete

Much of the research work upon which the freeze-thaw mechanism and the air void parameters were founded was conducted many years ago typically on low strength, high water/cement ratio mixtures. With the advent of the high range water reducer and the subsequent ability to place high strength concrete with extremely low water/cement ratios, it is only natural to question the applicability of these mechanisms and parameters to these newer concrete materials. The main thrust of this study is to determine whether well-cured concrete having a water/cement ratio below 0.35 is indeed immune to freezing damage as Powers and others have suggested and if so, at what age and under what curing conditions. If not true and an air void system is required at these low water/cement ratios, are the current parameter values still applicable for these materials?

CHAPTER III REVIEW OF PREVIOUS RESEARCH

3.1 Introduction

While the amount of research on freeze-thaw resistance of concrete is voluminous, studies dealing with the durability of high strength concrete produced using very low water/cement ratios, fly ash, and silica fume are not nearly as abundant. The reason for this can be traced primarily to the advent of superplasticizers in the 1970s. Widespread acceptance of superplasticizers which made possible the production of high strength, low water/cement ratio concrete has only occurred in the past 10 years so the research into its durability performance is still in the infant stage.

Most of the studies reviewed utilized water/cement ratios in the 0.40 to 0.60 range by weight and were primarily directed at investigating the superplasticizer's effect on the air void system in the hardened concrete. The literature review for this study focused on previous research in freeze-thaw resistance, chloride ion permeability, and deicer scaling resistance of high strength concrete. A summary of selected works is presented in this chapter which provided the starting point from which the test procedures, material selections, curing conditions, and data analysis techniques were chosen to guide this investigation.

3.2 Freeze-Thaw Resistance

The summation of all the studies researched for this investigation clearly brings forth the fact that while the mechanism by which freeze-thaw damage occurs in concrete is somewhat understood, its application to high strength, low water/cement ratio concrete is clearly new ground about which very limited information is available. The previous research is herein summarized and presented according to the name of the primary author of the work. Where one author has published multiple studies, they are combined and categorized by year published.

3.2.1 Malhotra (1979,1983,1986,1988). V. Mohan Malhotra has conducted a host of concrete durability studies in the last decade at the Construction Materials Section of the Canada Center for Mineral and Energy Technology (CANMET). In 1979, Malhotra³⁶ investigated the performance of several superplasticizers in high strength concrete having a water/cement ratio of 0.42 by weight. A total of 12 different mixtures were cast with one non-air entrained and one air entrained control mixture, and 10 air entrained mixtures. Three different superplasticizers were used: a sulphonated melamine formaldehyde condensate at a dosage rate of 1 to 3 percent by weight of cement, a sulphonated naphthalene formaldehyde condensate at a dosage rate of 0.5 to 10 percent by weight of cement, and a modified lignosulphonate at a dose of 1 to 3 percent by weight of cement.

The 28-day moist cured compressive strength varied from 5000 psi to 7000 psi and the total air contents varied from 2 percent in the non-air entrained mixture to a maximum of 6.8 percent in the air entrained mixtures. The freeze-thaw prisms were tested after 14 days of moist curing in accordance with ASTM C 666 Procedure B which consists of freezing in air and thawing in water. The test data consisted of visual inspection, fundamental longitudinal frequency, ultrasonic pulse velocity, and mass and length change measurements. The test results were then correlated to data obtained from a microscopic air void analysis performed on each mixture.

The results of this study showed that concrete specimens from mixtures with total air contents of 3.8 percent to 6.8 percent endured 700 freeze-thaw cycles without suffering any significant distress. Additionally, Malhotra found that the mixtures contained an adequate air void system despite varying dosage levels of superplasticizer. It should be noted that the testing was conducted according to ASTM C 666 Procedure B which consists of freezing in air instead of water. This is a much less severe freeze-thaw test because the test prisms have the opportunity to dry during the freezing cycle thus preventing the concrete from reaching critical saturation.

In 1983 Malhotra and Carrette¹⁴ conducted a study of the durability of portland cement concrete containing increasing amounts of silica fume (SF). A total of 12 mixtures having a water/cement ratio of 0.40 by weight were cast and tested for strength, freeze-thaw resistance, and drying shrinkage. The total air content of the mixtures ranged from 3.8 to 6.4 percent with a mean value of 4.9 percent. The results of microscopic analysis indicated that the addition of silica fume hindered the development of an adequate air void system and resulted in higher spacing factors as the silica fume content increased from 5 to 30 percent. All freeze-thaw specimens were tested according to ASTM C 666 Procedure A and those with up to 15 percent silica fume and air contents from 3.8 to 4.5 percent achieved durability factors (DF) greater than 94 percent after 300 cycles. The test specimens with 20 percent and 30 percent silica fume began showing signs of serious distress after 250 cycles and only attained durability factors of 83 percent and 68 percent respectively as shown in Figure 3.1.

All mixtures had air void parameters which were unacceptable when measured according to ASTM C 457 "Standard Practice for Microscopical Determination of Air Void Content and Parameters of the Air Void System in Hardened Concrete". Of interest was the fact that the higher silica fume content mixtures had slightly better air void parameters than the lower content mixtures and yet exhibited worse freeze-thaw resistance. The key conclusion drawn from this study was that the high silica fume content produces a very impermeable paste which severely restricts the movement of water in the matrix. This restriction increases the pressure upon freezing and, coupled with the high spacing factors, results in poor freeze-thaw resistance.

In 1986 Malhotra³⁷ conducted an extensive program which studied strength and freeze-thaw durability of high strength silica fume concrete this time utilizing very low

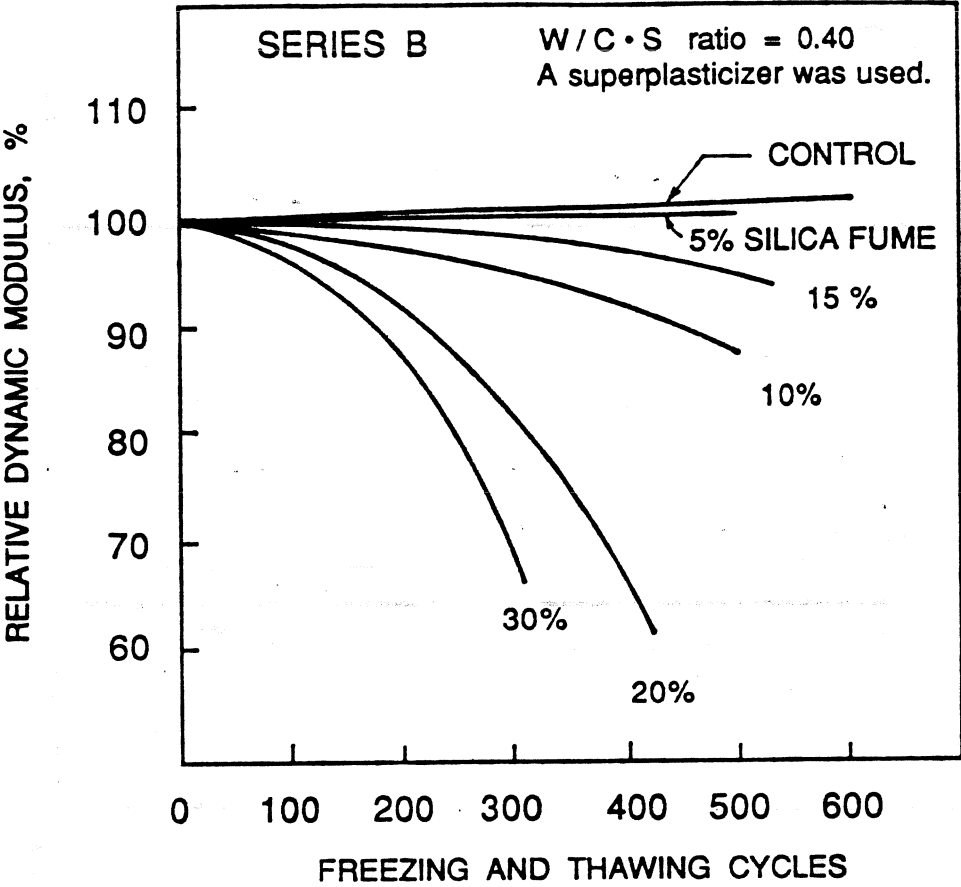


Figure 3.1 Durability Factors vs. Freeze-thaw Cycles for Silica Fume Concrete Mixtures from Malhotra¹⁴.

water/cement ratios. A total of 18 non-air entrained mixtures and 6 air entrained mixtures were cast with water/cement ratios varying from 0.25 to 0.36 by weight and silica fume contents ranging from 0 to 20 percent by weight of portland cement. By lowering the water content of the concrete and adding silica fume to densify the paste, it was anticipated that freeze-thaw resistance could be attained without air entrainment. The 28-day compressive strength of the non-air entrained mixtures ranged from 7,300 psi to 12,400 psi with an average entrapped air content of 1.7 percent. The air entrained mixtures averaged 4.7 percent total air content and ranged from 6,200 psi to 8,700 psi in compressive strength. All specimens were tested after 14 days of moist curing according to ASTM C 666 Procedure A.

The results of this testing program showed that all non-air entrained mixtures performed poorly with no specimen lasting longer than 90 cycles or developing a durability factor (DF) greater than 12 percent. The air entrained specimens developed higher durability factors than the non-air entrained companion specimens however performance

declined significantly with increasing silica fume content as can be seen in Table 3.1. Malhotra stated that the reason for the deterioration was due to the decreasing permeability of the cement/silica fume paste restricting the water movement and thus raising the pressure within the paste upon freezing. The air void parameters shown in Table 3.1 also confirmed the difficulty obtaining adequate air void spacing factors when casting silica fume concrete using superplasticizer. These increased spacing factors also contributed to the low durability values.

Malhotra's conclusions from this study were that non-air entrained concrete even at very low water/cement ratios exhibits poor freeze-thaw resistance when tested according to ASTM C 666 Procedure A. He suggested that perhaps testing these mixtures at later ages when the concrete is more mature, and allowing the concrete to dry prior to testing might improve performance. He also found that even concrete containing up to 4.5 percent total air performed poorly when large amounts of silica fume are used. This he concluded was due to the large spacing factors generated by the superplasticizer.

In 1988 Malhotra³⁵ published a study describing the current status of a long term durability study involving concrete samples exposed to a marine environment. A series of 175 large prisms (305x305x915mm) were cast over a 9 year period starting in 1978 and placed on a rack at mid-tide level on Treat Island, Maine. The specimens are exposed to daily wetting and drying cycles and have averaged about 80 cycles of freezing and thawing per year. Phase V of this study commenced in 1982 involving concretes having a 0.60 water/cement ratio by weight and silica fume contents of 0, 10, 15, and 20 percent replacement by weight of cement. Performance was monitored on the basis of pulse velocity and visual inspection. Malhotra found that in just 5 years both the air entrained and non-air entrained blocks showed increasing levels of distress with increasing amounts of silica fume compared to the control blocks containing no silica fume. Malhotra maintains that it is too early to draw firm conclusions, however the early trends seem to agree with similar findings from laboratory studies. When silica fume concrete is exposed to a natural freeze-thaw environment, its frost resistance decreases with increasing silica fume content due to decreased permeability and its effect on restricting water movement in the paste.

3.2.2 Whiting (1979,1987). Whiting has conducted several studies on concrete durability during the last decade at the Concrete Materials/Technology Services Department of the Construction Technologies Laboratory. In 1979, Whiting, Perenchio, and Kantro⁷⁹ published the results of a study which investigated the effect of superplasticizers on several properties of concrete including frost resistance. A total of 54 mixtures were prepared with cement contents ranging from 376 to 658 lbs/cy and water/cement ratios ranging from 0.70 to 0.32 by weight. Thirty four of the mixtures were air entrained with total air contents ranging from 5 percent to 7 percent. The mixtures were tested for slump loss, time of set, shrinkage, strength, freeze-thaw resistance, deicer scaling resistance, and microscopic air void analysis. Freeze-thaw specimens were submerged in water and subjected to two complete cycles of freezing and thawing per day. The cycle temperature ranged from 10 to 55°F and the cooling rate was approximately 20°F per hour. Upon completion of testing, Whiting

Table 3.1 Durability Factors and Air-Void Parameters of Hardened Concrete
(from Malhotra³⁷)

Mixture No.	Mixture Type	W/C + S	Silica Fume Replacement, %	Air Content of Fresh Concrete, %	No. of Freezing and Thawing Cycles	Durability Factor	Air-Void Parameters			
							Voids in Concrete, %	Specific Surface, mm ⁻¹	Spacing Factor, mm	
1	Non-Air Entrained	0.35	0	2.0	66	6	1.2	8.7	0.912	
2		0.35	10	1.8	70	6	1.4	5.4	1.506	
3		0.35	20	1.2	70	10	1.1	6.6	1.438	
7		0.30	0	1.9	67	12	2.8	6.7	0.907	
8		0.30	10	1.3	67	3	1.1	8.6	1.047	
9		0.30	20	1.1	70	3	0.8	14.7	0.746	
13		0.25	0	2.0	89	11	2.0	7.2	1.015	
14		0.25	10	1.3	89	5	1.3	8.9	0.964	
15		0.25	20	1.5	89	8	1.5	5.1	1.677	
16		0.25	0	1.8	79	3	----	----	----	
17		0.25	10	1.5	79	2	----	----	----	
18		0.25	20	1.8	79	2	----	----	----	
19*		0.25	0	2.0	47	6	----	----	----	
20*		0.25	10	1.6	47	7	----	----	----	
21*		0.25	20	1.8	47	2	----	----	----	
22		0.25	0	2.2	70	4	----	----	----	
23		0.25	10	1.0	70	3	----	----	----	
24		0.25	20	2.0	7.0	3	----	----	----	
4		Air Entrained	0.35	0	5.4	300	97	7.2	14.9	0.230
5			0.36	10	5.6	265	59	5.5	15.9	0.269
6			0.36	20	4.9	203	36	4.3	10.2	0.502
10			0.30	0	3.7	300	99	6.7	13.9	0.267
11			0.30	10	4.2	170	33	5.4	12.8	0.325
12			0.32	20	4.5	138	16	5.6	10.6	0.428

the cooling rate was approximately 20°F per hour. Upon completion of testing, Whiting found results similar to Malhotra's in that use of the superplasticizers resulted in unacceptable air void parameters when measured according to ASTM C 457. Despite these 'unsatisfactory' air void systems however, no specimens showed signs of distress from freezing and thawing or scaling, even after 300 cycles.

In 1987 Whiting⁷¹ investigated the durability of high strength, superplasticized concrete having strengths of 6,000, 8,000, and 10,000 psi. A total of 12 mixtures were cast with one non-air entrained and 3 air entrained mixtures at each strength level and total air contents varying between 3.5 and 7.5 percent. All specimens were tested at 28 days of age after either continuous moist curing until testing or 7 days moist curing followed by 21 days air curing. The results of the testing showed that all of the non-air entrained specimens failed prior to completing 170 cycles with the exception of the 10,000 psi air cured mixture which exhibited a DF of 70 percent at 300 cycles. Whiting noted a definite correlation between air content and performance for the moist cured specimens. The performance of the air entrained mixtures was excellent even at the relatively low air content of 3.5 percent with all specimens achieving a DF greater than 99 percent after 300 cycles. Microscopic analysis revealed all of the air entrained mixtures produced air void systems very close to or exceeding the requirements of ASTM C 457. Whiting concluded that while the freeze-thaw resistance of the non-air entrained mixtures was poor, as low as 3.5 percent total air produced a very durable mixture. He also found that a period of drying prior to the start of testing was beneficial to the performance of the concrete.

In 1987 Whiting and Schmitt⁷⁸ completed a report for the National Cooperative Highway Research Program which studied the durability of in place concrete containing superplasticizer. The purpose of the study was to survey the use of concrete containing superplasticizer, inspect and test some in place structures, and report on their long term durability. The program consisted of: (1) a questionnaire surveying highway agencies throughout the US, Canada, and Europe, (2) development of information on superplasticizer applications, (3) selection of structures to evaluate, and (4) laboratory testing of samples taken from these structures.

The major finding after evaluating 48 core samples taken from 12 different structures with an average concrete age of 7 to 9 years was that there are no widespread durability problems associated with use of superplasticizer in concrete. This study did find many instances where the use of a superplasticizer altered the air void parameters significantly however this did not appear to affect the structure's freeze-thaw resistance. On many sites concrete without superplasticizer was placed adjacent to sections containing concrete with superplasticizer and little difference was observed with regard to scaling. Whiting also stated that the air void parameters in the bulk concrete did not appear as critical to durability as the water/cement ratio and air content in the near surface zone.

3.2.3 Mather and WES (1979,1984,1986,1987). Bryant Mather at the structures laboratory of the U.S. Army Corps of Engineers Waterway Experiments Station in

Vicksburg, Mississippi has both conducted and supervised an extensive amount of concrete durability research in the past 40 years including several studies dealing with high strength concrete. Of these, only four studies are reviewed here.

In 1979, Mather⁴¹ conducted a study on concrete containing superplasticizers with the main objective of investigating their influence on strength, slump, air content loss, and frost resistance. The study consisted of 34 air entrained mixtures of which 18 contained any of 4 different superplasticizers and 16 air entrained control mixtures. The control concretes were all cast with water/cement ratios equal to 0.45 by weight. Companion specimens were cast from similar mixtures containing superplasticizers which resulted in a reduction in the water/cement ratios from 0.45 to from 0.34 to 0.37. The compressive strength of the superplasticized mixtures tested between 132 and 155 percent of the 28-day control concrete strengths. Two freeze-thaw specimens were cast from each mixture and tested according to ASTM C 666 Procedure A. The control specimens had durability factors ranging from 57 to 89 percent averaging 76 percent while the superplasticized concrete specimens had durability factors ranging from 5 to 77 percent. Mather reported that the universal reason for failure of the test specimens was the larger spacing factors and lower air contents resulting from the use of the superplasticizer.

In 1984 Saucier⁶³ published the results of an investigation into the use of high strength concrete for defense related construction. The purpose of the investigation was to study the necessary materials and techniques required to produce 15,000 psi concrete and develop physical property data including freeze-thaw resistance on the concrete produced. Saucier proportioned 76 mixtures involving 4 different coarse aggregates, an ASTM Class F and Class C fly ash, silica fume, and Type II portland cement. The water/cement ratio varied between 0.22 and 0.30 by weight and 28-day concrete strengths in excess of 15,000 psi were achieved with many of the mixtures. Freeze-thaw tests were conducted on three mixtures containing 0.8 percent, 4.0 percent, and 5.8 percent total air which had attained 28-day compressive strengths of 14,200, 13,350, and 16,600 psi respectively. All specimens were moist cured for 28-days prior to testing. The test results showed that each of mixtures performed adequately according to ASTM C 666 Procedure A with a durability factor exceeding 80 percent after 300 cycles. All three mixtures had a water/cement ratio equal to 0.24 by weight and coarse aggregate with absorption capacities ranging from 0.4 to 0.6 percent. Saucier's conclusion with regard to durability of high strength concrete was that durable concrete could in fact be made using conventional methods and materials without air entrainment.

In 1986, S.A. Ragan⁶¹ from WES published a study on the frost resistance of Roller Compacted Concrete (RCC). RCC is typically placed at very low water/cement ratios and low slumps and achieving normal quantities of air entrainment is usually difficult in this concrete. Nine RCC pavements were sampled and tested for microscopic air void content, resistance to freezing and thawing, critical dilation, and compressive and flexural strength. Water/cement ratios ranged from 0.31 to 0.43 by weight and mixture proportions, production, and delivery equipment varied widely from pavement to pavement. The

concrete strength varied from as low as 2900 psi at 40 days for one batch to 8900 psi at 90 days for another.

The results from the freeze-thaw tests and microscopic air void analysis indicated a strong correlation between the durability factor and the air void spacing factor (L). Ragan found, however, that spacing factor values as high as 0.012 inches could be tolerated and still achieve durability factors equal to 60 percent after 300 cycles. Ragan also found that L values of 0.010 to 0.016 consistently resulted in concrete DF's ranging 40 to 60 percent thus showing some degree of frost resistance. This the author attributed to the low water/cement ratio of the concrete. Ragan stated that the method of mixing, specifically the use of a pug mill type mixer, appeared to have the largest effect on the generation of an adequate air void system for the RCC projects studied. The conclusion of this study was that some resistance to freezing and thawing can be achieved without using an air entraining agent due to the low water/cement ratio inherent in an RCC mixture, especially when a pug mill is used in the mixing operation.

In 1987, Buck et al¹² reported on a continuation of the work published earlier by Saucier which further evaluated four of the high strength mixtures that Saucier developed. Buck analyzed two pairs of mixtures, one air entrained and one non-air entrained, having identical components with the exception of coarse aggregate. Each mixture contained identical contents of cement and silica fume, and a water/cement ratio of 0.24 by weight. Table 3.2 contains detailed information on the durability data on the two pairs. Buck performed microscopic air void analysis on the non-air entrained granite mixture and found a spacing factor equal to 0.013 inch which, under normal circumstances, should not result in a durable paste. A photographic evaluation showed no microcracking at all in the matrix of the granite coarse aggregate concrete. The excellent performance of this concrete, Buck reasoned, was due to the self desiccation of the paste which then provided such low permeability that the specimen was never saturated during the test.

Both coarse aggregates were tested in both air entrained and non-air entrained mixtures and had average durability factors of 92 and 95 percent for the granite aggregate concrete and 55 and 17 percent for the limestone aggregate concrete respectively. From this, Buck concluded that either the pore size distribution or the thermal and elastic properties of the limestone were unable to handle the stresses caused by the freezing temperatures during the test. While Buck did not determine the exact cause of failure, the results clearly showed the importance of the coarse aggregate properties in determining the durability of high strength concrete.

3.2.4 Khalil (1979). S.M. Khalil et al²⁷ studied the durability performance of low water/cement ratio, non-air entrained concrete mixtures typical of precast plant operations in western Canada. Six non-air entrained mixtures were cast with a constant cement content of 540 lb/cy and water/cement ratios varying from 0.32 to 0.46 by weight. Strength cylinders were broken at 7 and 28 days with the 28-day compressive strength ranging from 5500 psi to 8400 psi. An identical air entrained control mixture was cast containing a total air

Table 3.2 Freeze-Thaw Results from Buck¹².

Mixture No.	Specimen No.	Average DFE ₃₀₀ ‡	Air Content, %, of Fresh Concrete (ASTM Designation: C231)	28-Day Compressive Strength psi (MPa)	Coarse Aggregate
68	9787-9789 (9789 examined in detail)	95	0.8	16,590 (114.4)	Granite
67	9784-9786 (9784 examined in detail)	92	5.8	13,350 (92.0)	Granite
66	9781-9783	83	4.0	14,220 (98.0)	Limestone (P)†
64	9775-9777	55	4.6	14,260** (98.3)	Limestone (L)†
65	9778-9780 (9779 examined in detail)	17	1.0	16,440 (113.4)	Limestone (L)†
** 35-day age †P = project; L = laboratory stock ‡ = Durability Factor					

content of 5.3 percent and a water/cement ratio of 0.45 by weight. The 28-day compressive strength of the control mixture was 6100 psi. Durability was measured using two methods: Procedure A of ASTM C 666 and the Critical Dilation Method under ASTM C 671. All mixtures were moist cured for 14 days followed by immersion in 35°F water for ASTM C 671 or 71°F water for ASTM C 666 for 7 days prior to the first freezing cycle.

The measure of frost resistance in the Critical Dilation Test is based upon the net expansion of the specimen as the temperature is slowly lowered from 35°F to 15°F. In fact, frost resistant concrete contracts in a nearly linear fashion during the test, as shown in Figure 3.2. When testing non-air entrained concrete, at a point just below freezing, a sharp increase in the specimen length is usually recorded. This is attributable to the hydraulic

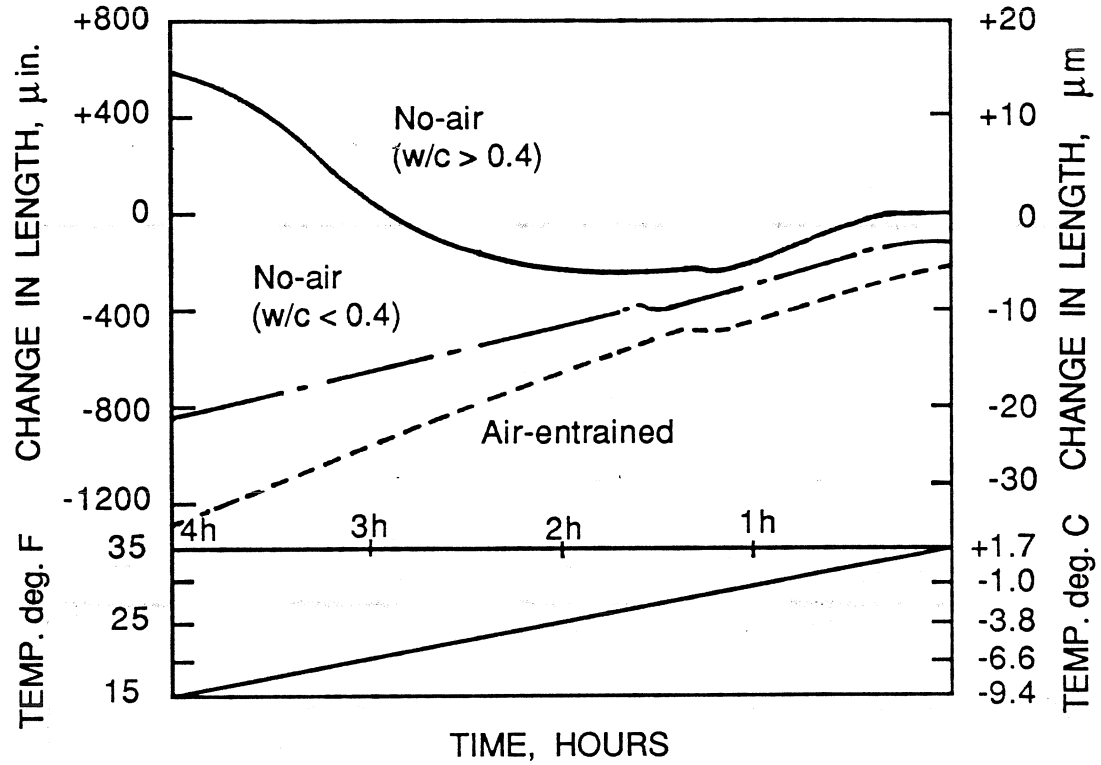


Figure 3.2 Typical Results from Critical Dilation Tests According to ASTM C 671 from Khalil²⁷.

pressure which is generated as the capillary water turns to ice and strains the paste. Once the initial formation of ice has occurred, the water held in the gel pores now has a higher vapor pressure than the ice in the capillaries and is not in equilibrium with it. This causes the gel water to diffuse to the ice seeds causing them to enlarge thus creating more expansion. Length measurements are recorded continuously until the target temperature of 15°F is reached. The net expansions are recorded for each test and the concrete is considered non-durable when it expands more than twice the previous cycle's expansion. This is termed the 'critical dilation' and the test is terminated. The specimen is kept immersed in water and tested once every two weeks until critical dilation is reached. There is no failure criterion based upon the number of cycles required to reach critical dilation.

If the specimen is adequately air entrained, the water freezes in the air bubbles thus creating no pressure on the concrete and the concrete contracts as the water is withdrawn from the gel pores. This is shown in Figure 3.2 by the dashed line marked "Air-entrained". If the concrete is not air entrained the water continues diffusing to the ice crystals and this results in continued expansion with subsequent cycles. Khalil found this behavior to be common among the higher water/cement ratio mixtures tested and depicted this in Figure 3.2 by the line marked "No-air (w/c > 0.4)". For two of three non-air entrained mixtures with

by weight water/cement ratios less than 0.40 however, Khalil found frost resistant behavior conforming to lines marked "No-air ($w/c < 0.4$)" in Figure 3.2.

Table 3.3 Properties of Hardened Concrete Subjected to ASTM C 671 "Critical Dilation Test" from Khalil²⁷.

Mix Designation	A (Control)	B	C	D	E	F	G
Aggregate Source	S1			S2	S3		S4
Compressive Strength, N/mm ² (psi)							
7 days	33.8 (4900)	46.7 (6770)	49.6 (7190)	35.3 (5115)	36.6 (5310)	----	42.7 (6200)
28 days	42.1 (6110)	55.7 (8080)	57.8 (8390)	38.2 (5540)	42.8 (6210)	46.0 (6670)	----
Air Void Analysis							
Air Content, %	8.4	3.2	2.74	0.98	1.24	1.82	1.36
Spacing factor, mm (in.)	0.132 (0.0052)	0.71 (0.028)	1.37 (0.054)	1.14 (0.045)	0.81 (0.032)	0.81 (0.032)	1.85 (0.073)
Specific Surface, cm ² /cm ³ (in. ² /in. ³)	222 (565)	74 (189)	42 (106)	87 (220)	119 (302)	124 (314)	52 (131)
Paste Content, %	24.9	21.3	21.3	27.0	33.1	28.5	35.1
Critical Dilation							
Frost Immunity, (weeks) ^a	34.3 ± 1.8	18.3 ± 1	18 ± 1.0	2.3 ± 0.8	6.3 ± 1.0	1.0	1.0
Critical Dilation, μm (μin.)	1.14 ± 0.12 (45 ± 5)	1.27 ± 0.12 (50 ± 5)	1.14 ± 0.12 (45 ± 5)	2.79 ± 0.89 (10 ± 35)	4.16 ± 0.89 (164 ± 35)	1.02 ± 0.12 (40 ± 5)	4.27 ± 1.09 (168 ± 43)
Number of Cycles ^b	17.0	10.0	9.0	2.0	4.0	1.0	1.0
Rapid Freeze-Thaw							
Durability Factor, %	85.5	15.6	20	4.4	38	5	6.4
Number of Cycles ^c	>300	78	102	24	186	25	32
W/C	.45	.32	.36	.42	.33	.46	.44

^a 95% confidence interval of the mean

^b Number of cycles completed to reach critical dilation.

^c Number of cycles completed to reach 60% relative dynamic modulus.

Although the test method has no failure criterion based upon number of cycles to critical dilation, Powers⁵⁹ stated that any concrete which could withstand freezing under continually wet conditions such as those prescribed by ASTM C 671 for 16 weeks could be considered frost resistant for normal winter exposure. Table 3.3 shows that two of Khalil's three non-air entrained, low water/cement ratio mixtures exceeded that mark. The fact that the air entrained control mixture did not reach its critical dilation until 34 weeks of testing is clear evidence that a low water/cement ratio is not as effective as entrained air in rendering the concrete freeze-thaw resistant.

Figure 3.3 plots the dilation vs cycles endured for the ASTM C 671 test results shown in Table 3.3. Figure 3.4 plots the loss of dynamic modulus vs cycles Khalil found for the same mixtures when tested under ASTM C 666 Procedure A and Table 3.3 shows the durability factors obtained. The results again clearly demonstrate the effect of the water/cement ratio on the durability of concrete. The low water/cement ratio mix exhibited adequate frost resistance according to ASTM C 671 but not according to ASTM C 666. Khalil concluded that, while not disproving the fact that air entrainment is necessary to obtain durable concrete, the concept of lowering the water/cement ratio provides excellent durability when the concrete is tested according to ASTM C 671. Many investigators believe this is a more realistic representation of existing conditions in service and, therefore, a more accurate test.

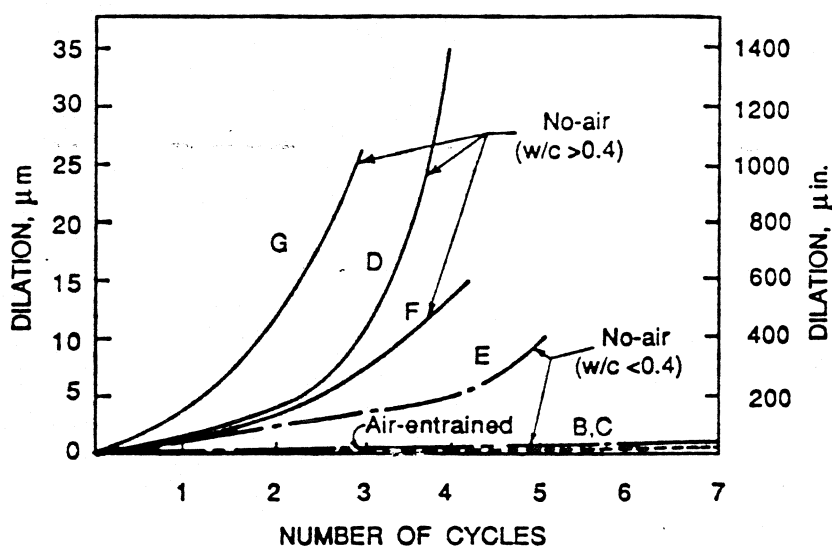


Figure 3.3 Plot of Dilation vs. Number of Cycles for Mixes Tested Under ASTM C 671 by Khalil²⁷.

3.2.5 Sturup (1987). Sturup⁶⁵ published a report in 1987 summarizing the durability of concrete test blocks and actual structures dating back nearly 30 years. Sturup discussed the discrepancies discovered between performance under accelerated laboratory test procedures such as ASTM C 666 Procedures A and B and long term performance in an outdoor exposure facility. The study was divided into three categories by subject: water/cement ratio and air entrainment, fly ash replacement, and aggregate evaluations. While none of the studies utilized high strength, low water/cement concrete, the material response to the testing procedures are of importance to this study.

The initial tests involved both air and non-air entrained concretes with water/cement ratios varying from 0.5 to 1.0 by weight and air contents from 1.0 to 15.0 percent. Curing varied between moist and air dry for some of the mixtures. Companion specimens from all

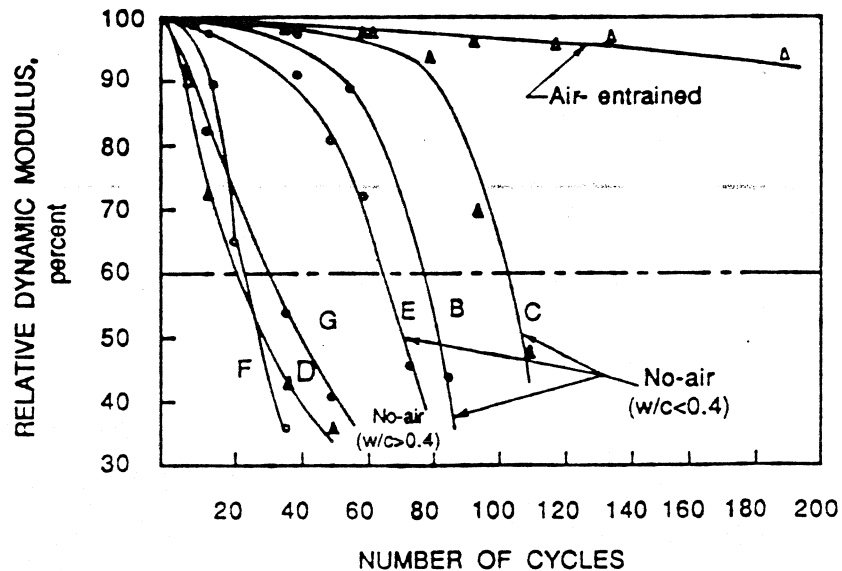


Figure 3.4 Plot of Freeze-Thaw Durability vs. Cycles for Mixes Tested Under ASTM C 666 from Khalil²⁷.

mixtures were subjected to laboratory freeze-thaw tests and field tests in which specimens were half submerged in water filled tubs and left at the outdoor exposure site. Tests conducted according to ASTM C 666 Procedure A showed all non-air entrained concretes to be non-durable, but could not distinguish between the performance of concretes with water/cement ratios of 0.5 and 1.0 by weight. For the air entrained specimens, Procedure A showed the high water/cement ratio mixture ($w/c=1.0$ by weight) to be more durable than those with water/cement ratios of 0.5 and 0.6 by weight. This data was in direct conflict with the results obtained from the outdoor exposure facility for the companion specimens.

Results of laboratory freeze-thaw tests conducted according to ASTM C 666 Procedure B (thawing in air) generally agreed with the measured performance of the outdoor exposure specimens for water/cement ratios equal to 0.5 and 0.6 by weight. For mixtures with by weight water/cement ratios equal to 0.8 and 1.0 however, Procedure B data was closer to Procedure A results. Sturup noted that when inspected for scaling after 10 years exposure, except for some very low air content mixtures (0.7 percent) and some very high water/cement ratio specimens, only minor visual differences exist between the remaining specimens, regardless of water/cement ratio or air content.

The fly ash studies commenced at the outdoor exposure site in 1960 and consisted initially of several fly ash replacement level mixtures ranging from 0 to 60 percent by weight of cement at a constant water/cement ratio of 0.60 by weight and total air content of 6 percent. Laboratory freeze-thaw tests were not performed on this initial air entrained series

but the outdoor exposure test showed a strong correlation between increasing fly ash content and increased scaling of the block faces.

In the aggregate evaluation phase of the study, Sturup selected concrete mixtures with proven durable aggregates and replaced them with varying percentages of two aggregates considered marginal in freeze-thaw performance. These mixtures were then cast with adequate air entrainment along with non-air entrained control mixtures. Laboratory testing was done according to ASTM C 666 Procedure A and companion specimens were placed in the outdoor exposure facility. Sturup reported that the laboratory test results greatly underestimated the durability especially at the lower fly ash replacement levels. This, he reported, was probably due to the relative size of the specimens since a strategically located piece of chert in a laboratory specimen could result in fracture whereas it would only cause a pop out in the much larger outdoor block. Sturup also found that air entrainment did not prevent failure of the marginal aggregate mixtures but only served to delay deterioration. This delay period also became shorter with increased replacement levels of marginal aggregates.

In conclusion, Sturup stated that the laboratory test ASTM C 666 Procedure A is very severe and does not always provide accurate results as he points to many non-air entrained mixtures at the outdoor site which have performed adequately for 20 years. Procedure A also cannot differentiate between concrete without air entrainment and concrete with poor aggregates. A much clearer difference between these modes of failure is evident in the outdoor exposure tests. In summary, if laboratory results based on ASTM C 666 Procedure A indicate adequate performance, field performance will be better. If poor laboratory results are obtained, however, field performance cannot necessarily be predicted, especially if the problem is in fact caused by marginal aggregates.

3.2.6 Hudec (1987). Peter Hudec²⁵ published a report in 1987 summarizing the underlying causes of the deterioration of aggregate when used in concrete. This paper summarized over 15 years of research conducted by Hudec and his students. In this work, he explained the volumetric changes that aggregates undergo in response to changing conditions of temperature, moisture, and salt content. Hudec classified aggregates by predominant pore size into three groups as shown in Table 3.4.

By comparing Table 3.4 with Figure 2.1, it is seen that the fine pores in the aggregate approximate the size of the larger capillary pores in the concrete paste. Hudec disagrees with Young and Mindess on the behavior of water in pores this size. Hudec states that all surfaces have an electric charge on them due to broken bonds at the material surface and for most minerals this charge is negative. For this reason, aggregates will attract water and dissolved salts to their surfaces and adsorb them thus balancing their surface charge. Cations from dissolved salts also bind themselves to water molecules and then are attracted to the surfaces of the aggregate particles by an even stronger bond than to the water itself. This is why salts in the pore water lower the freezing temperature of an aggregate-water system.

Table 3.4 Pore Size Classification for Aggregates from Hudec.

Pore Class	Force Pores	Micro Capillary	Macro Capillary	Bulk Pores
Pore Size	< 1 μm	1-5 μm	5 μm - 1 mm	> 1 mm
Dominant In:	shale, chert	fine grained volcanics, argill, dolomite and limestone	medium grained dolomite, limestone, sandstone, metamorphic & igneous rocks	coarse grained dolomite, limestone, sandstone, Metamorphic & igneous rocks

Hudec explained that the initial effect of water upon contact with a rock is contraction of the rock. The rock attracts the water into its pores through capillary suction and this places the rock particles between the capillaries in tension which physically contracts the rock. As the capillaries fill to saturation, the tension decreases until the rock regains its initial dry volume. If the rock is fine grained, the difference in vapor pressure between the adsorbed water and the pore water farther from the pore surfaces will set up osmotic pressure differentials which can then create water movement within the rock or from the water outside. The presence of salts such as deicing salts on pavements increase this osmotic potential by further lowering the vapor pressure within the pores. The failure mechanism then is caused by the volume changes within the rock as it cycles through periods of wetting and drying. Hudec found that in fine grained rocks, these contractions and expansions due to osmotic potentials are sufficient to cause fracture even in the absence of freezing temperatures.

Hudec also studied the freezing phenomenon in rocks and reported results very similar to Powers' ⁵⁴ work with cement paste. In fine grained rocks, the water in the smallest pores never freezes during typical winter temperatures. Likewise rocks containing mostly coarse pores drain or expel water easily upon freezing and are also unlikely to suffer damage. Hudec states that it is the rocks with predominantly microcapillary sized pores of 1 to 5 μm which will be least durable. Hudec states that the freezing of aggregates especially in the presence of deicing salts does not cause failure due to expansion upon freezing but due to the movement of water because of the osmotic pressures generated by the ice formation.

3.2.7 Teodoro (1987). Teodoro⁶⁶ published the results of a study investigating the role of aggregate in determining the frost resistance of concrete. Specifically, Teodoro investigated the mineralogical effect of coarse aggregate and the effect of fines of diameter

less than 0.1 mm in the fine aggregate. A total of 12 mixtures were cast in four series and only the results of the freeze-thaw testing was reported. The cement content of the first series of three mixtures was 660 lb/cy with a water/cement ratio of 0.5 by weight. One of the mixtures contained a coarse aggregate with a high content of silicic acid in the form of opal. All specimens were tested according to STAS 3518-68 which is similar to ASTM C 666 Procedure A except that each freeze-thaw cycle is each four hours in length.

When subjected to the freeze-thaw test, the mixture containing the opal coarse aggregate performed very poorly compared to the other two mixtures containing more durable aggregates. In the second series, the original Type I cement was replaced with a Type III cement and the test repeated with similar results. In the third series, the author increased the cement content in an attempt to improve the performance however this did not overcome the aggregate's lack of durability. In the final series two identical mixtures were cast with the exception that one had 5 percent of the fine aggregate with a diameter less than 0.1 mm while the other had 1.7 percent fines. The freeze-thaw results clearly showed the mixture with excessive fines performed poorly compared to that of the mix with the low fines content.

The conclusions of this study stated that the mineralogical makeup and size fraction of the aggregates have a significant effect on the freeze-thaw performance of the concrete and neither cement type or content, nor the presence of "adequate" air entrainment can overcome an aggregate's deficiency. Limits on the fines content of the sand and testing of the mineralogical makeup and pore distribution of the coarse aggregate is critical to ensuring frost resistant concrete.

3.2.8 Yamato (1986). In 1986 Yamato⁸¹ completed an investigation into the freezing and thawing resistance of silica fume concrete. A total of 23 concrete mixtures were cast with water/cement ratios ranging from 0.25 to 0.55 by weight and silica fume contents of 0, 5, 10, 20, and 30 percent by weight of cement. Twenty of the mixtures were non-air entrained and three 0.55 water/cement ratio mixtures were air entrained with silica fume contents of 0, 20, and 30 percent. Each mixture was tested for compressive strength, freeze-thaw resistance, pore size distribution, water permeability, drying shrinkage, and microscopic air void parameters. Only the results of the freeze-thaw testing are reported here. The curing conditions for the freeze-thaw specimens consisted of 28-days submersion in 20°C water prior to testing. All testing was conducted according to ASTM C 666 Procedure A.

Yamato found that at water/cement ratios of 0.45 to 0.55, non-air entrained mixtures performed poorly with respect to the reference air entrained concrete and performance decreased with increasing silica fume content. As the water/cement ratio decreased to 0.35, the performance improved to where the 0 percent and 5 percent non-air entrained silica fume mixtures both tested satisfactorily with durability factors of 82 and 64 percent, respectively, after 300 cycles. When Yamato lowered the water/cement ratio to 0.25, he reported that all non-air entrained mixtures performed satisfactorily regardless of silica fume

content with an average durability factor of 95 percent. This occurred in spite of an average spacing factor L of 0.8 mm which is 4 times that recommended by ASTM C 457. Yamato's conclusion was that 0.25 water/cement ratio silica fume concrete can be produced without air entrainment to have adequate resistance to freezing and thawing which is contrary to much of the published literature.

3.3 Rapid Chloride Ion Permeability

There are many ways to obtain an indication of the relative permeability of concrete with the different measurement techniques being geared particularly to the permeating agent whose movement is being monitored. As stated in Chapter II, concrete permeability can be measured with regard to its resistance to movement of liquids or gases which utilize pressure flow as the transport mechanism or the movement of ions which is governed by the mechanism of diffusion. The transport mechanism of ion diffusion was selected in this study and the test procedure used and researched in the following pages is the Rapid Chloride Ion Permeability Test (RCPT). This test was recently developed in the United States by Whiting [] and is recognized as AASHTO T-277. The following material reviews the research completed utilizing this technique especially with regard to high strength concrete containing fly ash and silica fume.

3.3.1 Whiting (1981,1987,1988,1989). In 1981 David Whiting⁷⁷ published a report for the Federal Highway Administration outlining the development of a new test procedure to be used as a rapid means of assessing the permeability of concrete to chloride ions. The test consists of first conditioning a 4-inch diameter by 2-inch thick slice of concrete by vacuum saturation after which each face is immersed in known solutions of sodium chloride (NaCl) and sodium hydroxide (NaOH) respectively. A potential of 60V dc is then applied across the thickness of the slice and utilizing a calibrated resistor of known resistance, the current is measured at 30 minute intervals over a six hour period. Upon completion of the test, the total amount of electric charge measured in coulombs that has passed through the specimen is obtained by integrating over time the measured values of current. Thus the test is not a direct measure of permeability but a comparative one.

The value of the RCPT lies in the correlation of the permeability values obtained through this test with results from long term chloride penetration tests performed on companion slabs through ponding. Whiting showed that the results correlated very well with 90-day ponding tests from which he devised Table 3.5 which categorizes concrete permeability into qualitative classes based on the absolute value obtained from the RCPT test. The primary benefit derived from using the RCPT is its rapid return of results. The RCPT method takes 3 days typically whereas ponding tests require 90 days to complete.

In 1987, Whiting and Kuhlman⁷⁵ investigated the effect of curing on the chloride permeability of different concretes. Four mixtures were cast, a latex-modified concrete (LMC), a low slump dense concrete (LSDC), a superplasticized dense concrete, and a

Table 3.5 Permeability Ratings Devised by Whiting⁷⁷.

Relative Permeability	Charge Passed (Coulombs)	Type of Concrete
High	> 4000	High water / cement ratios (≥ 0.60)
Moderate	2000 to 4000	Moderate water / cement ratios (0.40 to 0.50)
Low	1000 to 2000	Low water / cement ratios "lowa" dense concrete
Very low	100 to 1000	Latex modified concrete Internally sealed concrete
Negligible	< 100	Polymer impregnated concrete Polymer concrete

reference control concrete. The initial water/cement ratios for these mixtures were all by weight and ranged from 0.26 for the LMC to 0.42 for the control and the 28-day compressive strengths ranged from 5000 psi to 6800 psi. An identical set of 4 mixtures was also cast and then retempered with additional mixture water and tested to study the effect of retempering on chloride permeability. To test the effect of curing conditions, standard moist cured laboratory cylinders were cast along with slabs which were field cured and then cored to obtain the test specimens. Both the laboratory specimens and the field cores from each mixture were tested for permeability and compressive strength at 14, 30, 60, 180, and 365 days of age.

The results of the study showed that the latex modified concrete exhibited the lowest chloride ion permeability of all the mixtures at all ages with values under 1000 coulombs. Not surprisingly, the laboratory cylinders showed lower permeabilities than the cores from the field cured slabs and the addition of retempering water resulted in significant increases in permeability ranging from 50 percent in SDC to 200 to 300 percent for the LMC. The study also showed that the permeability of all concretes reduced dramatically with time especially the superplasticized dense concrete (SDC) during early ages up to two months after casting.

In 1988 Whiting⁷³ published an extensive study on the permeability of six different concretes with water/cement ratios ranging from 0.26 to 0.75 by weight. Specimens were tested for permeability to water and air, permeability to chloride ions both rapid and long term, and volume of permeable voids and porosity. High range water reducers and silica fume were used in the low water/cement ratio mixtures. Curing consisted of a standard 7 day moist cure for all mixtures with some specimens from each mixture being given only one day of moist curing. The results of 90-day compressive strength tests ranged from 4800 to 15,000 psi. Only the results of the Rapid Chloride Ion Permeability Test and the 90-day ponding tests are discussed here. Table 3.6 shows the test results of the six mixtures.

Table 3.6 Permeability Test Results from Whiting⁷³.

Mix No.	W/C	Cure Time	RCPT (Coulombs)	90-Day Ponding (% Cl)	Permeability		Porosity	Vol. Permeable Voids (%)
					Hydraulic (μ Darcys*)	Air (μ Darcys*)		
1	0.26	1 day	44	0.013	**	37	8.3	6.3
		7 days	65	0.013	**	29	7.5	6.2
2	0.28	1 day	942	0.017	**	28	9.1	8.1
		7 days	852	0.022	**	33	8.8	8.0
3	0.4	1 day	3897	0.062	0.030	130	11.3	11.4
		7 days	3242	0.058	0.027	120	11.3	12.2
4	0.5	1 day	5703	0.103	0.560	120	12.4	13.0
		7 days	4315	0.076	0.200	170	12.5	12.7
5	0.6	1 day	5911	0.104	0.740	200	13.0	12.8
		7 days	4526	0.077	0.230	150	12.7	12.5
6	0.75	1 day	7065	0.112	4.100	270	13.0	14.2
		7 days	5915	0.085	0.860	150	13.0	13.3
Coefficient of Variation, %			7.0	12.9	20.9	14.0	2.5	2.4

* To convert from μ Darcys* to m^2 , multiply by 9.87×10^{-7}

** Permeability too small to measure.

Whiting found that water/cement ratio has the largest single effect on the concrete permeability as evidenced in the more than 100 fold increase in chloride ion permeability when the water/cement ratio is increased from 0.26 to 0.75. Likewise, Whiting found the

percentage of chlorides in the hardened concrete rose 7-9 fold when the water/cement ratio was tripled. The beneficial effect of the 7 day vs 1 day moist curing period was especially obvious for the higher water/cement ratio mixtures, reducing the total charge passed by over 15 percent. Probably the most significant finding in Whiting's study was the correlation between the 3 day Rapid Chloride Ion Test (RCPT) and 90 day ponding studies. Whiting found that the RCPT test had a correlation coefficient of 0.99 and the standard error of the estimated value of permeability was less than 10 percent. The results of this correlation are shown in Figure 3.5

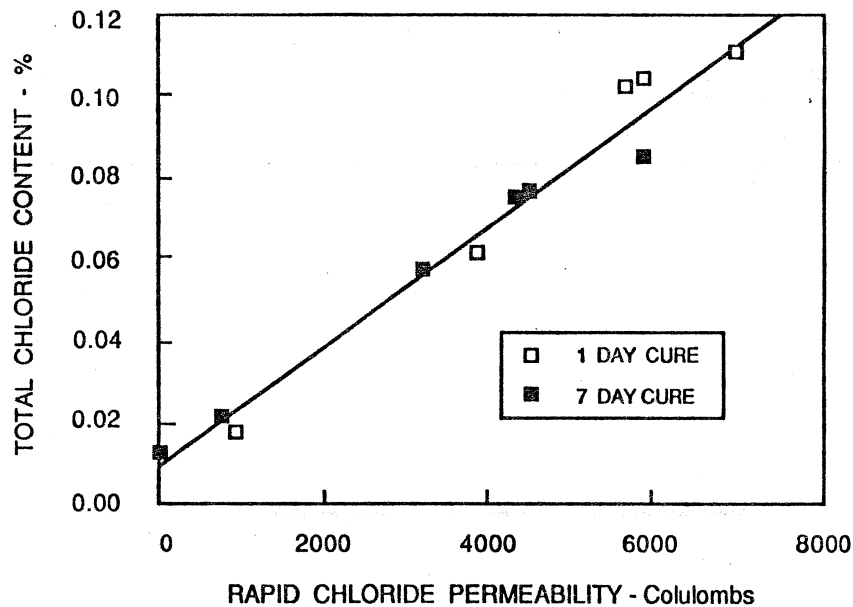


Figure 3.5 Relationship Between Results of Rapid Chloride in Permeability and 90-Day Chloride Ponding Tests from Whiting.

In 1989 Whiting⁷⁴ published the results of a permeability study investigating the effectiveness of various materials in rigid pavement bridge deck overlays. Twenty-five bridge decks were tested including 13 at existing sites and 12 new construction overlays cast during the summer of 1987. Overlay materials chosen for testing included latex-modified concrete (LMC), superplasticized dense concrete, and condensed silica fume concrete (CSFC) and construction methods ranged from 2-inch overlays to full depth repairs. The age of the in-place concretes ranged from 2 months to 13 years. Concrete cores taken from the in-place sites were tested for RCPT and total chloride ion content in the concrete at different depths from the surface. At new placement sites, 4-inch by 8-inch cylinders were

cast and cured for a specified period before being subjected to either the RCPT or the 90-day ponding test.

The test results showed the CSFC pavement to be far superior to both LMC and SDC in both permeability and chloride ion content in both in-place and new placement specimens. Whiting also verified his laboratory study described earlier in that the field LMC pavements showed consistently lower permeabilities regardless of age than SDC pavements; however, LMC showed more variability in samples taken across a structure. SDC pavements start out with much higher permeability values than LMC; however, over a period of years the permeability decreases. The most significant result from the study was again the establishment of the correlation between the results from the RCPT and chloride ion content tests. Whiting found that, despite the variations that can occur in field construction techniques and the varying ages of the structures involved, the correlation coefficient between the two test results was relatively good at 0.81 with a standard error of only 16 percent. Whiting felt that this demonstrated that RCPT could be used effectively as a reliable indicator of the long term permeability of concrete to chloride ions.

3.3.2 *Plante and Bilodeau (1988)*. This study⁵¹ presents the results of an investigation by the authors into the effect of supplementary cementing materials on the permeability of concrete when tested using the Rapid Chloride Permeability Test (RCPT). A total of eighteen mixtures were made in three series. The first series consisted of four reference concretes having by weight water/cement ratios from 0.21 to 0.71 and four companion mixtures incorporating the addition of 8 percent silica fume by weight of cement. In the second series, the water/cement ratio was held constant and a reference concrete and three mixtures incorporating silica fume, fly ash, and blast furnace slag were cast. In the third series, different slags were compared along with one slag at different fineness levels. Compressive strength and RCPT testing was performed on all mixtures at 1 day, 7 days, and 28 days of age.

Plante found results similar to others in that the water/cement ratio and length of curing have the most significant effects on the permeability of the concrete. Based upon the test results, the silica fume most effectively reduced the porosity of the concrete and this is reflected in the decreased permeability values. Contrary to some research, however, Plante did find occasions where, at relatively high water/cement ratios of 0.55 by weight, slag mixtures had lower permeability values than silica fume mixtures. Plante also found that the finer slag mixtures were much less permeable than their coarser counterparts. These last two findings need further research.

3.4 Deicer Scaling

Although not the main focus of this dissertation, the deicer scaling resistance of concrete was evaluated in this study because the scaling mechanism is similar in some respects to the freeze-thaw mechanism. Investigators often test and report on both

mechanisms in the same study. No attempt is made here to report the extensive amount of research published on the deicer scaling phenomenon. The literature review presented here focuses primarily upon the research performed on high strength and silica fume concrete since these topics are most relevant to the present study.

3.4.1 *Brown and Cady (1975)*. These authors¹⁰ conducted this investigation in the early 1970's at Pennsylvania State University with the intent to study two separate mechanisms in the concrete: (1) the generally accepted hydraulic pressure method and its dependence on deicer concentration and saturation depth, and (2) the chemical mechanism that occurs between the concrete and the calcium chloride solution. The first experiment performed by the authors was to immerse concrete and mortar specimens in deicer solutions of varying concentrations and measure absorption over time. These specimens were then subjected to freeze-thaw cycles while exposing their surfaces to the same deicer solutions of varying concentration. These results verified what others^{33,34,69} had found that a three percent solution of calcium chloride resulted in much faster saturation of the concrete which produced much more deterioration during freeze-thaw cycling than either pure water or higher concentration solutions.

The authors then subjected both concrete and mortar specimens to freeze-thaw tests with varying concentrations of deicer solution on their surfaces and measured surface scaling visually and the penetration of chloride ions through the depth of the slab. The authors found that in all cases the chloride level decreased steadily with depth from the concrete surface however they found little correlation between chloride level and surface deterioration. This they reasoned was due in large part to the sampling technique which reused sampled specimens which may have altered the test results.

The final experiment conducted focused on the chemical interaction between the deicer solution and the concrete in the absence of temperature changes. Test specimens were cast and submerged in equal concentrations of either calcium chloride or sodium chloride solutions for periods varying from 0 to 84 days. Upon completion of the soaking they were tested for tensile strength and evaporable water content and compared to previously tested control specimens. The tests revealed that initially an osmotic cell develops in between the internal concrete water and the deicer solution which effectively removes evaporable water from the matrix. This was evidenced by early increases in the tensile strength. At later ages, however, the concrete continuously lost strength without any changes in its evaporable water content. This strength loss was solely due to the reduction in surface area of the specimen resulting from the chemical attack by the deicer solution in the absence of freeze-thaw cycles.

3.4.2 *Adkins and Christianson (1988)*. The authors⁴ conducted an investigation at Utah State University in the late 1980's which studied the solar effects on deicer deterioration of concrete pavements. Deicer scaling deterioration is caused by both thermal and hydraulic stresses. The temperature gradient across the depth of the pavement also plays a significant role. The authors theorized that a fully frozen pavement will experience

thawing in its upper layers on a winter day due to solar effects. Upon nightfall as temperature drop below freezing, the partially thawed pavement begins freezing from the top down and this traps a layer of unfrozen water just below the surface which then expands upon freezing and places stress on the matrix. Unfrozen water left within the concrete then starts flowing to the frozen sites as described by Powers⁵⁷. This migration also causes stress which breaks bonds and a portion of the surface flakes off.

To test this theory of converging temperature gradients, the authors cast several instrumented specimens and after initial saturation and freezing, alternated thawing and freezing cycles using heat lamps and refrigeration units and monitored the temperature gradients through the depth of the slab. Their results shown in Figure 3.6 indicate that the last area to freeze when the pavement is subjected to cycling temperatures is a plane about 1/4 inch below the surface and when this area does finally freeze, there is no unfrozen capillary space for its water to move to. The authors then applied deicer solutions to the surface and found that the solutions aggravated the scaling because of their surface drying effect and their ability to maintain saturation levels immediately below the surface.

The author's laboratory findings were confirmed by the results of a field study performed in Canada in 1984 on a vertical barrier wall which was instrumented with thermocouples and exhibited rapid scaling. Data was taken from January through March and the results were very similar to those obtained in the laboratory. The authors concluded that the solar effects of thawing the surface and creating the temperature gradient in the pavement slab had a definite effect on the deicer scaling mechanism.

3.4.3 Sorenson (1983). This investigation⁶⁴ studied the effect of deicer scaling on concrete made with silica fume. Sixteen mixtures were cast in eight air entrained/non-air entrained pairs with the silica fume content varying from 0 to 40 percent by weight of cement. The water/cement ratio of the mixtures varied from 0.37 to 0.67 by weight and the 28-day compressive strengths ranged from 3800 psi to 9200 psi. The test procedure applied during this study was RILEM Recommendation CDC2 which is similar to ASTM C-672 "Standard Test for Resistance of Concrete to Deicer Scaling". All test specimens were demolded after one day and cured under water for thirteen days whereupon three specimens from each mixture were given a standard 20°C (70°F) air cure and three others were cured at 45°C (113°F) until 28 days of age. The severe drying was done to simulate an extreme climatic condition and investigate its effect on the freezable water content of the concrete. The specimens were then ponded with 3 percent NaCl solution and subjected to daily cycles of freezing and thawing. At the completion of 10, 20, and 25 cycles, all specimens were photographed, visually rated, and the scaled material washed off and weighed.

The results Sorenson found were that, compared to the 0.39 water/cement ratio control concrete with no silica fume, the 10 percent silica fume mixtures showed less scaling at water/cement ratios as high as 0.52. The control concrete also showed serious deterioration after exposure to the elevated temperature curing while the silica fume mixtures showed little effect. The air entrainment improved the deicer scaling resistance

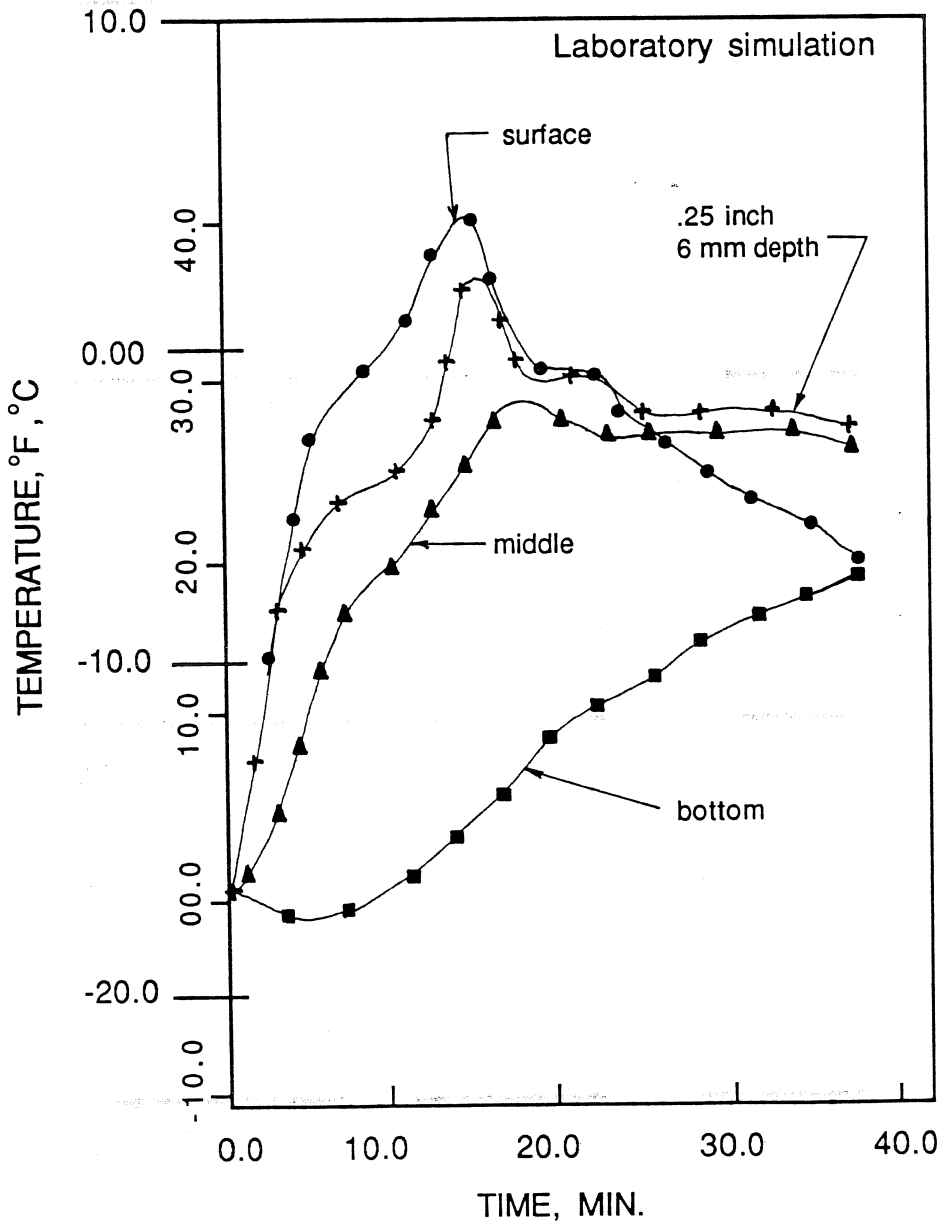


Figure 3.6 Concrete Temperature vs Time Measured at Varying Depths from Adkins⁴.

of all the mixtures both with and without silica fume. Sorensen's final conclusion was that a 10 percent silica fume mixture with 500 lb of cement could exhibit excellent deicer scaling resistance without the need for air entrainment.

3.4.4 Pigeon (1987). This investigation⁵⁰ was conducted at Laval University in Quebec City, Canada and studied the relationship between deicer scaling resistance and critical spacing factor of silica fume concrete. The author wished to determine if the air void parameters which made silica fume concrete durable under freeze-thaw testing by ASTM C 666 also provided durability with regard to scaling resistance. Three series of mixtures were cast with a constant water/cement ratio of 0.45 by weight and silica fume replacements of 0, 5, and 10 percent by weight of cement. In each series, one mixture had a typical amount of entrained air and one had a higher than normal amount of entrained air. This was done in an effort to obtain concrete specimens with adequate spacing factors equal to approximately 0.2 mm and concretes with spacing factors much smaller than that. Two curing methods were used, one employing 7 days moist curing and the other, the use of a curing compound. All specimens were tested for scaling according to ASTM C 672 using both a 2.5 percent NaCl solution and pure water.

Pigeon found that the scaling resistance of the concrete decreased with increasing silica fume content. Surprisingly, the use of a curing compound resulted in higher scaling resistance than 7 days of moist curing for all mixtures. Microscopic analysis of each concrete showed that the spacing factors ranged from 0.09 mm to 0.18 mm which are well under the recommended value of 0.2 mm necessary for frost resistance according to ASTM C 457. Despite the excellent spacing factors obtained, there was no visible difference in scaling performance as a function of the spacing factor. This is interesting from the standpoint that many authors including Pigeon have published work indicating that using silica fume in concrete can allow higher values of the critical spacing factor and still achieve freeze-thaw durability. These results indicate that the damage mechanism in scaling is different from that in freeze-thaw testing and that spacing factor is not as critical a parameter.

3.4.5 Johnston (1987). This author²⁶ conducted an investigation similar to Pigeon's in which he compared performance obtained using ASTM C 666 Procedure A with the performance obtained using ASTM C 672 on mixtures containing both fly ash and silica fume at water/cement ratios varying from 0.53 to 0.88 by weight. Johnston found that, when testing fly ash or silica fume concretes for durability, resistance to freezing and thawing under ASTM C 666 does not ensure resistance to scaling under ASTM C 672, even if adequate air void parameters are obtained. Johnston was able to produce concrete containing 42 percent replacement fly ash having a water/cement ratio of 0.59 by weight which performed well under ASTM C 666 Procedure A testing yet scaled severely under ASTM C 672. Similarly, silica fume mixtures with replacement values up to 15 percent by weight and by weight water/cement ratios up to 0.88 also showed excellent performance in ASTM C 666 Procedure A yet failed when tested for scaling. Johnston concluded that, with regard to water/cement ratio and replacement percentages, fly ash and silica fume concretes

need stricter limits in order to resist deicer scaling than is required to resist freeze-thaw damage.

CHAPTER IV EXPERIMENTAL PROGRAM

4.1 Materials and Test Procedures

The materials and standardized testing procedures used in this study adhere to approved Texas State Department of Highways and Public Transportation (SDHPT) procedures. All testing procedures and materials standards met one or more of the following: Texas SDHPT Manual of Testing Procedures Physical Section 400-A Series⁶⁷, the American Society for Testing and Materials 1987 Annual Book of ASTM Standards, Volume 04.01, "Cement, Lime, and Gypsum"⁶, and Volume 04.02, "Concrete and Aggregates"⁷, and the AASHTO Standard Specification for Methods of Sampling and Testing⁵.

4.2 Materials

The materials used in this study were typical of those used in the production of commercial portland cement concrete. No attempt was made to obtain or use exotic materials to increase strength or enhance concrete performance. The materials are all commercially available, approved for use in Texas by the Texas SDHPT Materials and Test Division, and are currently being used by local concrete suppliers. These materials included portland cement, fly ash, and coarse and fine aggregate. A commercially-available condensed silica fume (CSF) which is not currently approved for use by the Texas SDHPT was used for one phase of the study. Chemical admixtures used in this study consisted of commercial air entraining and high range water reducing admixtures which met applicable ASTM and SDHPT standards.

4.2.1 Portland Cement. Since variability between cements was not an issue being addressed in this study, only one portland cement was used throughout the investigation. It consisted of an ASTM Type II portland cement meeting the requirements of ASTM C 150 "Standard Specification for Portland Cement". The specific gravity of the cement was assumed to be 3.15 for mixture design purposes. Table 4.1 shows the chemical and physical properties of the cement.

4.2.2 Coarse Aggregate. The two types of coarse aggregate used in this study were a 3/4 inch nominal maximum size crushed limestone obtained locally from Georgetown, Texas, and a 3/4 inch crushed dolomitic limestone from Marble Falls, Texas. A 3/8 inch nominal maximum size dolomitic limestone was also used for a limited portion of the study. The dolomitic limestone had a specific gravity of 2.78 and an absorption capacity of 0.7%. It is referred to on the graphs in the following chapters as 'LOW AC AGG'. The limestone from Georgetown, Texas, referred to as 'HIGH AC AGG' in the graphs, had more variable material characteristics. Its specific gravity was 2.46 and absorption capacity

Table 4.1 Chemical and Physical Analyses of Cement

CHEMICAL DATA		PHYSICAL DATA	
Composition	Percent	Specific Surface	
Silicon Dioxide	21.8	Blaine (sq. cm/gm)	3350
Aluminum Dioxide	4.2	Wagner (sq. cm/gm)	1890
Ferric Oxide	3.3	Compressive Strength	
Calcium Oxide	65.2	1 Day	2030 psi
Magnesium Oxide	0.6	3 Day	3640 psi
Sulfur Trioxide	2.8	7 Day	4670 psi
Loss on Ignition	0.9	Set Time	
Insoluble Residue	0.2	Vicat/Gilmore	
Free Lime	0.9	Initial Set (min)	91/132
Tricalcium Silicate	57	Final Set (min)	210/244
Tricalcium Aluminate	6		
Total Alkalies	0.63		

Table 4.2 Coarse Aggregate Properties

PROPERTY	AGGREGATE A	AGGREGATE B
Description	Limestone	Dolomitic Limestone
Nominal Size	3/4 inch	3/4 inch
Bulk Specific Gravity	2.46	2.78
Absorption Capacity	2.2% - 4.5%	0.7%
Dry Rodded Unit Weight	91 lb/cf	99 lb/cf

varied from 2.2 to 4.5 percent. Table 4.2 lists the characteristics of the coarse aggregates used in the program.

4.2.3 Fine Aggregate. The fine aggregate was a natural siliceous sand from the Colorado River Basin obtained from a local supplier. The sand had a specific gravity of 2.56 and was rather coarse with a fineness modulus of 3.04. The same sand was used throughout the project. A sieve analysis of the fine aggregate is shown in Table 4.3.

4.2.4 Fly Ash and Silica Fume. Two fly ashes were used in the study. Both ashes were ASTM C 618 Class C, or Texas SDHPT Type B high calcium content ashes produced from sub-bituminous coal mined in Wyoming. Table 4.4 shows the chemical and physical test data on the fly ashes used. Silica fume from a single source was used throughout the study. The silica fume was used in a slurry form and contained greater than 98 percent SiO₂.

4.2.5 Chemical Admixtures. Two chemical admixtures were used in this study: an air entraining agent and a high range water reducing (HRWR) admixture. The air entraining agent was a neutralized vinsol resin complying with the requirements of ASTM C 260 "Air Entraining Admixtures For Concrete", while the high range water reducer complied with the requirements of ASTM C 494 "Chemical Admixtures for Concrete". Both admixtures are commercially available and approved by the Texas SHDPT Materials and Test Division for use in concrete.

4.2.6 Water. The mixture water used throughout the experimental program was potable tap water obtained from the city water supply. The specific gravity of the water was assumed to be 62.4 lb/cy and the pH was measured to be 8.14. The temperature of the mixture water ranged from 70 - 75°F.

4.3 Mixture Proportioning

A total of fifty six mixtures were designed in the study and a listing of the mixture proportions is presented in Appendix A. Since high strength was of primary interest, a cement content of 940 lb/cy was chosen and kept constant throughout the study. The water/cement ratio was varied by weight from 0.26 to 0.30 in order to obtain varying

Table 4.3 Sieve Analysis of Fine Aggregate

Sieve Size	Percent Retained	ASTM C-33 Limits
#4	0	0 - 5
#8	11 (11)	0 - 20
#16	26 (37)	15 - 50
#30	31 (68)	40 - 75
#50	22 (90)	70 - 90
#100	8 (98)	90 - 98
#200	2 (100)	

Table 4.4 Chemical and Physical Analyses of Fly Ashes

OXIDE COMPOSITION	PERCENT FLY ASH #1	PERCENT FLY ASH #2
Calcium Oxide	27.95	31.34
Silicon Dioxide	31.34	30.8
Aluminum Oxide	22.51	21.94
Ferric Oxide	4.98	4.66
Oxide Sum	58.83	57.4
Magnesium Oxide	4.34	6.14
Sulfur Trioxide	2.28	1.97
Average Alkalies	1.56	1.67

Physical Analysis	Fly Ash #1	Fly Ash #2
Pozzolanic Activity	100	105
Retained on #325	17	15.7
Blaine (sq. cm/gm)	3930	3940
Specific Gravity	2.7	2.73
Moisture Content	0.01	0.06

strength levels. All mixtures were cast using fly ash at replacement levels of 0, 27, and 33 percent by weight of cement in the early phase of the program and at later phases only 0 and 27 percent was used. Silica fume was added in addition to portland cement at rates of 7 and 10 percent by weight of cement. All mixtures were cast once with the low absorption dolomitic limestone coarse aggregate and once using the higher absorption limestone. Each mixture was initially cast without entrained air, followed by identical mixtures with 3 percent, and 6 percent entrained air contents. Later in the study, mixtures were cast with only 0 percent and 3 percent air since the early results showed the 6 percent air mixtures performed satisfactorily.

4.4 Mix Procedures

All mixing was conducted under laboratory conditions in a 9-cubic foot capacity rotary drum mixer in accordance with the provisions of ASTM C 192 "Standard Method of Making and Curing Concrete Test Specimens in the Laboratory". All batches ranged in size from 5 to 6 cubic feet in volume. Aggregates were stored outside and batched the day prior to mixing in order to bring them to room temperature. Moisture contents for both aggregates were determined prior to mixing by drying a sample of the aggregate in a microwave oven and then adjusting the mixture water.

Mixing times were as per ASTM C 192: three minutes of initial mixing followed by three minutes of rest, followed by two minutes of mixing. At the end of mixing, an initial slump was taken followed by the addition of the superplasticizer to the mixture and 2 to 3 more minutes of mixing. At this time, a second slump test and an air content test were performed on the mixture. For the air entrained mixtures, the air entraining admixture was added at the end of the batching sequence after the HRWR had increased the slump of the mixture. This procedure resulted in more consistency between air content and dosage rate of air entraining agent.

Four different concrete molds were used depending upon the testing requirements. Strength specimens were cast in single use, 6-inch by 12-inch plastic cylindrical molds with air tight lids. Permeability specimens were cast in 4-inch by 8-inch plastic molds. Freeze-thaw specimens were cast in steel molds measuring 3 inches by 4 inches by 16 inches and deicer scaling blocks were cast in reusable PVC plastic cylinders measuring 12 inches in diameter by 3 inches deep. Upon completion of casting, all molds were struck off, wood floated, and then steel trowelled after initial set. Cylinder molds were sealed and the remaining molds were covered with wet burlap and sealed in plastic for 24 hours after casting. After 24 hours, specimens were demolded, marked, and immediately placed in a moist curing room meeting the requirements of ASTM C 511 "Standard Specification for Moist Cabinets, Moist Rooms, and Water Storage used in the Testing of Hydraulic Cements and Concretes".

4.5 Curing Procedures

Due to the number of parameters tested in this study, the curing procedures were quite varied. In all cases, the curing conditions complied with the requirements of the applicable ASTM, AASHTO, or SDHPT specification except where the effect of varying these conditions was being examined. All compressive strength cylinders were moist cured at 73°F and 100 percent relative humidity continuously until time of testing. Deicer scaling specimens were cured in accordance with ASTM C 672 "Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals" which prescribes 14 days of moist curing at 73°F followed by 14 days of air curing at 73°F and 50 percent relative humidity prior to testing. The freeze-thaw and permeability specimens were cured

identically as outlined in Table 4.5. Test ages of 7 days and 91 days were chosen along with two curing methods for each age: a continuous moist cure, and a combination of moist and air curing. The temperature and humidity of these methods were identical to those stated above.

Figure 4.5 Curing Methods and Test Ages for Freeze-Thaw and Permeability Testing.

CURING METHOD DESIGNATION	DAYS OF MOIST CURING	DAYS OF AIR CURING	TEST AGE IN DAYS
AC-7	4	3	7
MC-7	7	0	7
AC-91	28	63	91
MC-91	91	0	91

4.6 Testing Procedures

4.6.1 Fresh Concrete Testing. Each mixture was tested for slump, air content, and concrete temperature in the plastic state. Slump tests were performed on each mixture in accordance with ASTM C 143 "Standard Test Method for Slump of Portland Cement Concrete". Mixtures containing air entraining admixture were also tested for fresh concrete air content according to ASTM C 231 "Standard Test Method for Air Content of Freshly Mixed Concrete by the Volume Method". Air tests were conducted periodically on non-air entrained mixtures in order to estimate the amount of entrapped air. The slump test was conducted twice, once before and once after the addition of the superplasticizer whereas the air test and the concrete temperature measurement were performed immediately before placement of the concrete in the molds.

Typical values of slump prior to adding superplasticizer ranged from 2 inches to 1/2 inch for water/cement ratios of 0.30 and 0.26, respectively. Values for the second slump taken after the addition of the superplasticizer ranged from 6 to 9 inches. The values for total air content ranged from 1.5 to 2 percent for non-air entrained mixtures to 8 percent for well air entrained mixtures. Concrete temperatures ranged from 75 to 90°F depending upon the season of the year in which it was cast. Appendix B shows a listing of each mixture and its fresh concrete properties.

4.6.2 Compressive Strength. The compressive strength of each concrete mixture was determined by testing 6-inch by 12-inch cylinders in accordance with ASTM C 39 "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens". Cylinders were capped using unbonded neoprene caps inside steel retaining rings and all testing was conducted using a Forney 600 kip capacity testing machine. Strength tests were conducted on all mixtures at 7, 28, and 91 days of age. Cylinders were moist cured until time of testing and the strength recorded refers to the average of three companion specimens at each test age. The strength loss per percent entrained air was calculated at 91 days for each air entrained mixture and the average loss was %. Figure 4.1 shows a plot of strength vs age for a typical mixture cast in this study. Appendix C gives a similar plot for each mixture cast along with a table showing a compiled list of strength tests and the strength loss per percent air for each mixture.

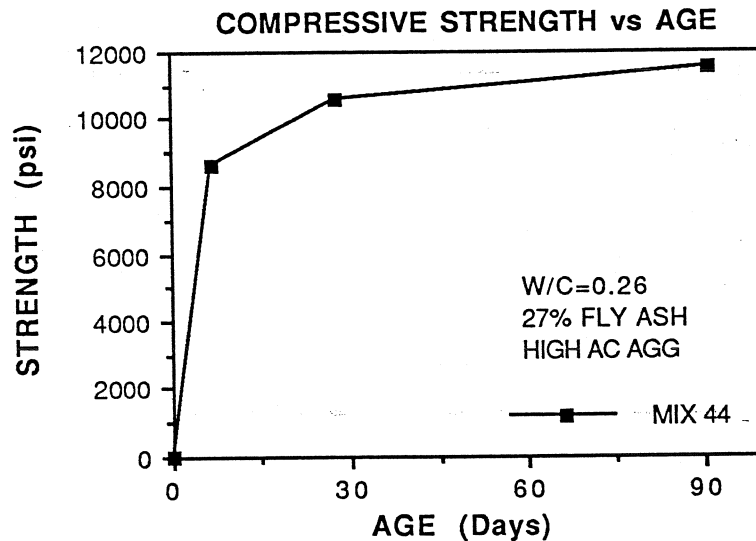


Figure 4.1 Plot of Compressive Strength vs. Age for Mix 44.

4.6.3 Freeze-Thaw Testing. The resistance to freezing and thawing of the concrete was determined by testing 3-inch by 4-inch by 16-inch concrete prisms in accordance with ASTM C 666 "Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing". This specification allows two procedural variations of the test: Procedure A requires the freezing and thawing be conducted with the specimens continuously surrounded by water whereas Procedure B allows the specimens to be surrounded by air during the freezing phase. Since Procedure A is by far the more severe of the two tests, it was chosen for use in this study so that any conclusions drawn would represent a conservative approximation of the expected performance of the concrete in service. The only modification to this test procedure was the altering of the curing methods and test ages prior to testing

Upon completion of the scheduled curing procedure outlined earlier, specimens were weighed and tested for fundamental transverse frequency according to ASTM C 215 "Standard Test Method for Fundamental Transverse, Longitudinal, and Torsional Frequencies of Concrete Specimens" prior to starting the test. Subsequent weights and frequency measurements were made every 36 cycles thereafter until either 300 cycles were completed or the squared value of the fundamental frequency was reduced to 60 percent of the square of the initial frequency value. The final freeze-thaw resistance value obtained, which is called the durability factor, represented the average of three specimens for each age and curing condition. The durability factor values ranged from 8 percent for some 7 day old, air cured, non-air entrained specimens to greater than 100 percent for well air entrained specimens. Figure 4.2 plots the loss of relative dynamic modulus vs cycles obtained for a typical mixture showing the effect of the different curing methods. Appendix G gives a detailed list of the durability factors for each mixture and curing condition along with the graphs showing individual mixture measurements.

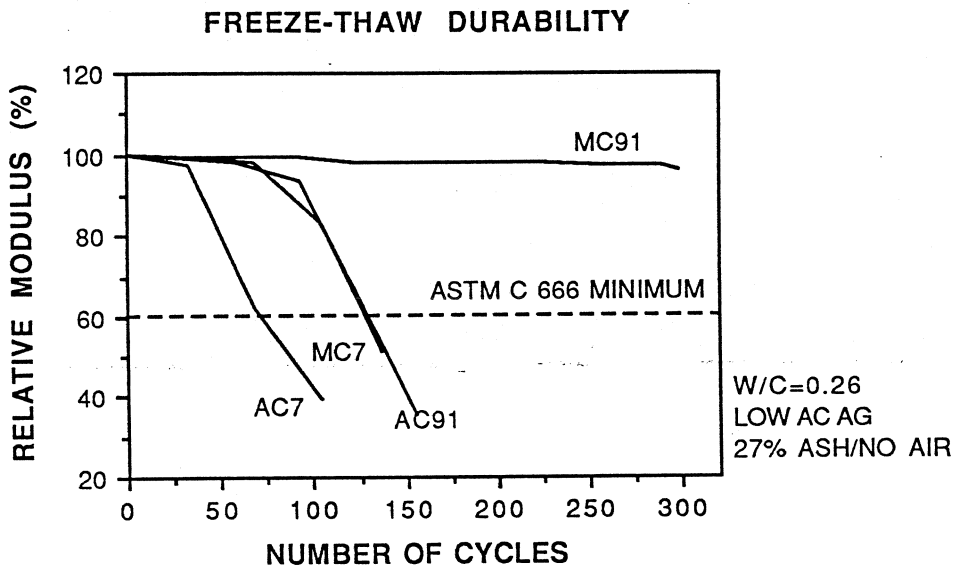


Figure 4.2 Plot of Relative Dynamic Modulus vs. Number of Freeze-Thaw Cycles

4.6.4 Permeability Testing. Each concrete mixture was tested for chloride ion permeability according to AASHTO T-277 "Standard Method of Test for Rapid Determination of the Chloride Permeability of Concrete". This test method is designed to measure the flow of DC current through a slice of saturated concrete placed between two electrolytic solutions. The current is measured at 30-minute intervals during a six-hour test period and the amount of coulombs passed is related to the concrete permeability. This procedure is more fully discussed in Chapter VI. The following modifications to the AASHTO T-277 procedure were observed during the testing: (1) tests were conducted on two samples from each cylinder instead of one from each core and; (2) specimens were kept

saturated in a sealed vacuum for one hour after evacuation instead of a forced vacuum as specified.

Since this test is designed to measure permeability of concrete extracted from existing structures, there is no specified curing period which must be followed prior to testing. In this study, it was desired to know the permeability at the same time as the freeze-thaw resistance so specimens were cured identically and tested simultaneously at ages shown in Table 4.5. Later in the study, two additional cylinders were cast with each mixture and moist cured for 14 and 21 days, respectively, prior to testing. The final permeability values obtained for each mixture represented the average of two slices from one 4-inch by 8-inch cylinder for each test age and curing method. Figure 4.3 shows the permeability test results from a typical mixture plotted against the curing conditions. A complete listing of the permeability results is shown in Appendix D.

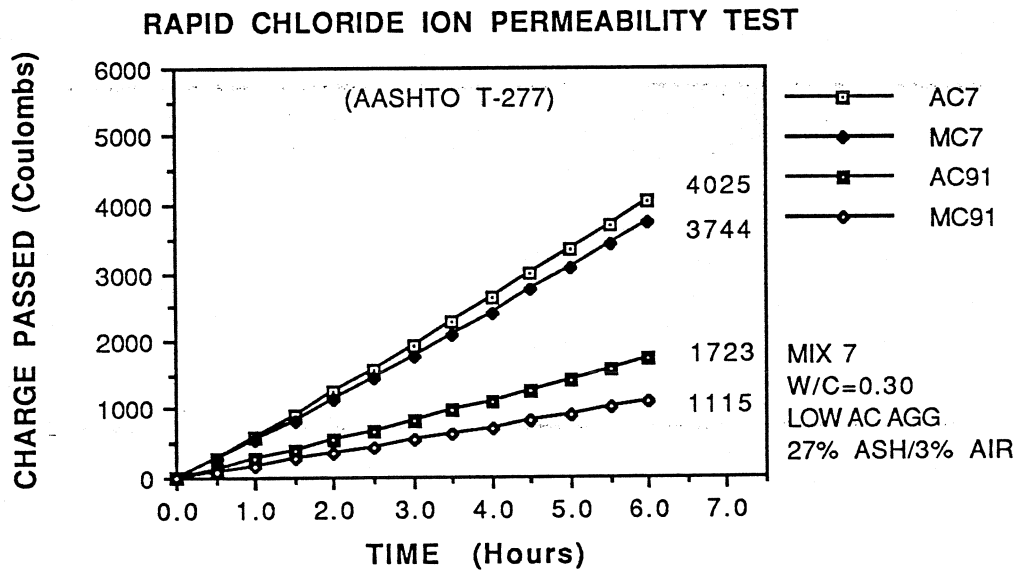


Figure 4.3 Chloride Ion Permeability Test Results for Mix 17

4.6.5 Deicer Scaling Resistance Testing. The resistance to scaling from exposure to deicing salts was tested according to ASTM C 672 "Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals". Three specimens from each mixture were moist cured for 14 days followed by air curing for 14 days. At 28 days of age, a four percent calcium chloride (CaCl_2) solution was ponded on the surface and the specimen subjected to one freeze-thaw cycle per day for 50 days. Deterioration of the concrete surface was measured by visual inspections giving each specimen a numerical rating from 0 to 5 with 0 defined as no scaling and 5 indicating very severe deterioration. Figure 4.4 shows the photograph used as a guideline for rating the deicer scaling specimens. The specimens were rated after 5, 10, 15, 25, and 50 cycles. After each rating, the specimens

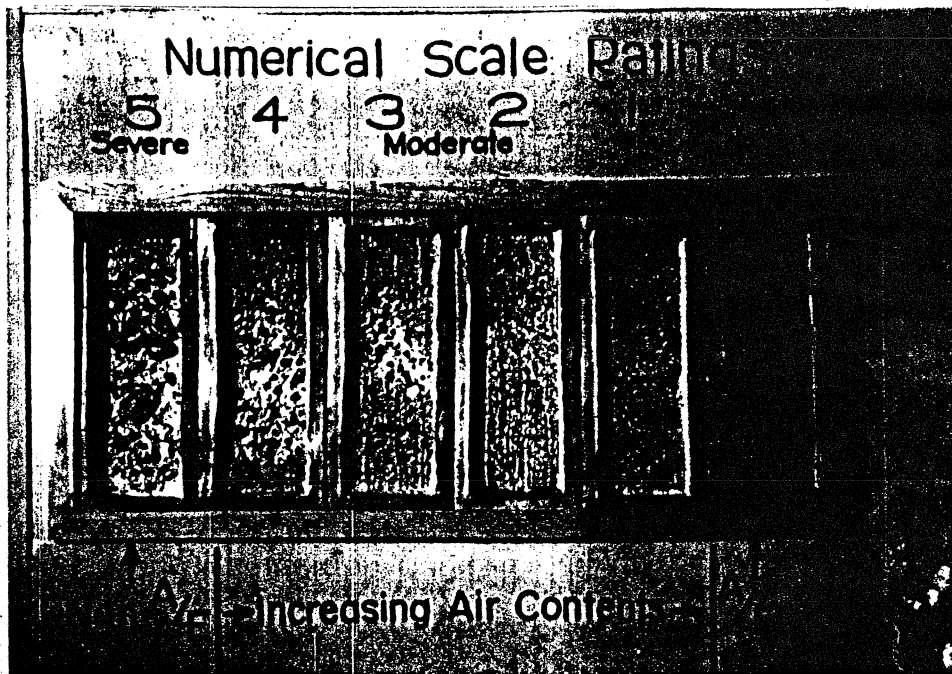


Figure 4.4 Reference Photograph Used in Rating Deicer Scaling Specimens.

were flushed with water and ponded with new solution. Figure 4.5 shows a plot of scaling vs. number of cycles for a typical mixture. A complete list of deicer scaling data can be found in Appendix E.

4.6.6 Chloride Ion Penetration. The penetration of chloride ions into the deicer scaling specimens was determined using a commercially available field test kit. Each of the deicer scaling specimens was sampled by drilling three holes to a predetermined depth and mixing the sampled concrete dust. Two samples were drawn from each of three specimens for a total of 6 samples per mixture at each depth. Samples were taken at depths of 1/2 to 3/4 inch and 1-1/4 to 1-1/2 inch. A specified weight of the sampled cement dust was then mixed with a specified volume of extraction fluid and allowed to sit overnight. The following day the fluid/powder mixtures were tested with a chloride electrode and a percent chloride level obtained from the displayed reading on a pre-calibrated digital voltmeter. These test kits are rapidly gaining acceptance and widespread use in the field due to their ease of use and accuracy at estimating the results of more elaborate laboratory test procedures such as potentiometric titration of chloride with silver nitrate as outlined in ASTM C 114 "Chemical Analysis of Hydraulic Cement". Figure 4.6 shows an example of chloride concentration level as a function of concrete depth for a typical mixture. A complete list of all chloride concentration measurements can be found in Appendix F.

4.6.7 Microscopical Air Void Analysis. Petrographic analysis of the air void system for many of the concrete mixtures was performed by a certified petrographer according to

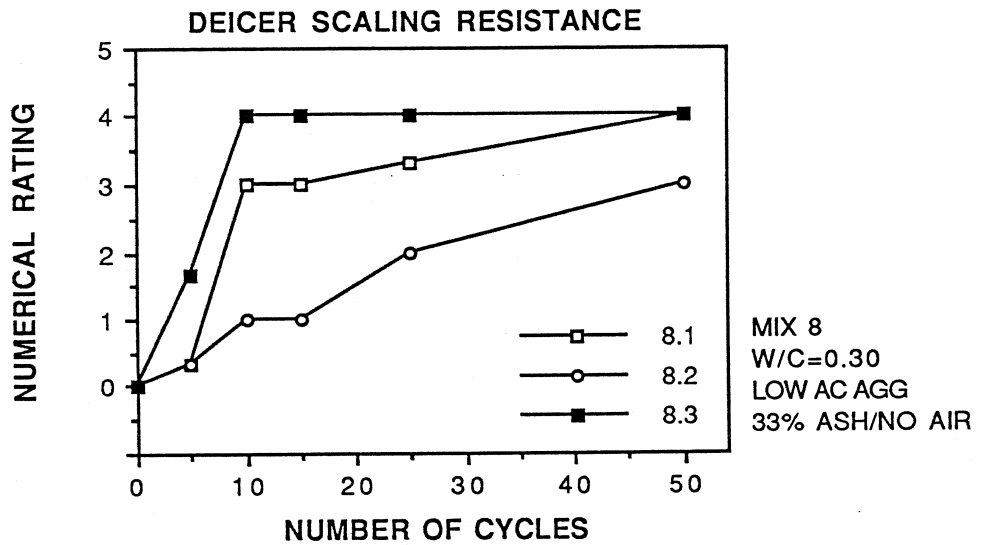


Figure 4.5 Typical Deicer Scaling Plot

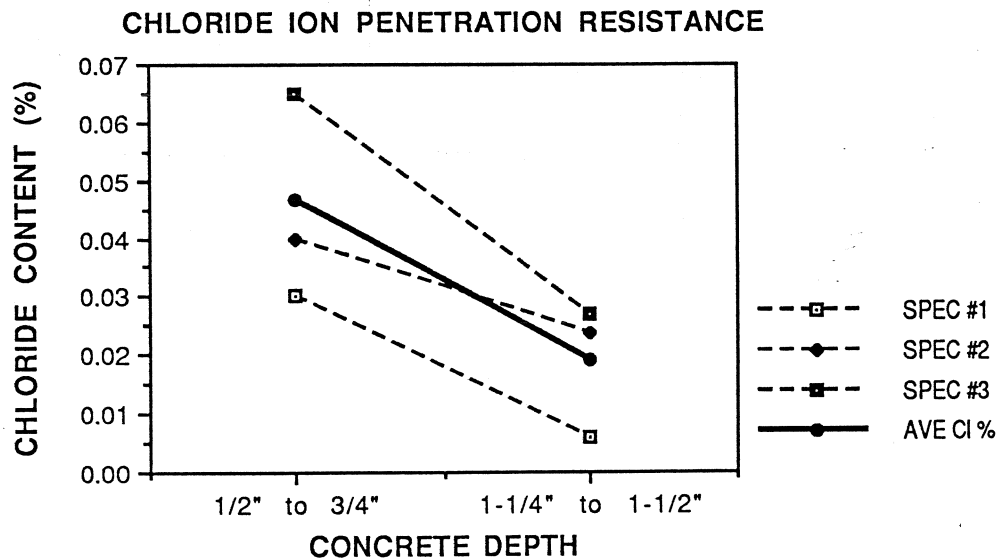


Figure 4.6 Chloride Ion Penetration for a Typical Mix

ASTM C 457 "Standard Practice for Microscopical Determination of Air Void Content and Parameters of the Air Void System in Hardened Concrete". Utilizing the Modified Point Count Method, petrographic analysis was performed upon 4-inch diameter polished sections obtained from the permeability cylinders. The air void system parameters reported included

total air content, spacing factor, specific surface of the air voids, average chord length, and a general description of the concrete. Further discussion of the petrography results are included in Chapter VII.

4.7 Testing Program Rationale

The testing program described in this chapter was chosen based upon established procedures and the results of previous research. Most of the concrete testing was conducted in strict accordance with established guidelines such as ASTM standards. In some areas, however, parameters or procedures were modified purposely in order to determine the effect of that change on the measured performance. This section provides the rationale behind the testing modifications made in this study.

Mixing and placing, fresh concrete testing, compressive strength testing, and deicer scaling testing was conducted in strict accordance with their respective ASTM specifications. The most significant departure from the specified standards occurred in the freeze-thaw test where the curing period was altered. ASTM C 666 specifies 14 days of moist curing followed by testing. Researchers^{8,13} have long criticized this practice as being non-representative of the natural environment and thus could give incorrect or misleading results. The arguments center around the maturity level and the saturation level of the concrete. Clearly the saturation level of the paste and the aggregate plays a critical role in freeze-thaw resistance. The reason ASTM C 666 Procedure B consistently gives more durable results than Procedure A is because the concrete has time to dry below the critical saturation level during the freezing period of each cycle.

These concepts of increased maturity and time for drying take on even greater importance when evaluating high strength, low water/cement ratio concrete. Greater maturity means more hydration which translates to less freezable water left in the concrete. Greater maturity also means lower permeability and thus less opportunities for saturation to occur. Drying time ensures that the specimens don't start the test in the saturated condition and this increases the chance for durable performance. For these reasons, the test ages and curing methods were developed for testing freeze-thaw durability and chloride ion permeability. As shown in Table 4.5, test ages were varied from a relatively short age of 7 days (typical of a normal construction sequence), to an unrealistically long age of 91 days. Within these two ages, the curing was varied to observe the benefit derived from drying the concrete prior to testing. Permeability testing was done concurrently with freeze-thaw testing in an effort to correlate these results and see what level of permeability corresponds to durable freeze-thaw performance.

Two minor modifications noted earlier in Section 4.6.4 were also made in the procedural steps taken during sample preparation for the Rapid Chloride Ion Permeability Test (RCPT). Since all permeability specimens were obtained from 4-inch by 8-inch cylinders, two slices were taken from each cylinder instead of one as prescribed in the test.

This was done for statistical purposes in order to guard against possible consolidation and placement errors affecting the data. Secondly, the specification requires the specimen to be evacuated for three hours, covered with deaerated water, and then evacuated for an additional hour. This procedure resulted in water entering the vacuum oil with each test which became expensive to change each time. For that reason, the vacuum was kept sealed over the covered specimen for the last hour without the pump operating. This alteration to the preparation was tested first to determine its effect on the permeability data and these effects were minimal. This was substantiated by a research study conducted by Mosbacher⁴⁷ who intentionally varied several of the preparation parameters on companion specimens and found that the test procedure was relatively insensitive to changes in the vacuum saturation and soaking phases of the test.

CHAPTER V PERMEABILITY RESULTS AND ANALYSIS

5.1 Permeability Testing

The testing procedure used to measure the permeability of the concrete was the Rapid Chloride Ion Permeability Test (RCPT) also known as AASHTO T-277. Permeability tests were conducted on each mixture for each of the test ages and curing conditions shown in Table 4.5. The results of these tests can be found in Appendix D. Figure 5.1 shows the organization of the testing which was divided into three phases. This chapter presents and analyzes the test results with respect to the effect of air entrainment, water/cement ratio, curing, coarse aggregate absorption, and fly ash, silica fume, and cement content on the permeability of high strength concrete.

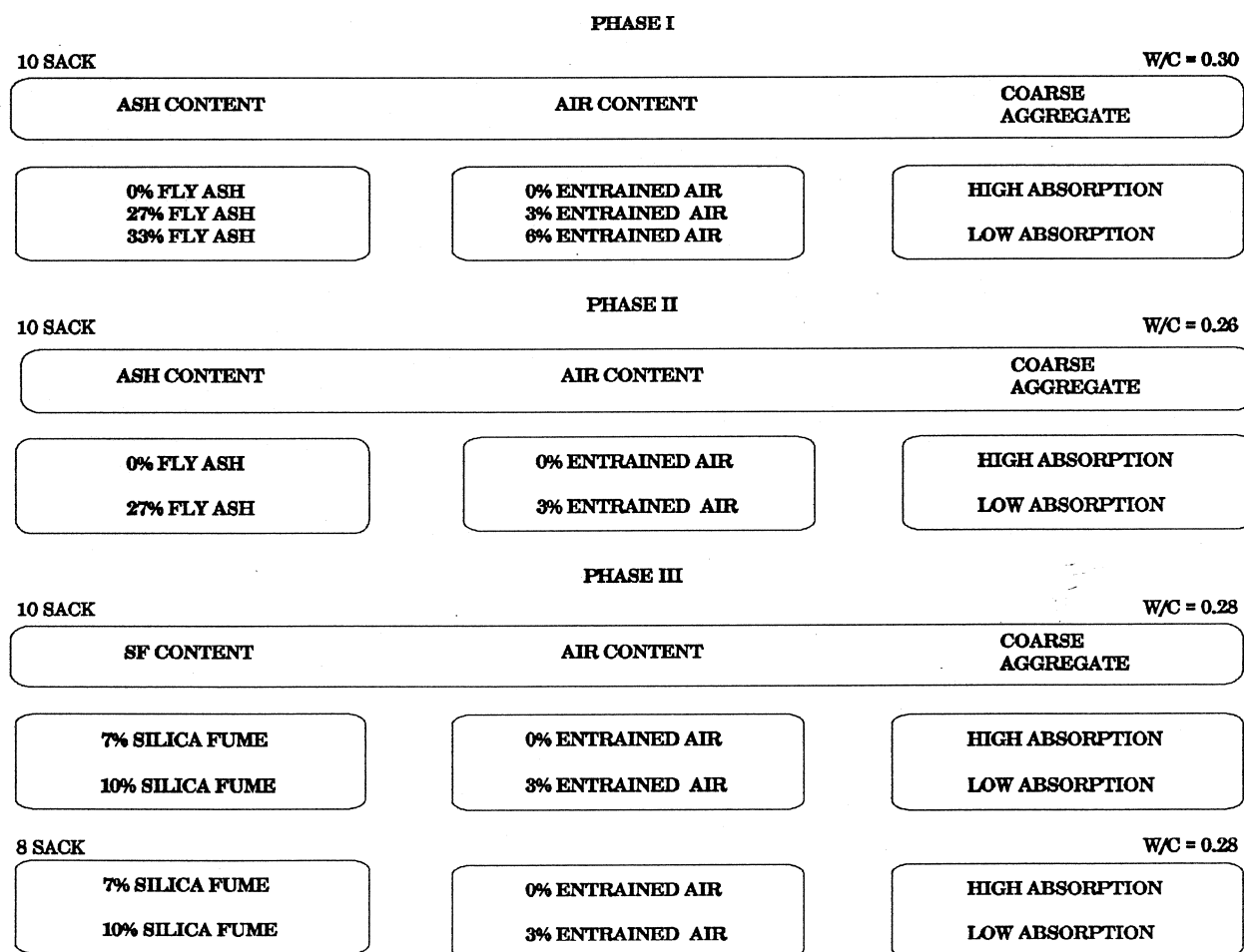


Figure 5.1 Organization of the Testing Program by Phase.

The AASHTO T-277 test does not give an absolute value of the permeability of concrete but is by design an indirect test which can be used for comparing the resistance to penetration of chloride salts of different concrete mixtures. Table 5.1 shows a table of values taken from AASHTO T-277 which gives a qualitative rating to the concrete based upon the numerical value of coulombs passed through the sample during the test. Due to the fact that all of the mixtures tested in this study were high strength concrete, the permeability values measured were expected to be low and the differences among concretes expected to be small. The permeability test results showed that most of the Phase I and II mixtures tested in the 'Moderate' and 'High' ranges at the early ages and in the 'Low' category after 91 days of moist curing. The Phase III silica fume mixtures tested in the 'Low' and 'Very Low' ranges at all test ages.

Table 5.1 Permeability Ratings According to AASHTO T-277

RELATIVE PERMEABILITY	CHARGE PASSED (Coulombs)	TYPE OF CONCRETE
High	> 4000	High water/cement ratios (≥ 0.60)
Moderate	2000 to 4000	Moderate water/cement ratios (0.40 to 0.50)
Low	1000 to 2000	Low water/cement ratios "Iowa" dense concrete
Very Low	100 to 1000	Latex modified concrete Internally sealed concrete
Negligible	< 100	Polymer impregnated concrete Polymer concrete

5.2 Effect of Air Entrainment

In normal strength concrete, the addition of entrained air typically results in a decrease in concrete permeability because the entrained air bubbles create discontinuities in the capillary pores within the paste. It is through the continuous capillary system that most fluids travel through concrete and the entrained air bubbles block these capillaries thus reducing the permeability of the concrete. As shown in Figure 2.3, the capillary porosity of the high strength, low water/cement ratio mixtures cast in this study, was very low from the outset so adding air entrainment was not expected to have a significant effect on the permeability of the mixtures tested.

Figures 5.2 through 5.7 show for each curing condition the ratio of the permeabilities of identical Phase I and II ash mixtures with the only difference being the presence of entrained air. In 40 percent of these mixtures, the specimen with entrained air had higher permeability and in the remaining 60 percent the entrained air specimen had lower permeability. Similar results were found when the Phase III silica fume mixtures were

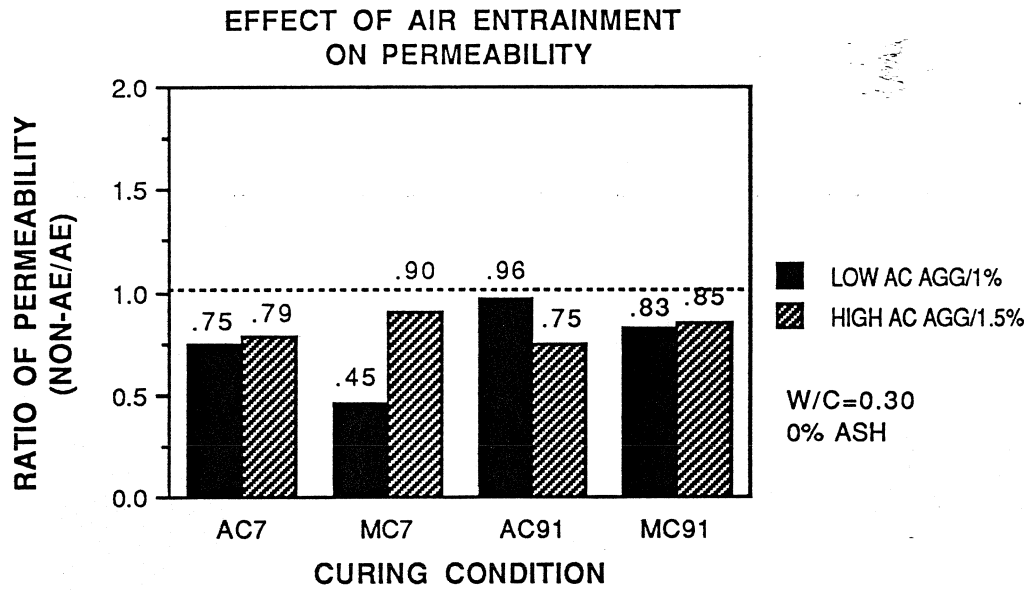


Figure 5.2 Effect of Air entrainment on Permeability.

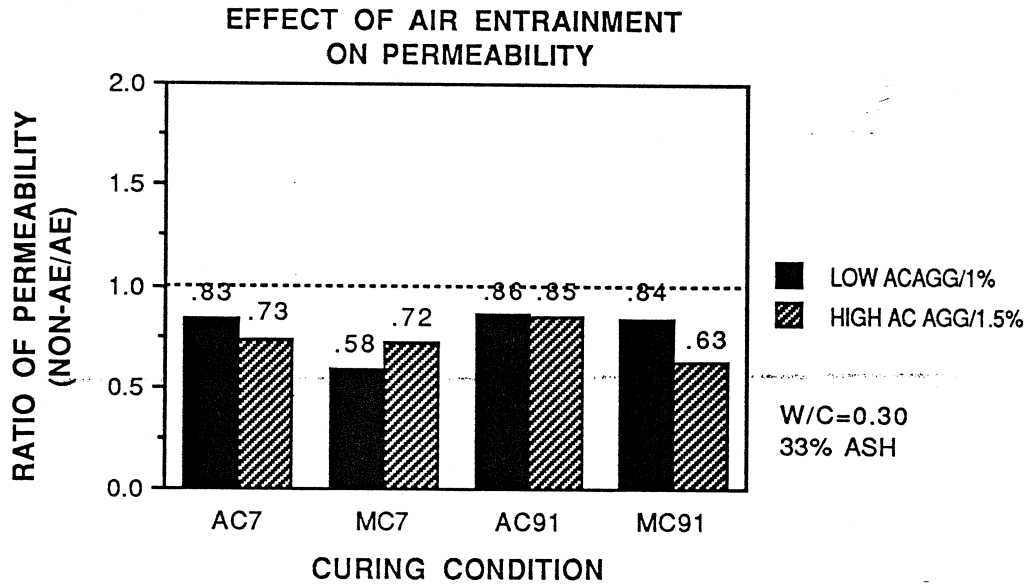


Figure 5.3 Effect of Air Entrainment on Permeability

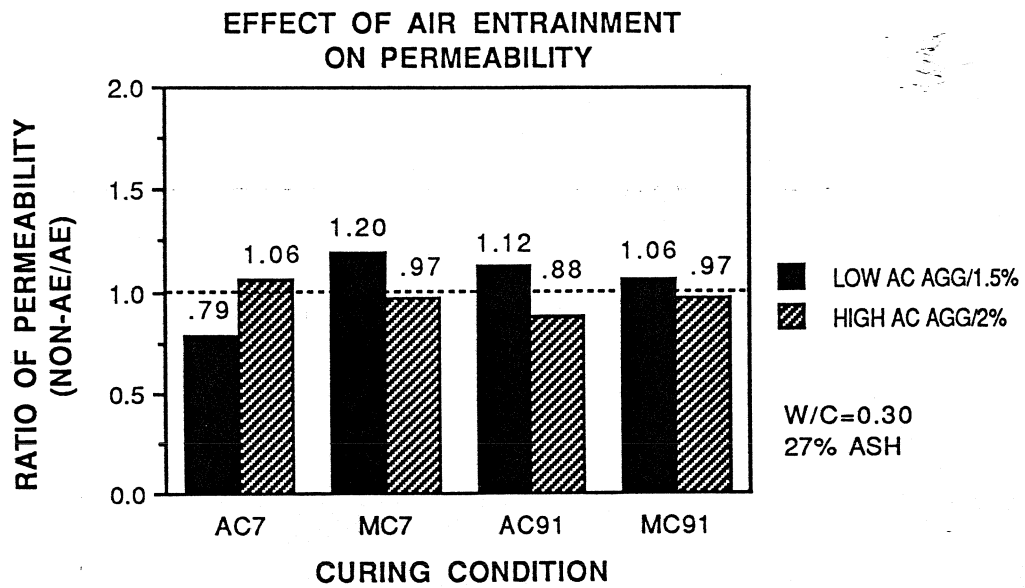


Figure 5.4 Effect of Air Entrainment on Permeability

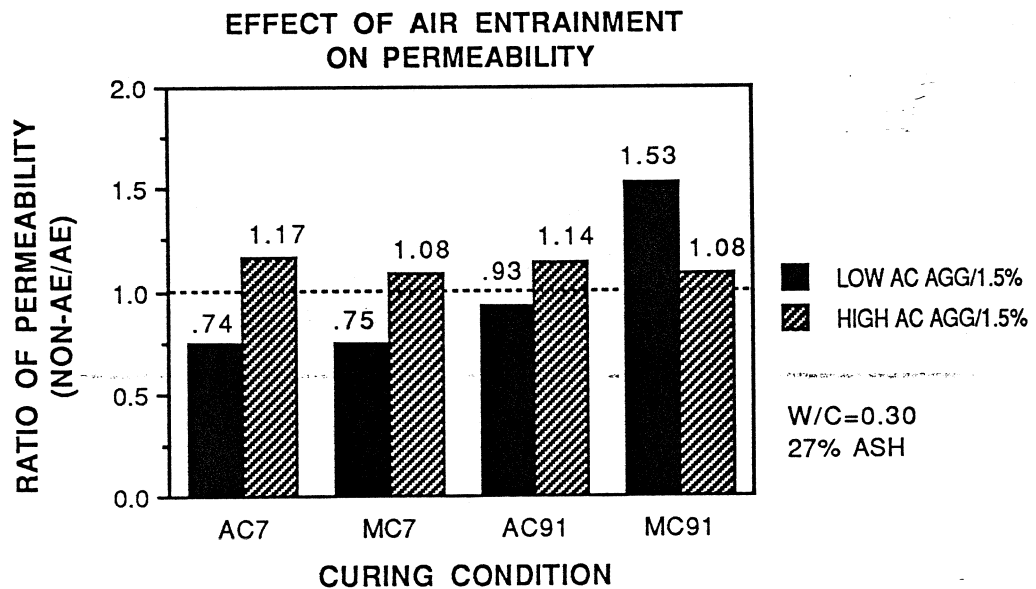


Figure 5.5 Effect of Air Entrainment on Permeability

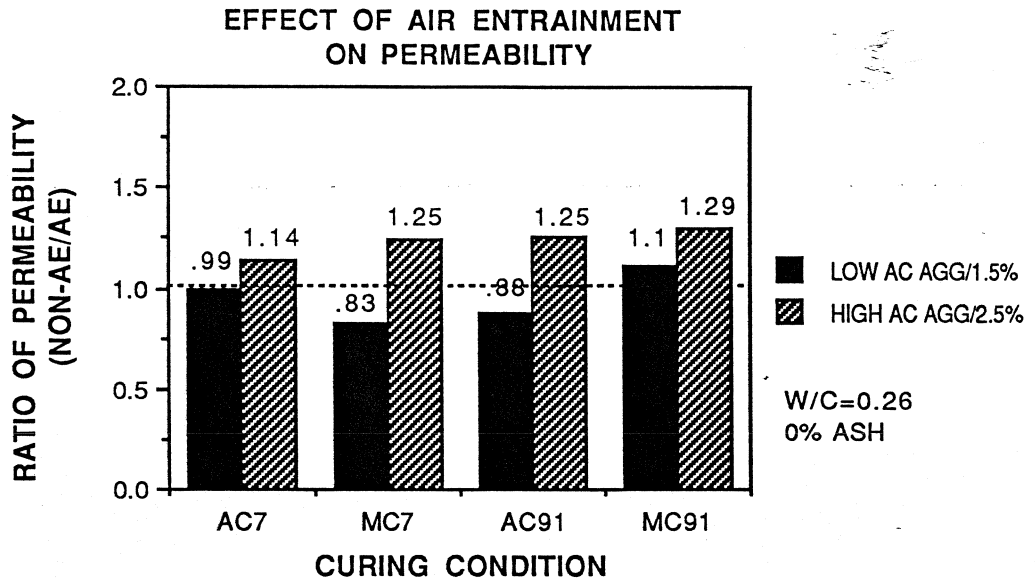


Figure 5.6 Effect of Air Entrainment on Permeability

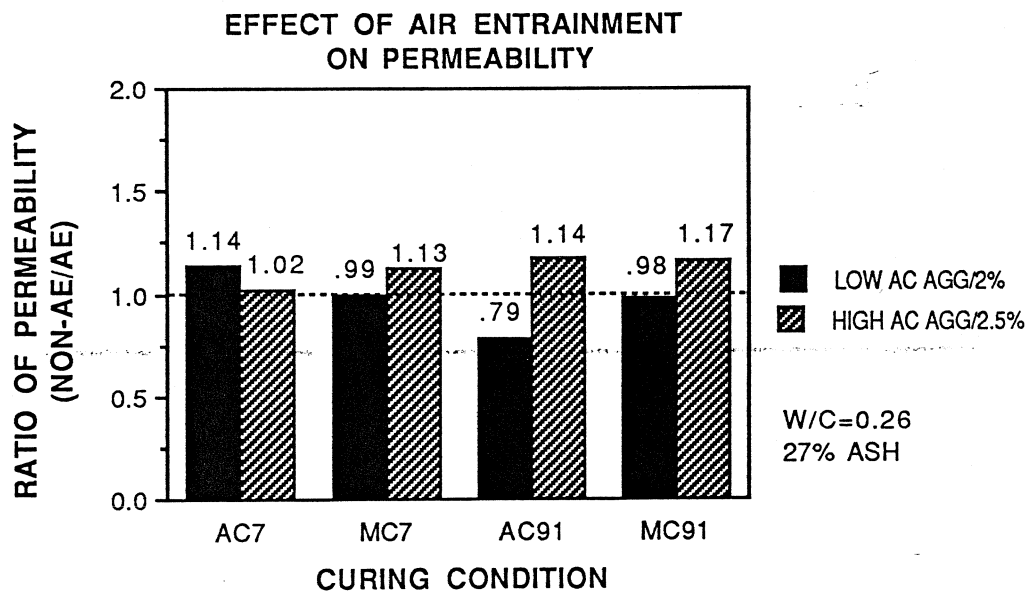


Figure 5.7 Effect of Air Entrainment on Permeability

compared. As shown in Figures 5.8 through 5.11, comparisons made between air entrained and non-air entrained specimens containing silica fume resulted in 52 percent of the air entrained specimens having higher permeability and 48 percent having lower permeability. From this evaluation it is clear that for high strength concrete having low water/cement ratios, the addition of entrained air had no effect on the permeability of the concrete.

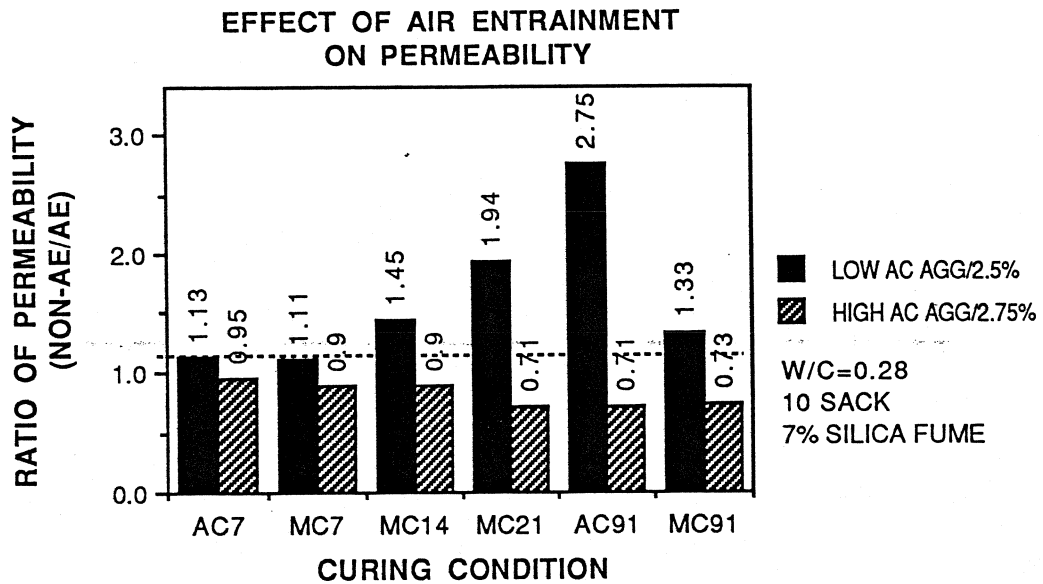


Figure 5.8 Effect of Air Entrainment on Permeability

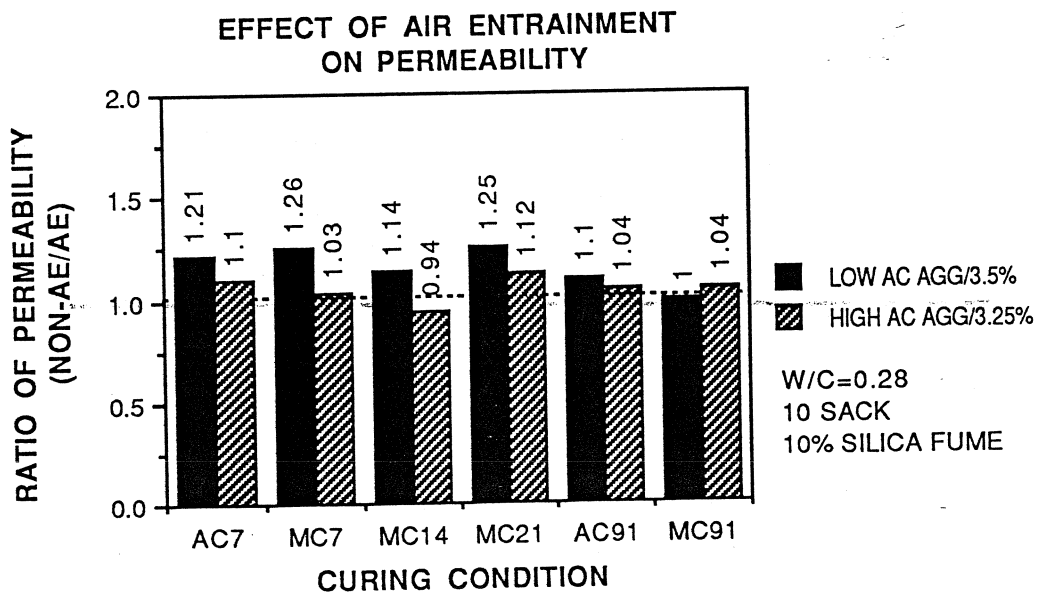


Figure 5.9 Effect of Air Entrainment on Permeability

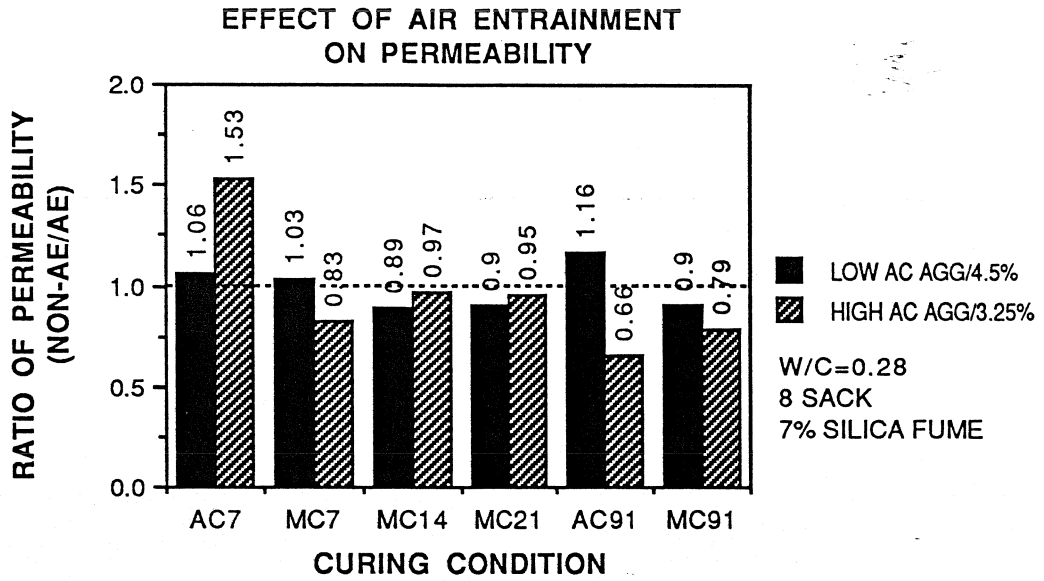


Figure 5.10 Effect of Air Entrainment on Permeability

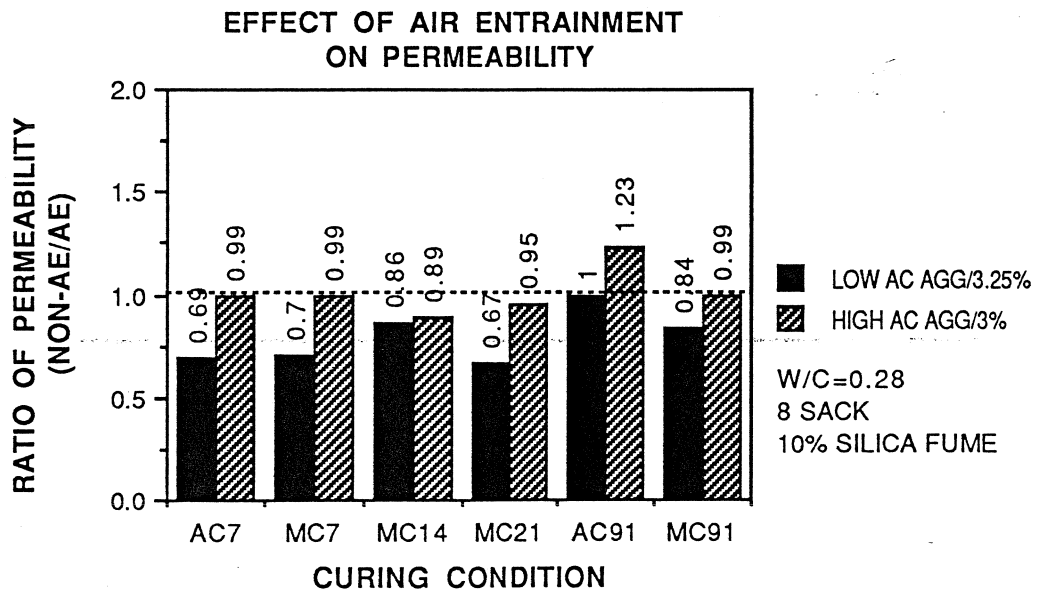


Figure 5.11 Effect of Air Entrainment on Permeability

5.3 Effect of Water/Cement Ratio

The water/cement ratios used in this study were 0.30, 0.28, and 0.26 for the fly ash mixtures in Phases I and II and 0.28 for the silica fume mixtures cast in Phase III. Throughout the study in mixtures where fly ash or silica fume were used, the water/cement ratio was calculated based upon the total weight of cement plus fly ash or cement plus silica fume. All further references in the study made to water/cement ratio include the weight of all cementitious materials in the mixture. Previous research^{73,75} has shown that lowering the water/cement ratio is the single most effective way to reduce the permeability of concrete. This is because lowering the amount of mix water reduces the volume of capillary voids in the hardened concrete. For the mixtures cast in this study, the volume of capillary voids was very low due to the low water/cement ratios chosen.

Figures 5.12 through 5.15 compare the effect of changing the water/cement ratio on the permeability of concrete mixtures cast without air entrainment. Except for the 7-day old test specimens in Figure 5.13, the reductions in permeability of the concrete without fly ash were fairly uniform for all the curing conditions averaging between 12 percent at 7 days and 30 percent at 91 days. When fly ash was added to the mixtures the average reduction in the permeability of the concrete at 7 days remained unchanged however the reduction at 91 days averaged 45 percent. The results clearly illustrate that lowering the water/cement ratio reduces the permeability of the concrete especially at later ages when fly ash is present. Figures 5.16 through 5.19 show the results of testing the previous mixtures proportioned with small amounts of entrained air. The permeability reductions for these mixtures averaged 21 percent at 7 days and 54 percent at 91 days of age.

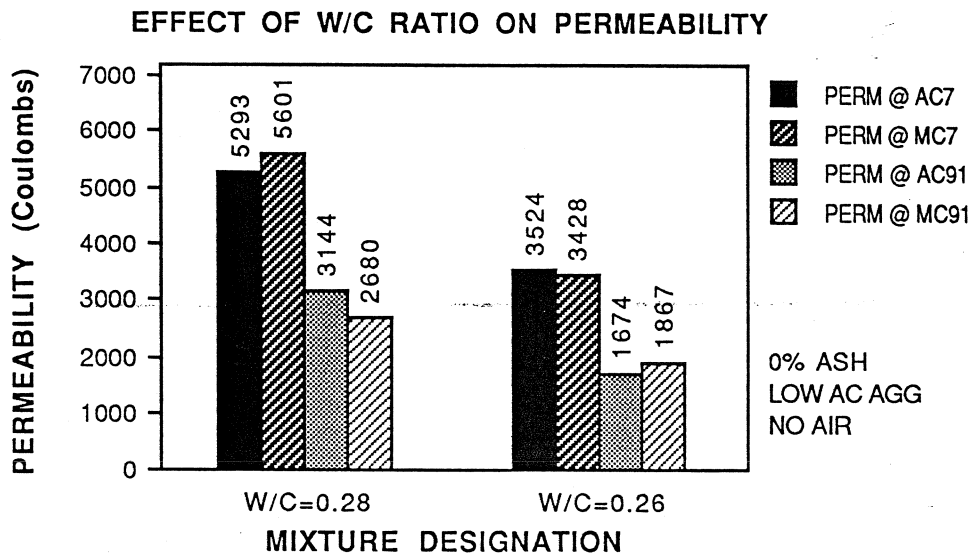


Figure 5.12 Effect of Water/Cement Ratio on Permeability

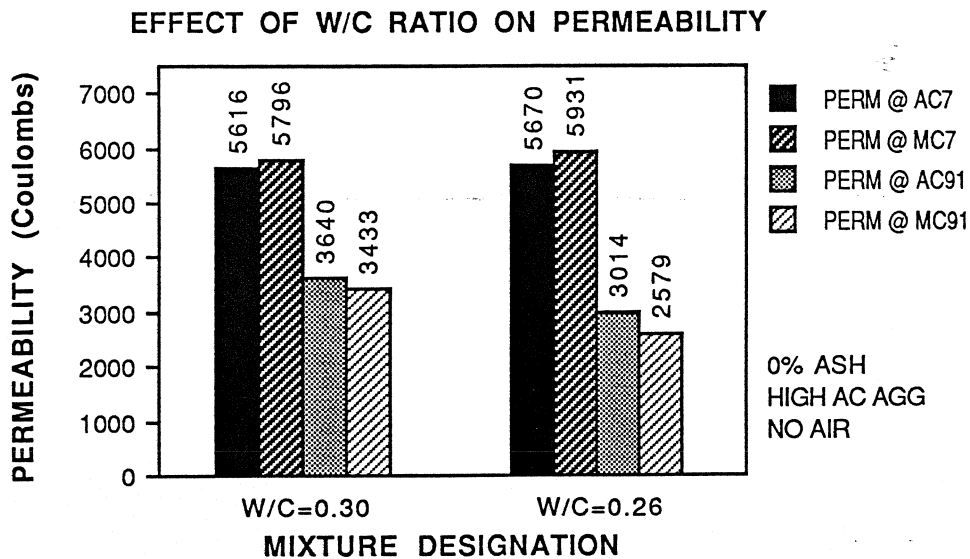


Figure 5.13 Effect of Water/Cement Ratio on Permeability

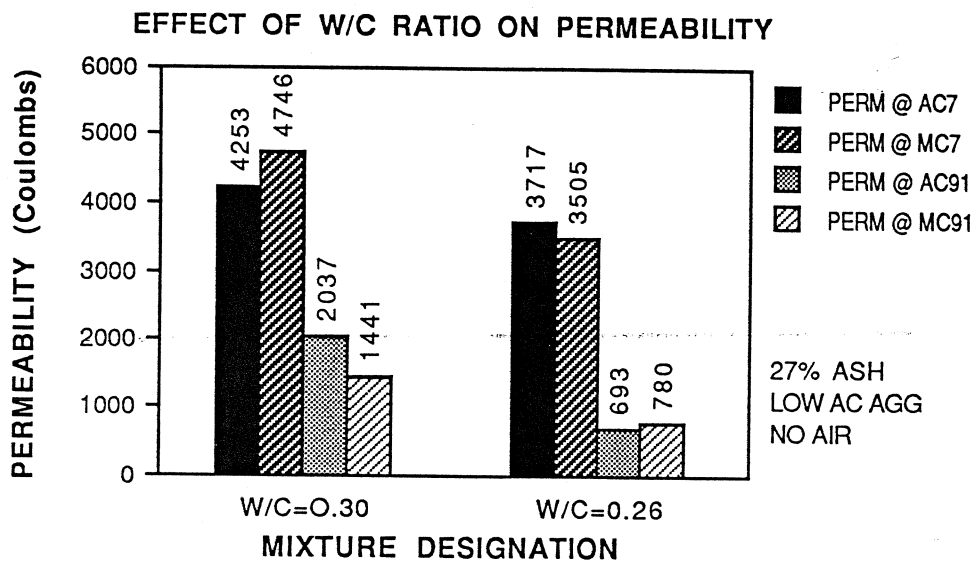


Figure 5.14 Effect of Water/Cement Ratio on Permeability

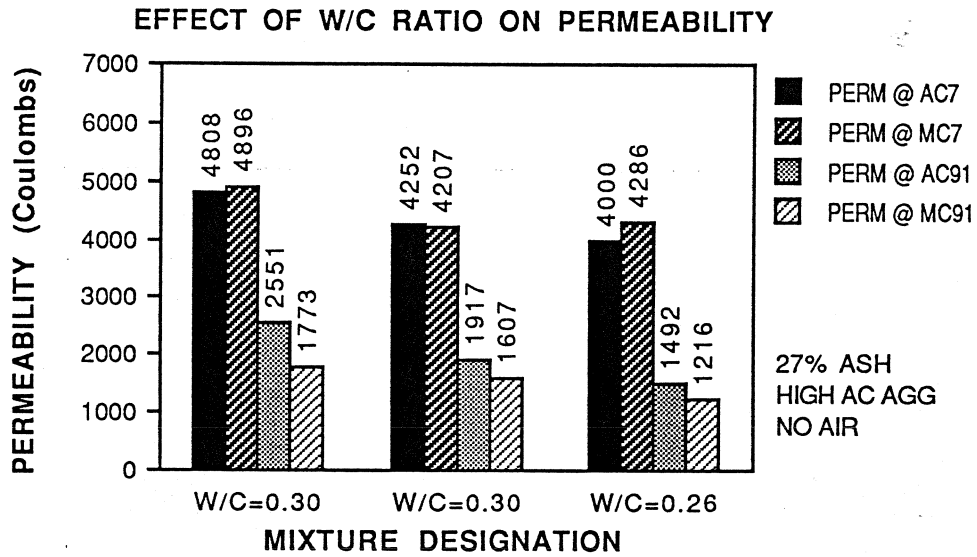


Figure 5.15 Effect of Water/Cement Ratio on Permeability

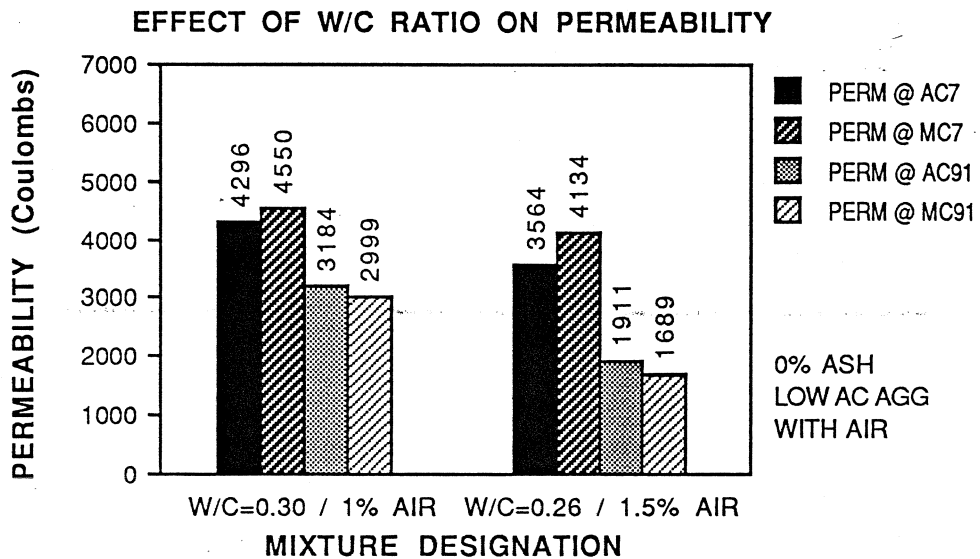


Figure 5.16 Effect of Water/Cement Ratio on Permeability

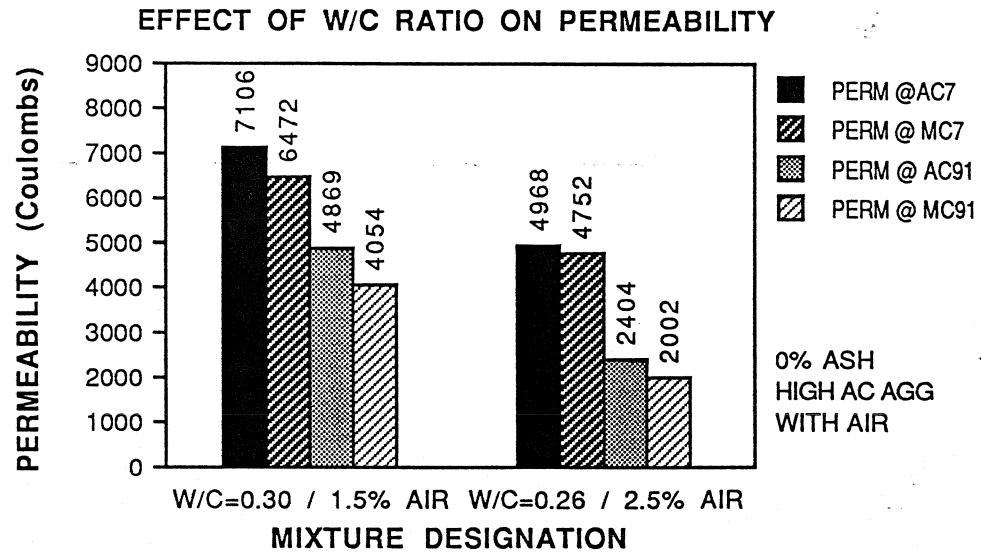


Figure 5.17 Effect of Water/Cement Ratio on Permeability

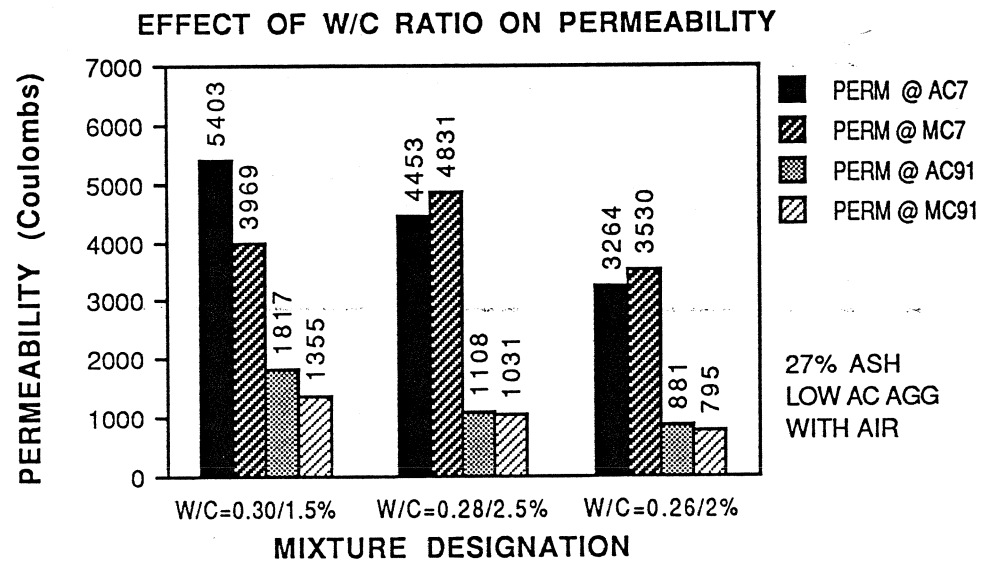


Figure 5.18 Effect of Water/Cement Ratio on Permeability

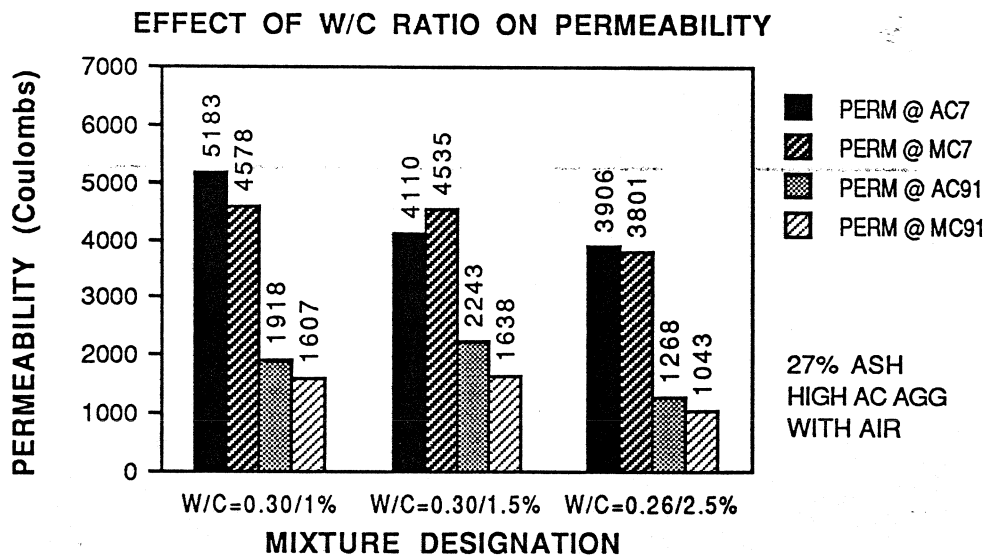


Figure 5.19 Effect of Water/Cement Ratio on Permeability

It can be concluded that lowering the water/cement ratio from 0.30 to 0.26 by weight results in reductions in concrete permeability of 10 to 25 percent at early ages but can cause 40 to 60 percent reductions at 91 days of age if moist curing is provided.

5.4 Effect of Curing

In order to illustrate the effect of curing on the permeability of concrete mixtures with so many different constituents, a reference point was established for each mixture. The permeability was measured for each mixture at 7 days of age after 4 days moist curing followed by 3 days air curing. This reference value was then used to evaluate the reduction in permeability at later ages for each curing condition. In this manner, the change in permeability due only to the different curing condition could be evaluated and compared among mixtures regardless of individual material differences. Average reference values are listed in Table 5.2 for all mixtures tested. Shown in the table are the average ratios of the permeability measurement for each curing condition divided by the reference permeability thus showing how the permeability changed with continued curing.

From the table it is clear that extending the moist curing period from 4 to 7 days did not significantly reduce the permeability of the concrete regardless of water/cement ratio or the presence of a mineral admixture. The data clearly shows the beneficial effect mineral admixtures such as fly ash and silica fume have in reducing the concrete permeability at later ages as evidenced the permeability ratios at 91 days of age.

Table 5.2 Effect of Curing on Permeability

Phase (w/c)	Description	Baseline Permeability Moist Cured 4 Days* (coulombs)	Ratio of PERMEABILITY ** BASELINE PERMEABILITY when moist cured for				
			7 Days	14 Days	21 Days	28 Days	91 Days
I (0.30)	w/o fly ash	5409	0.93	n/a	n/a	0.71	0.61
	with fly ash	4645	1.03	0.79	0.60	0.51	0.34
II (0.26)	w/o fly ash	4431	1.03	0.70	0.66	0.51	0.46
	with fly ash	3722	1.02	n/a	n/a	0.29	0.26
III	Silica Fume	775	0.92	0.60	0.45	0.32	0.37

* Specimens tested at 7 days after 3 days of air curing.

** Specimens tested at the end of the moist curing period except for the 28 day specimens which were tested at 91 days after 63 days of air curing.

5.5 Effect of Coarse Aggregate

Since the absorption of the coarse aggregate has been shown^{25,66} to have a significant effect on the freeze-thaw resistance of concrete, the permeability results were studied to determine the effect of coarse aggregate absorption on concrete permeability. Figures 5.20 and 5.21 compare the effect of coarse aggregate absorption on the permeability of non-fly ash mixtures at water/cement ratios of 0.30 and 0.26. The results show a significant increase in permeability at all ages and for all curing conditions when the concrete is made with the high absorption aggregate. The results obtained after substituting fly ash for 27 percent of the cement by weight at both water/cement ratios are shown in Figures 5.22 and 5.23. The mixtures containing low absorption aggregate were clearly less permeable for every curing condition however the differences at 7 days were not as large as when the mixtures contained no fly ash. At 91 days this difference sometimes reached 50 percent.

Figures 5.24 through 5.27 compare the effect of coarse aggregate absorption on the permeability test results for the air entrained mixtures. The graphs clearly show that the addition of entrained air did not offset the detrimental effect that the high absorption coarse aggregate had on the concrete permeability. For all curing conditions, the low absorption aggregate concrete was less permeable than the concrete cast with the high absorption aggregate.

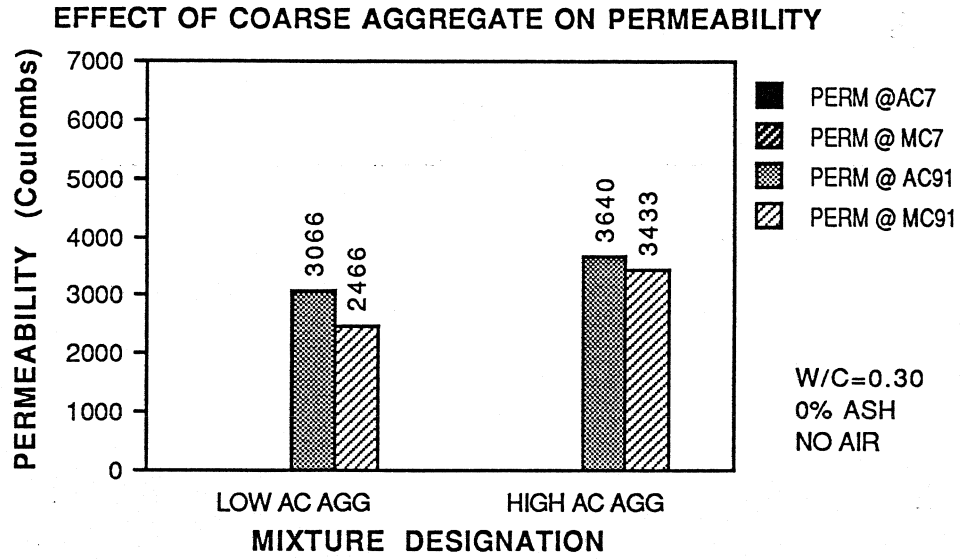


Figure 5.20 Effect of Coarse Aggregate on Permeability

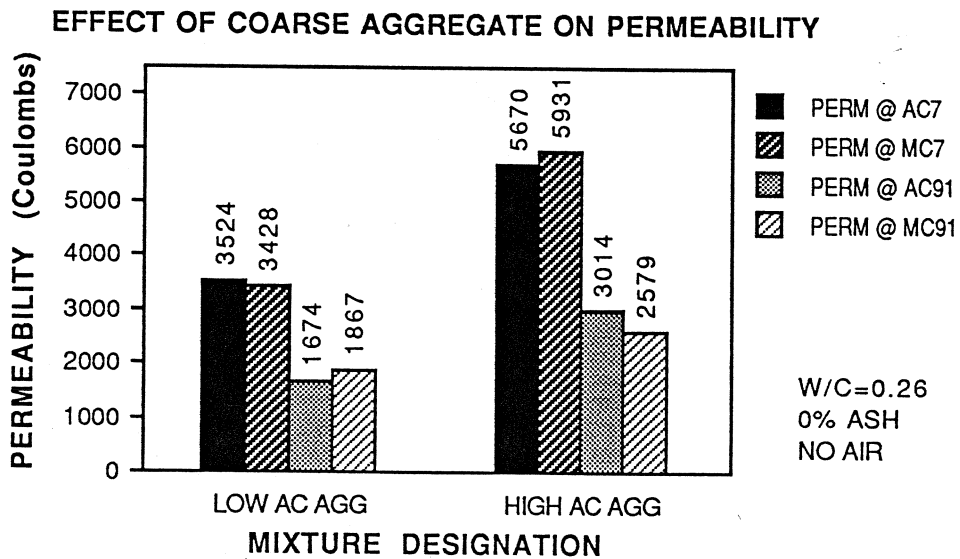


Figure 5.21 Effect of Coarse Aggregate on Permeability

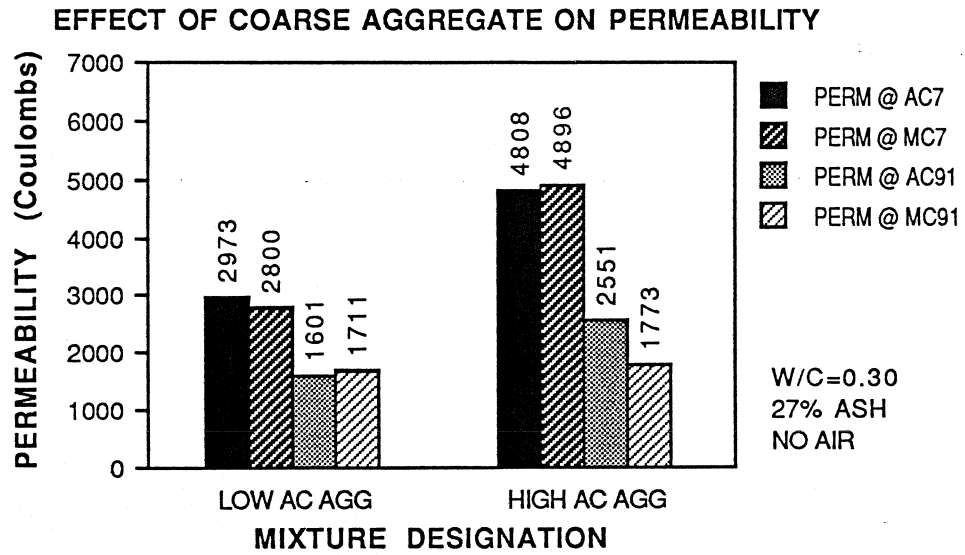


Figure 5.22 Effect of Coarse Aggregate on Permeability

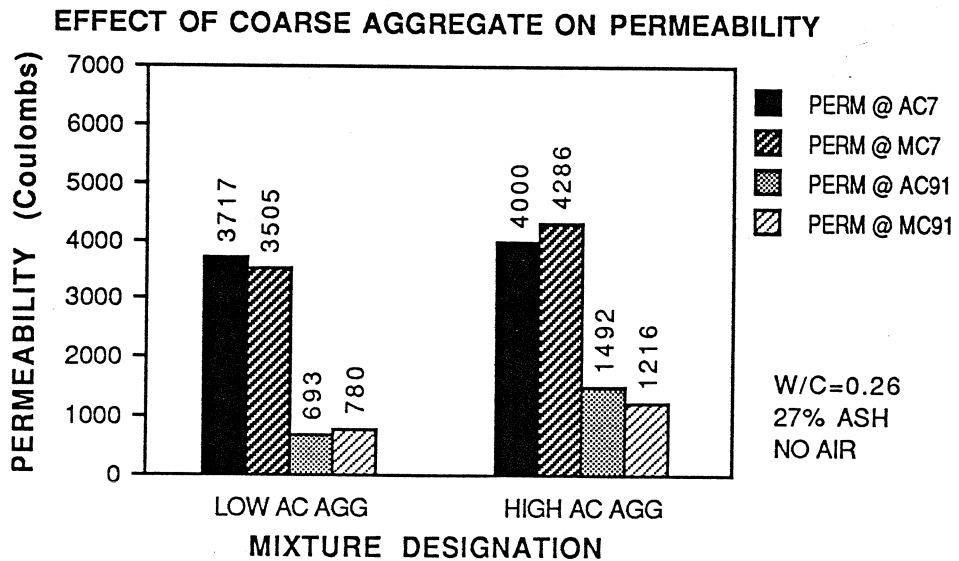


Figure 5.23 Effect of Coarse Aggregate on Permeability

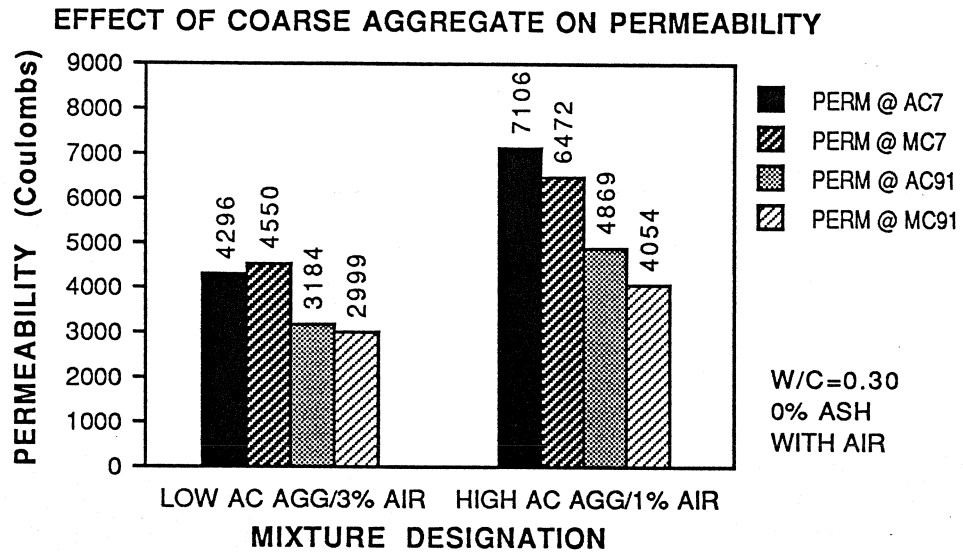


Figure 5.24 Effect of Coarse Aggregate on Permeability

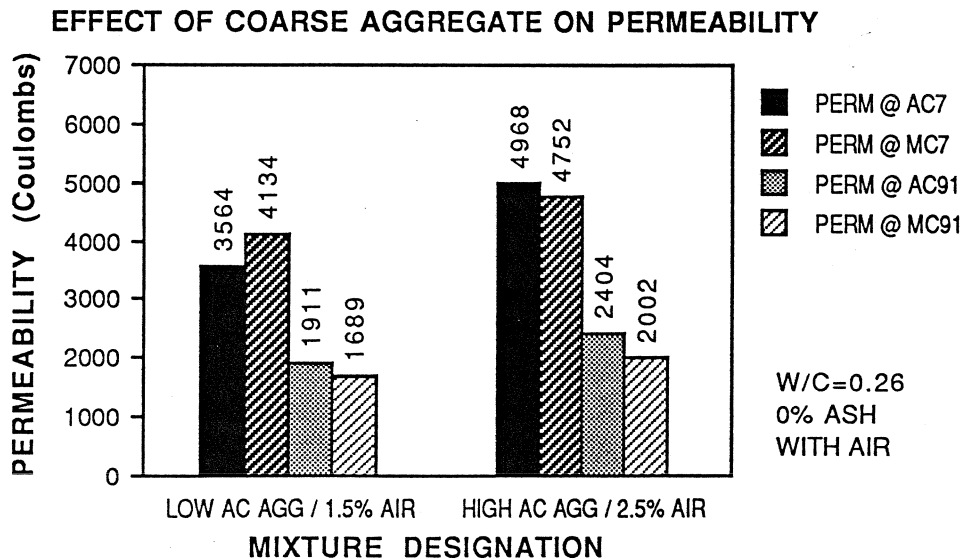


Figure 5.25 Effect of Coarse Aggregate on Permeability

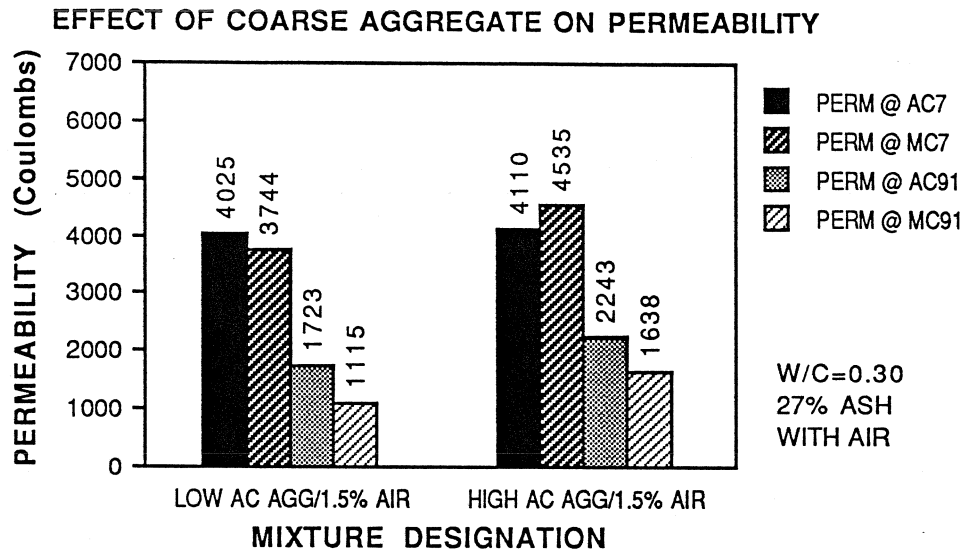


Figure 5.26 Effect of Coarse Aggregate on Permeability

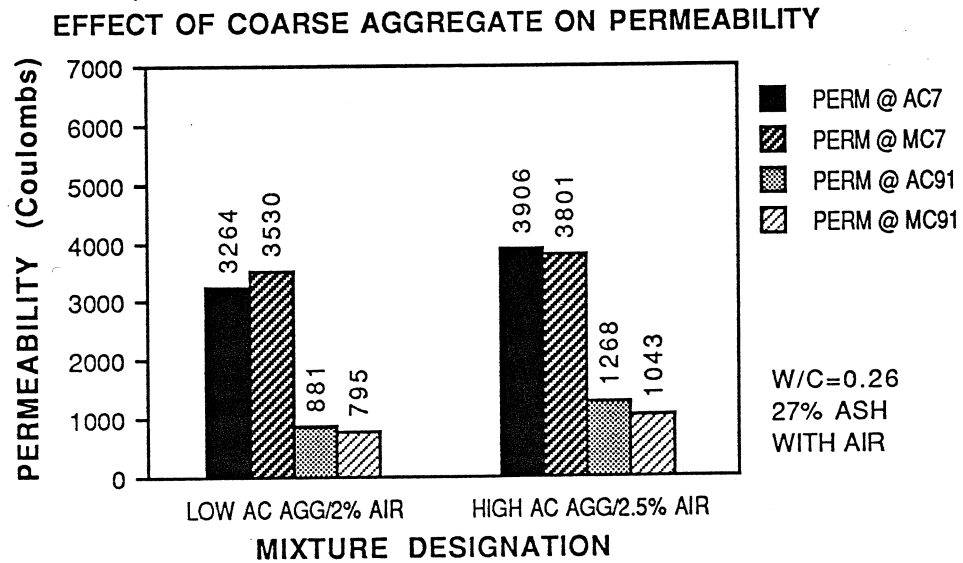


Figure 5.27 Effect of Coarse Aggregate on Permeability

These results highlight the importance of aggregate selection on producing low permeability concrete. To be durable, concrete must be able to control external sources of water which can eventually saturate the paste and cause freeze-thaw damage. The data show that regardless of initial water/cement ratio or the presence of entrained air, high coarse aggregate absorption can significantly increase concrete permeability and this could result in low freeze-thaw resistance.

5.6 Effect of Fly Ash

Much has been written^{43,44} describing the effect that the addition of fly ash has on concrete properties including permeability. Fly ash consists of fine particles of modified silicate glass that are formed after burning powdered coal. The process by which fly ash improves the permeability of concrete is both physical and chemical. The physical process is related to the particle size distribution of the solids in the mixture. The fine fly ash particles pack in between the larger fine aggregate pieces and hydrating cement grains during hydration. This process is called 'pore refinement' and results in denser concrete with less capillary channels and thus lower permeability. The chemical process is the pozzolanic reaction in which the amorphous, reactive silica phase within the fly ash combines with the calcium hydroxide created during hydration of the cement and forms additional calcium silicate hydrate. The process by which the large calcium hydroxide crystals are replaced in the matrix by the highly amorphous calcium silicate hydrates is called 'grain refinement'.

Fly ashes are classified by ASTM as either Class C or Class F depending upon the amount of calcium, silica, alumina, and iron oxides in the ash. High calcium ashes possess some cementitious properties in addition to their pozzolanic capability due to their high calcium content. Because of this, Class C fly ashes contribute calcium hydroxide to the matrix as well as remove it and thus are not as efficient at lowering permeability as Class F ashes which have less calcium oxide but more reactive silica. Class C ashes are typically preferred for use in high strength concrete because they contribute many of the benefits of fly ash without the loss in strength that occurs with the use of Class F fly ash. An ASTM Class C fly ash was used throughout this program of study.

The test results presented here verified the findings presented above especially with regard to permeability to chloride ions. Concrete permeability is directly related to concrete density which is dependent upon the quantity of hydrated cementitious material in the concrete. Compared to a non-fly ash mixture having the same total amount of cementitious material, at early ages (1 to 3 days) the amount of cementitious hydrates will be lower in a mixture where a portion of the cement has been replaced by Class C fly ash. At later ages, the pozzolanic reaction proceeds and eventually results in more cementitious hydrates than would have been possible had the fly ash been absent. The results obtained in this study showed that replacement of the cement with ASTM Class C fly ash resulted in equal

or lower permeability at 7 days and in significant reductions in permeability at 91 days for all curing conditions.

Figure 5.28 compares the permeability test results for three mixtures made with low absorption coarse aggregate, a water/cement ratio of 0.30, and varying amounts of fly ash. The 7-day results for the non-ash mixture were not reported due to equipment failure however the 91 day permeability results clearly show the reduction in permeability provided by the fly ash. Figure 5.29 shows the same test results for similar mixtures cast with the high absorption coarse aggregate. In every case, the addition of fly ash resulted in significant reductions in permeability when compared to the mixtures without fly ash. Figures 5.30 and 5.31 compare the effect of fly ash on the permeability of the non-air entrained, 0.26 water/cement ratio mixtures. The data shows that at 7 days, the fly ash mixtures are similar in permeability to the non-fly ash mixtures and much lower at 91 days as the pozzolanic reaction progresses.

The data conclusively showed that the addition of ASTM Class C fly ash in the amounts used in this study significantly lowered the chloride ion permeability of the concrete at both early and late ages regardless of water/cement ratio or coarse aggregate absorption. No significant rise in early age permeability was seen in the fly ash mixtures compared to non-fly ash mixtures due to the cementitious properties of the high calcium ASTM Class C fly ash used. At later ages the pozzolanic reaction resulted in large reductions in permeability. Although not shown graphically, the effect of fly ash on permeability was also examined for mixtures containing entrained air and similar results were obtained.

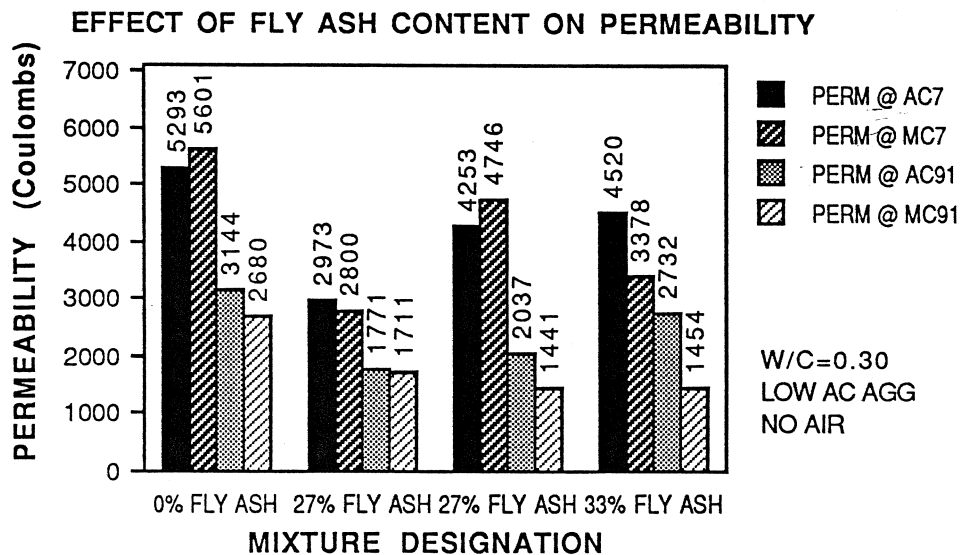


Figure 5.28 Effect of Fly Ash Content on Permeability

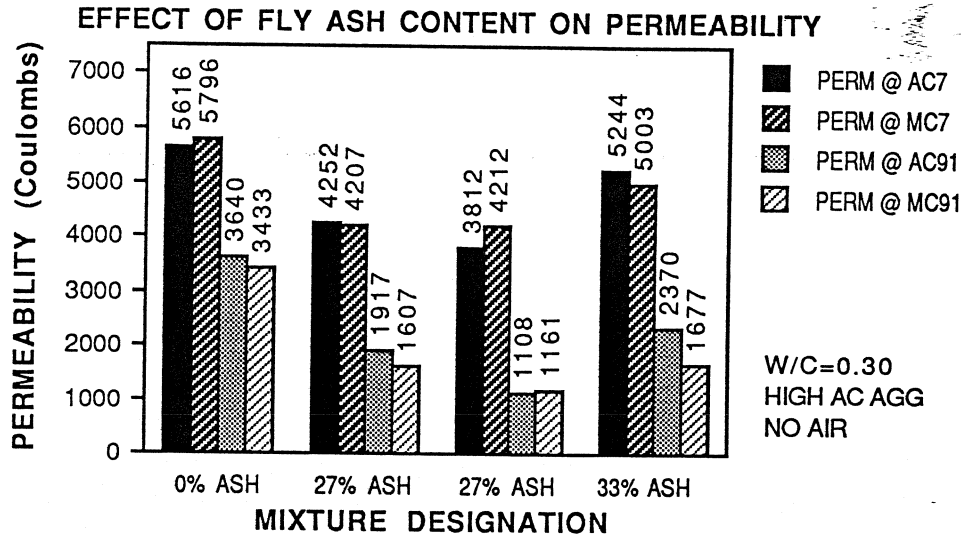


Figure 5.29 Effect of Fly Ash Content on Permeability

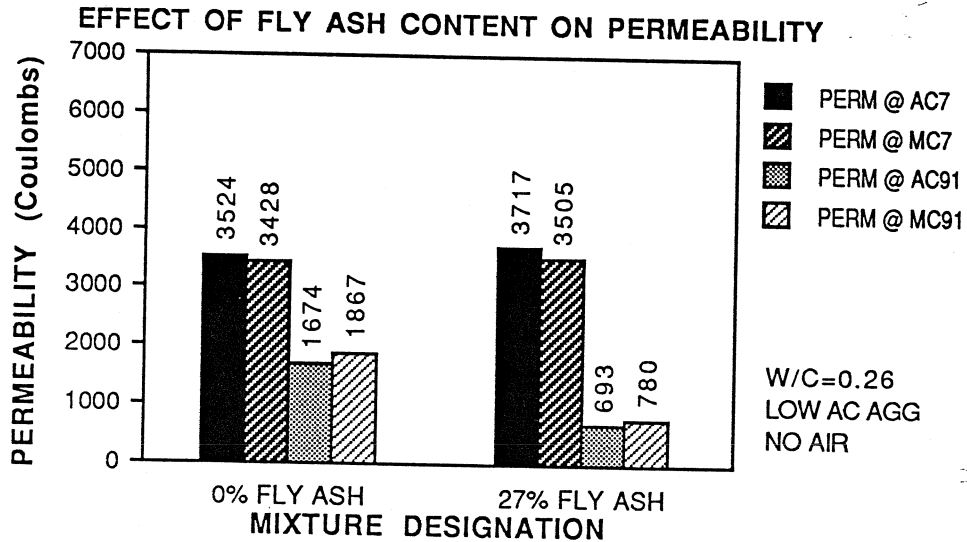


Figure 5.30 Effect of Fly Ash Content on Permeability

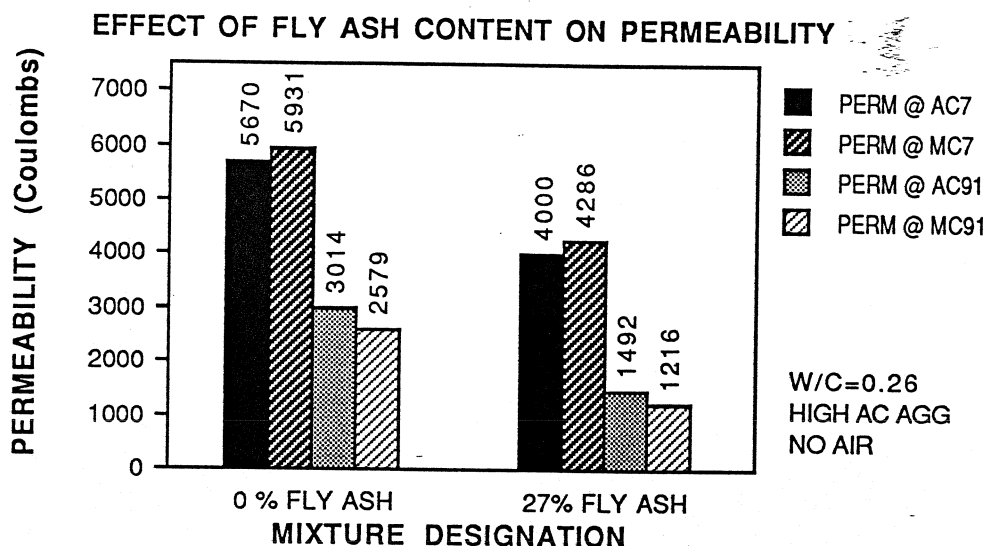


Figure 5.31 Effect of Fly Ash Content on Permeability

5.7 Effect of Silica Fume

The effect of silica fume on concrete permeability has been researched extensively in the past decade and its ability to prevent saturation of concrete exposed to external water is well documented⁶⁰. Research reviewed herein^{14,35,37} has also shown that very low permeability has a detrimental effect on the freeze-thaw resistance of concrete by restricting the movement of freezable water and thus resulting in increased pressures in the paste. In this study, silica fume was added to the concrete at levels of 7 and 10 percent by weight of cement. During this phase of the study, two additional permeability cylinders were cast from each mixture and tested after moist curing for 14 and 21 days.

5.7.1 Effect of Silica Fume Content. Figures 5.32 through 5.35 compare the permeability test results showing the effect of silica fume content for the mixtures with and without air and using both coarse aggregates. The cement content was held constant at 940 lb/cy. The results show that the concrete permeability was not affected by the silica fume content for the percentages of silica fume selected. The effect of silica fume content on permeability was also studied for mixtures having a cement content of 752 lbs/cy as shown in Figures 5.36 through 5.39. At this lower cement content, the results showed that at 7 days the silica fume content had no effect on the permeability of the concrete. After 7 days however, the concrete containing 10 percent silica fume exhibited average permeability values that were 30 percent less than identical concrete mixtures containing 7 percent silica fume.

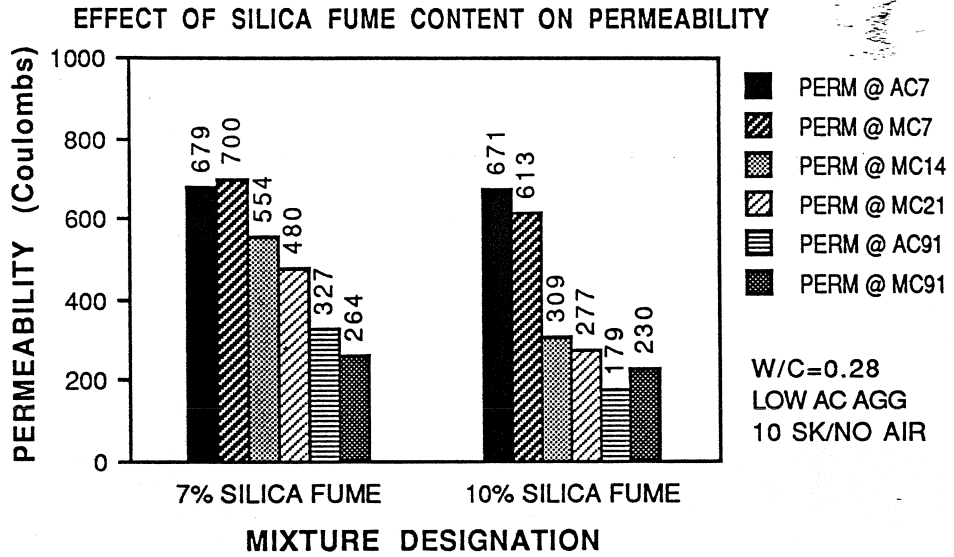


Figure 5.32 Effect of Silica Fume Content on Permeability

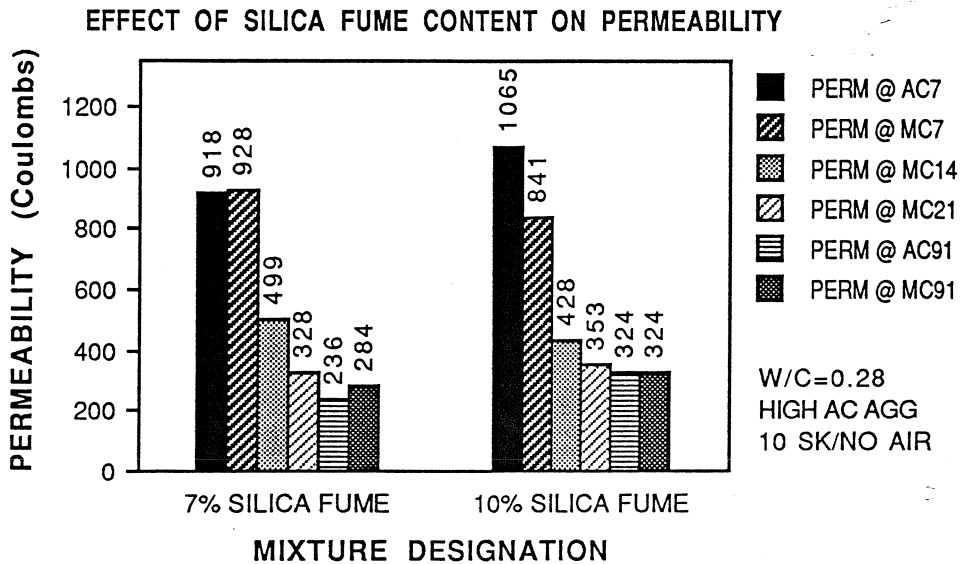


Figure 5.33 Effect of Silica Fume Content on Permeability

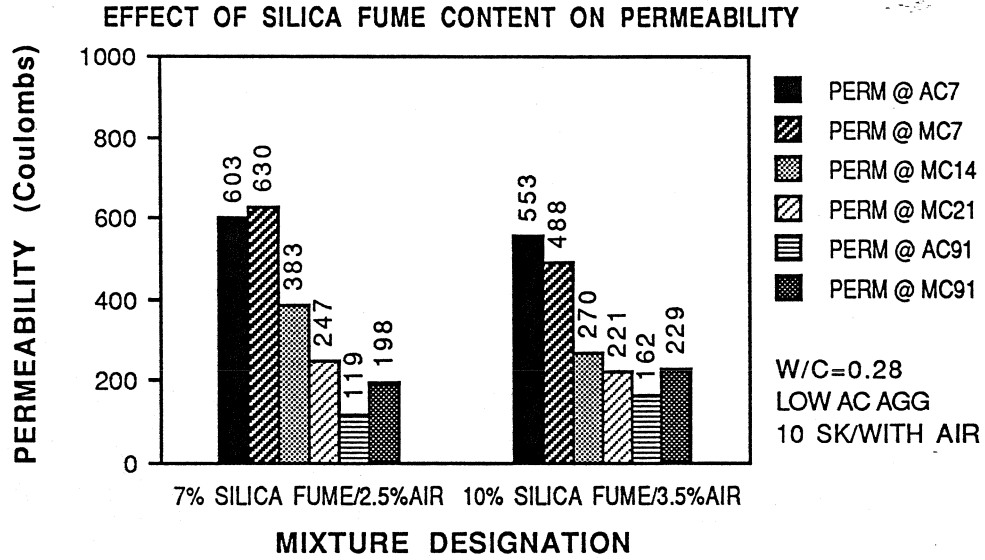


Figure 5.34 Effect of Silica Fume Content on Permeability

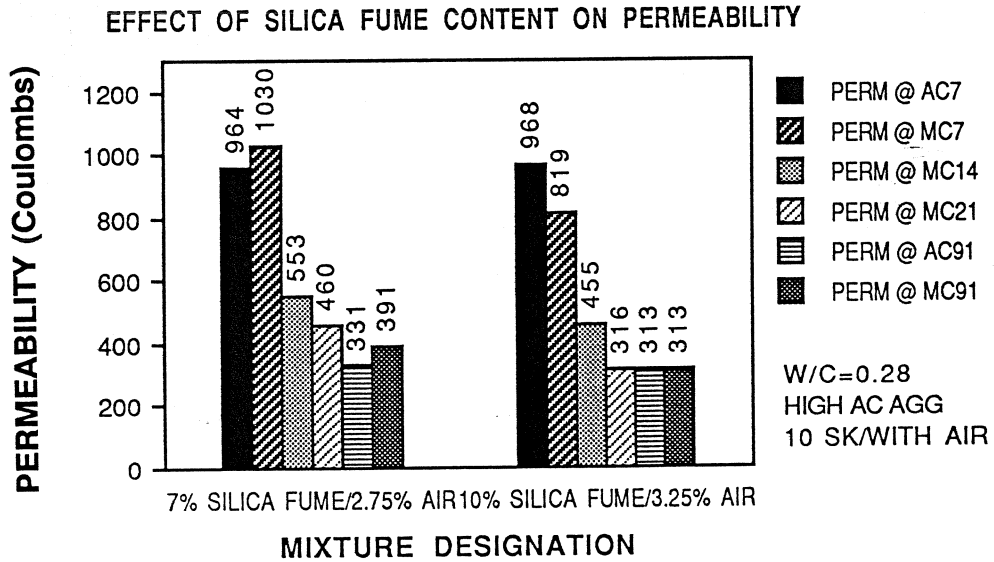


Figure 5.35 Effect of Silica Fume Content on Permeability

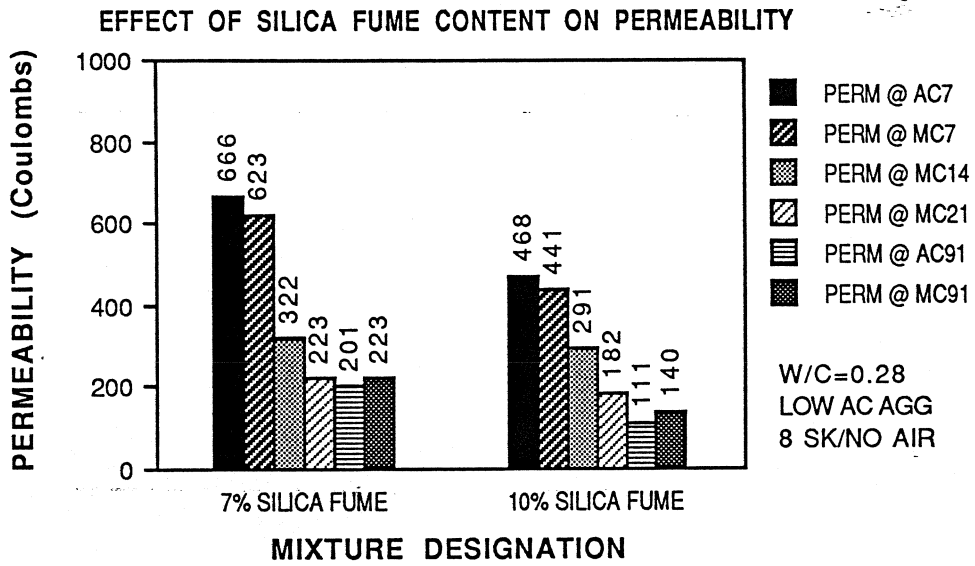


Figure 5.36 Effect of Silica Fume Content on Permeability

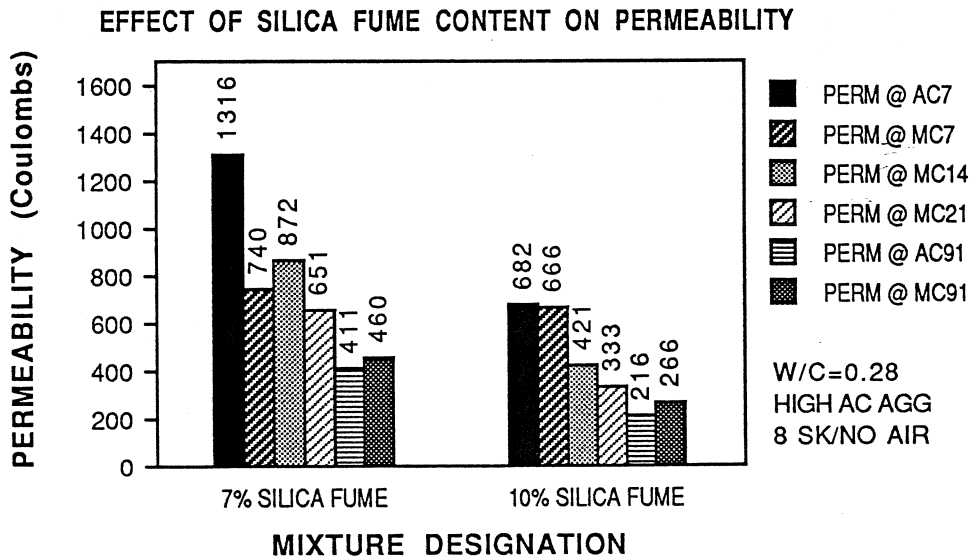


Figure 5.37 Effect of Silica Fume Content on Permeability

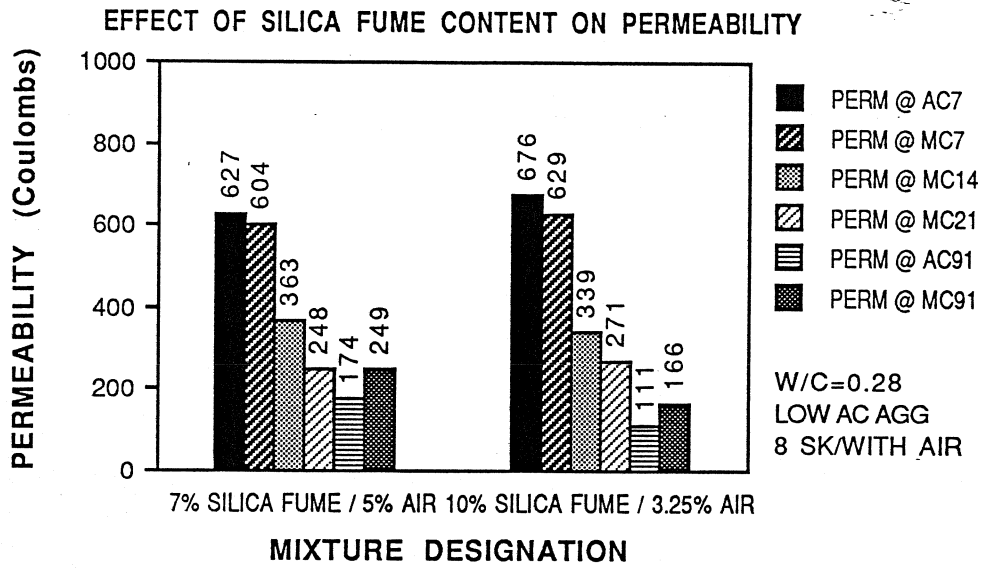


Figure 5.38 Effect of Silica Fume Content on Permeability

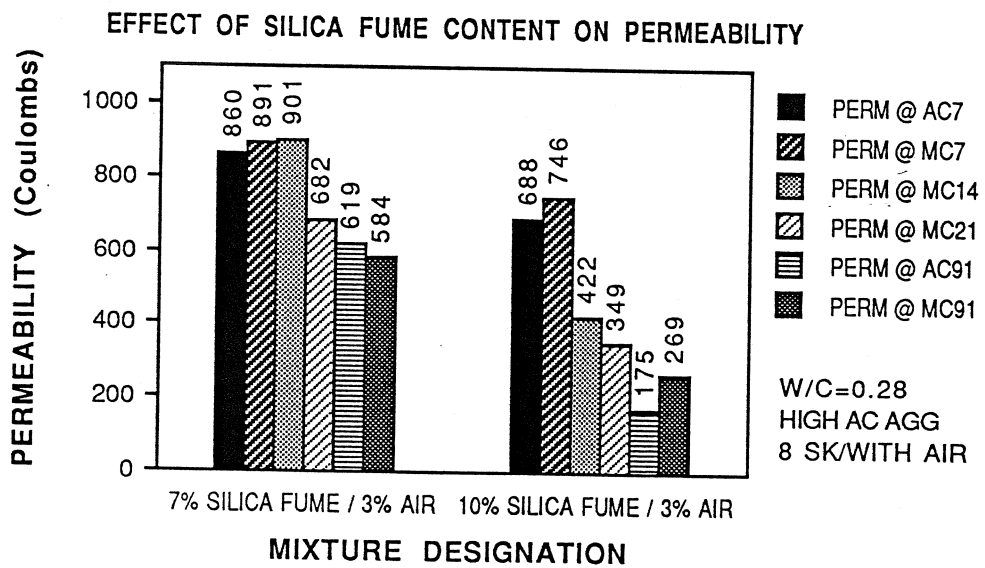


Figure 5.39 Effect of Silica Fume Content on Permeability

5.7.2 Effect of Cement Content. Figures 5.40 through 5.47 compare the permeability results of the 10-sack and 8-sack mixtures made with both aggregates, different silica fume contents, and with and without entrained air to evaluate the effect of cement content on the concrete permeability. The permeability readings ranged from a high of 1316 coulombs at 7 days of age to a low of 111 coulombs after 91 days. The results showed that in 66 percent of the cases, the 8-sack concrete mixtures were less permeable than the 10-sack mixtures by an average of 24 percent. This reduction in permeability was consistent for all curing conditions and test ages. This data indicates that while mixtures cast at both cement contents result in concrete with very low permeability, the concrete containing 8 sacks per cubic yard is less permeable so specifying a cement content greater than 752 lbs/cy is not an effective method of improving permeability performance

5.7.3 Effect of Coarse Aggregate. The effect of coarse aggregate absorption on the permeability of concrete containing silica fume was also evaluated. By comparing the permeability readings from identical mixtures in Figures 5.32 through 5.39, it is clear that use of the high absorption coarse aggregate increased the permeability of the silica fume concrete. In 40 of 42 cases compared, the silica fume concrete containing low absorption aggregate was less permeable by an average of 36 percent. In summary, the use of high absorption coarse aggregate in concrete containing silica fume results in increased permeability when compared to identical mixtures cast with low absorption aggregate.

Several important conclusions can be drawn from the permeability results of the Phase III mixtures containing silica fume. First the addition of silica fume to high strength concrete resulted in very dense, impermeable concrete. The level of silica fume used had

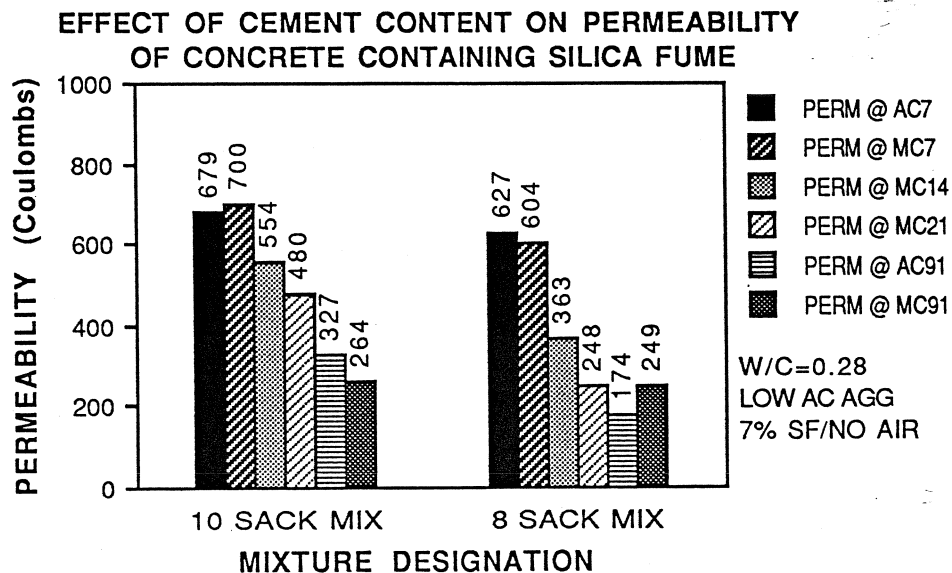


Figure 5.40 Effect of Cement Content on Permeability

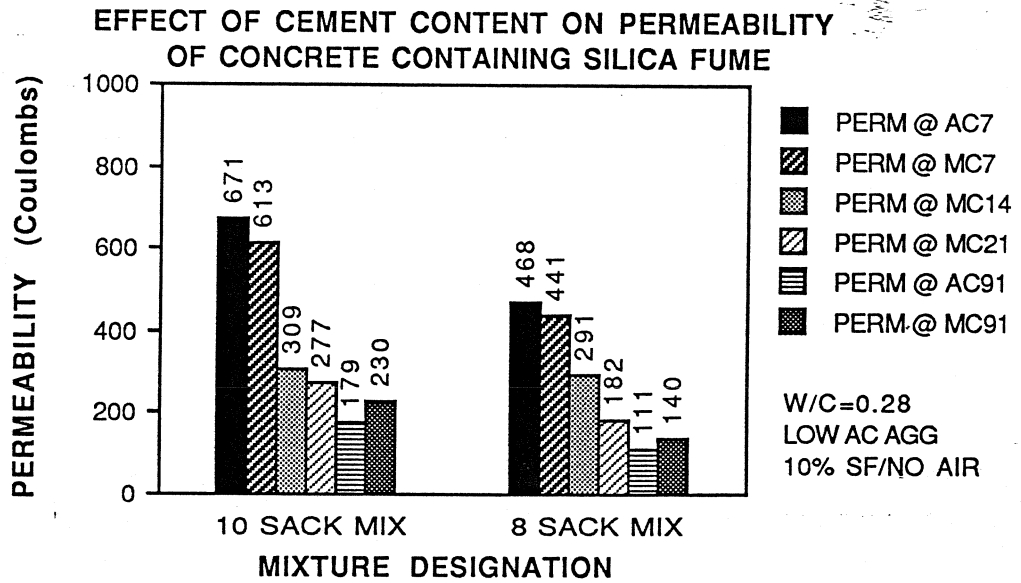


Figure 5.41 Effect of Cement Content on Permeability

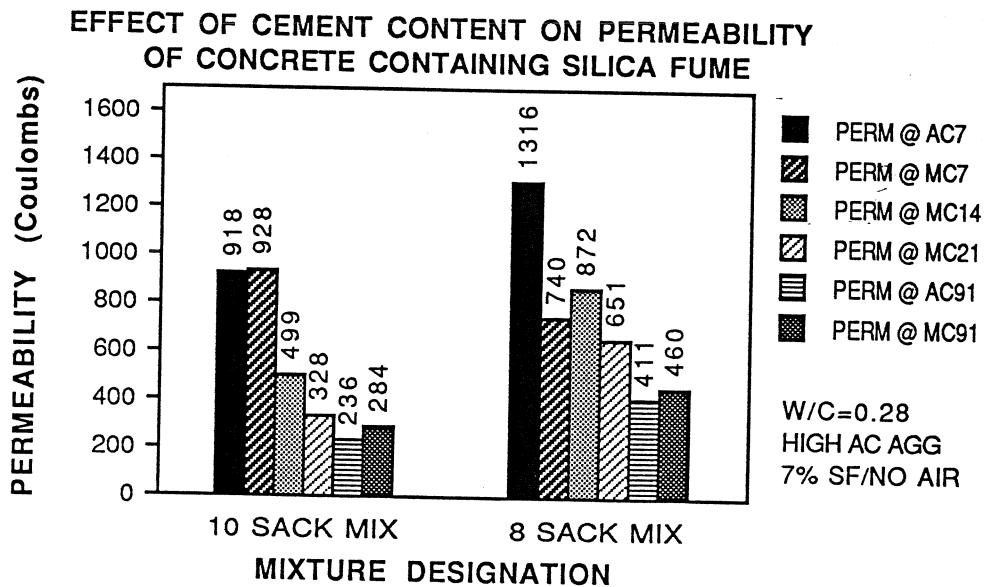


Figure 5.42 Effect of Cement Content on Permeability

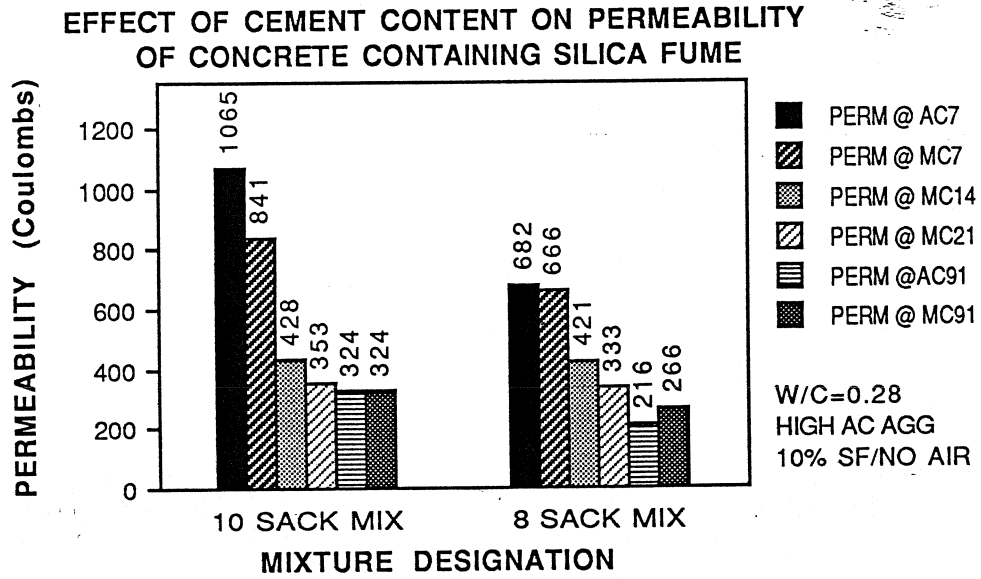


Figure 5.43 Effect of Cement Content on Permeability

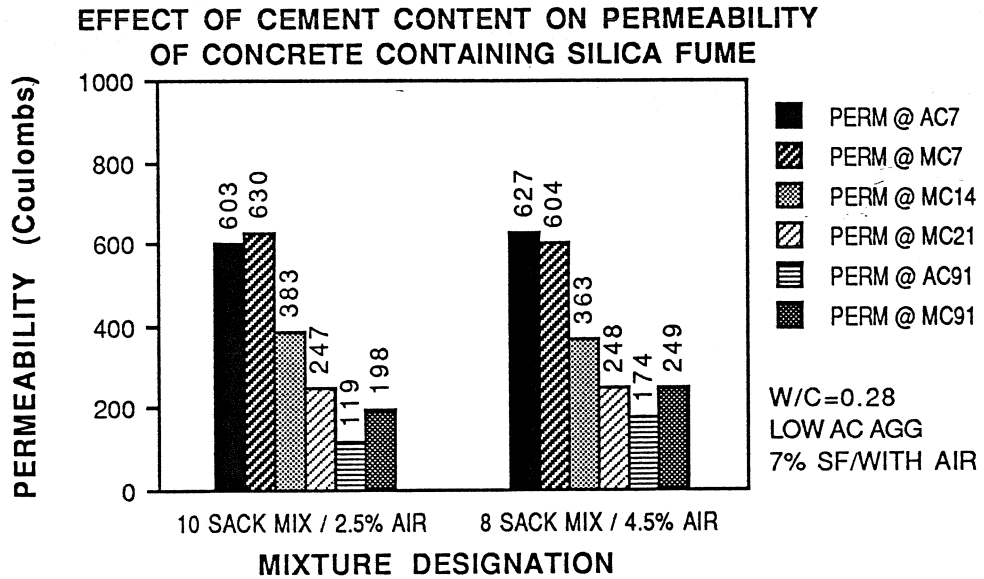


Figure 5.44 Effect of Cement Content on Permeability

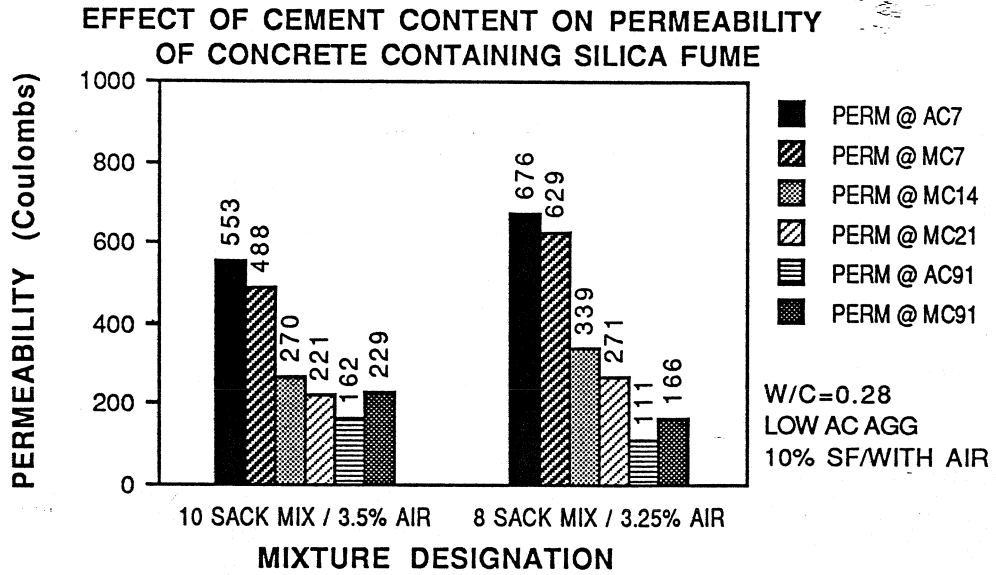


Figure 5.45 Effect of Cement Content on Permeability

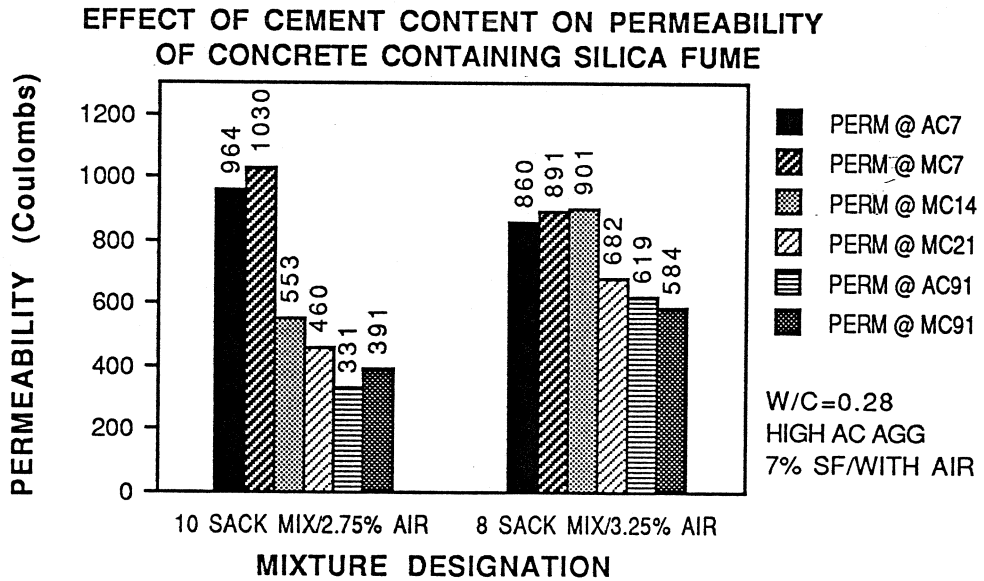


Figure 5.46 Effect of Cement Content on Permeability

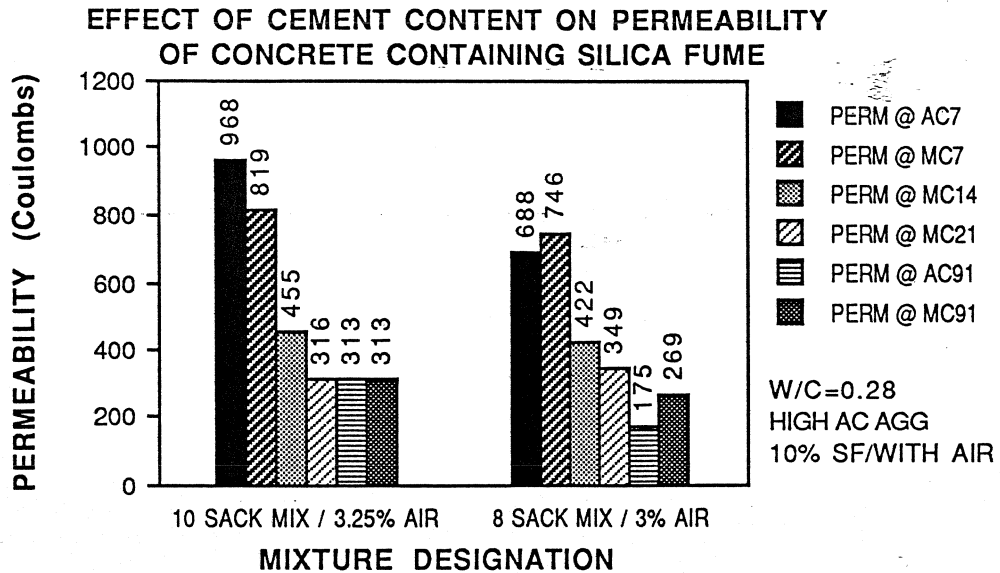


Figure 5.47 Effect of Cement Content on Permeability

no effect on the concrete permeability at 7 days however at later ages the mixtures with 10 percent silica fume were clearly less permeable. When comparing the effect of cement content on permeability, the 8-sack mixtures were less permeable in 66 percent of the cases.

5.8 Summary

The high strength concrete mixtures cast in this program of study were tested for chloride ion permeability and evaluated for the effect of air entrainment, water/cement ratio, curing, coarse aggregate absorption, cement, fly ash and silica fume content on this important parameter. It is clear from the data that the presence of air entrainment had no influence on permeability. This was attributed to the low volume of capillary voids present in the high strength paste. Reducing the water/cement ratio resulted in corresponding reductions in the concrete's permeability. Lowering the ratio from 0.30 to 0.26 by weight resulted in reductions in the permeability of 10 to 25 percent at early ages however this increased to 40 to 60 percent at 91 days.

Extending the moist curing period was strongly linked to reductions in concrete permeability but the reduction was not significant until later ages. The largest average reduction in permeability obtained by extending moist curing from 4 to 7 days was 8 percent. As curing progressed the reduction became greater and approached 60 to 70 percent for specimens moist cured 91 days. The addition of ASTM Class C fly ash to the mixture resulted in concrete which exhibited equal permeability at early ages and was much less permeable than identical mixtures without fly ash at 91 days. The concrete mixtures containing silica fume exhibited much lower initial permeability values than the fly ash

mixtures and experienced similar percent reductions in permeability with continued moist curing.

The absorption capacity of the coarse aggregate had a significant effect on the permeability of the concrete tested. For every mixture in Phase I and II, the high absorption aggregate mixtures exhibited higher permeability than identical mixtures made with low absorption aggregate. This is a significant finding in that this increased permeability could result in poor durability even in the presence of entrained air. The replacement of a portion of the cement with ASTM Class C fly ash resulted in greatly reduced permeability at later ages without sacrificing early age permeability due to cementitious qualities of the fly ash. The Phase III silica fume mixtures cast with high absorption coarse aggregate also exhibited higher permeabilities however these values were still less than 1000 coulombs due to the high density of the cement/silica fume paste.

The addition of silica fume to the mixtures in Phase III resulted in high strength concrete with permeability values several times lower than those obtained in Phases I and II. The Phase III mixtures were examined for the effect of silica fume and cement content on permeability. At 7 days the amount of silica fume added to the mixture had no effect however at later ages the mixtures containing 10 percent silica fume were consistently less permeable. In evaluating the effect of cement content on permeability, the 8-sack mixtures were less permeable in 66 percent of the cases than mixtures containing 10 sacks of cement.

CHAPTER VI

DEICER SCALING RESISTANCE AND CHLORIDE ION PENETRATION RESULTS AND ANALYSIS

6.1 Introduction

Each of the mixtures cast was tested for its resistance to deicer scaling and the resistance to chloride ion penetration of the concrete during the deicer scaling test. Scaling tests were conducted in accordance with ASTM C 672 "Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals". Chloride ion penetration tests were conducted using a commercially available test kit. This chapter presents the results of this testing and analyzes these results to evaluate the effect of water/cement ratio, air entrainment, coarse aggregate absorption, cement, fly ash, and silica fume content.

6.2 Deicer Scaling Test Results

Three specimens from each mixture were moist cured for 14 days and then air cured until tested at 28 days of age. The face of each specimen was ponded to a depth of approximately 1/4 inch with a solution of 4 percent anhydrous calcium chloride in water. The specimens were placed in a freezing environment at $0 \pm 5^\circ\text{F}$ for 16 to 18 hours after which they were placed in laboratory air at $73 \pm 3^\circ\text{F}$ and relative humidity of 45 to 55 percent for 6 to 8 hours. This cycle was repeated daily with water added as needed to replace losses due to evaporation. The specimens were removed from the test chamber after 5, 10, 15, 25, and 50 cycles, flushed with clean water, and visually rated for the extent of scaling from 0 to 5 according to the guidelines described in Table 6.1. After making the visual rating, the solution was replaced and the test continued until the completion of 50 cycles.

The author supplemented the accuracy of the rating scale by adding +/- signs to the numerical ratings in order to further differentiate scaling effects. To illustrate, a rating of 0+ indicated that very slight scaling had begun on a portion of the surface. A rating of 1- was given when this condition had progressed over more than half of the surface of the specimen. A rating of 1 was assigned when the condition existed over the entire surface area of the specimen. Final numerical ratings for each mixture were the arithmetic average of the ratings for the three specimens.

Table 6.1 Visual Rating Scheme from ASTM C 672

RATING	CONDITION OF SURFACE
0	No scaling
1	Very slight scaling (1/8 in. depth maximum with no coarse aggregate visible)
2	Slight to moderate scaling
3	Moderate scaling (some coarse aggregate visible)
4	Moderate to severe scaling
5	Severe scaling (coarse aggregate visible over entire surface)

In general the performance of all of the mixtures tested in the study was very good. Of the 58 mixtures tested involving 174 specimens, only three mixtures exhibited an average rating of 4 or higher which represents moderate to severe scaling and only nine mixtures were rated between 3 and 4 as moderately scaled. The large majority of the specimens were rated between 0 and 2 indicating slight to moderate scaling after 50 cycles.

6.2.1 Effect of Air Entrainment. The mechanism of deicer scaling in concrete is a physical phenomenon involving expansion upon freezing of the water in the top layer of concrete surface which is magnified by the presence of the salt in solution. Research [] has shown that the presence of entrained air, especially in the near surface zone, is necessary to prevent scaling of the concrete. Accordingly, the addition of entrained air to the high strength concrete mixtures in this program was expected to have a beneficial effect on the deicer scaling resistance and this occurred in every mixture to which air entrainment was added.

Figures 6.1 and 6.2 show the effect of adding 1.5 percent entrained air to two Phase I mixtures having a water/cement ratio of 0.30, without fly ash. In each case, the presence of 1.5 percent entrained air resulted in either no scaling or very slight scaling at the completion of the 50 cycle test. Figures 6.3 and 6.4 show the results obtained after repeating this test with identical Phase II mixtures having a water/cement ratio of 0.26. The addition of entrained air resulted in no scaling for both mixtures tested.

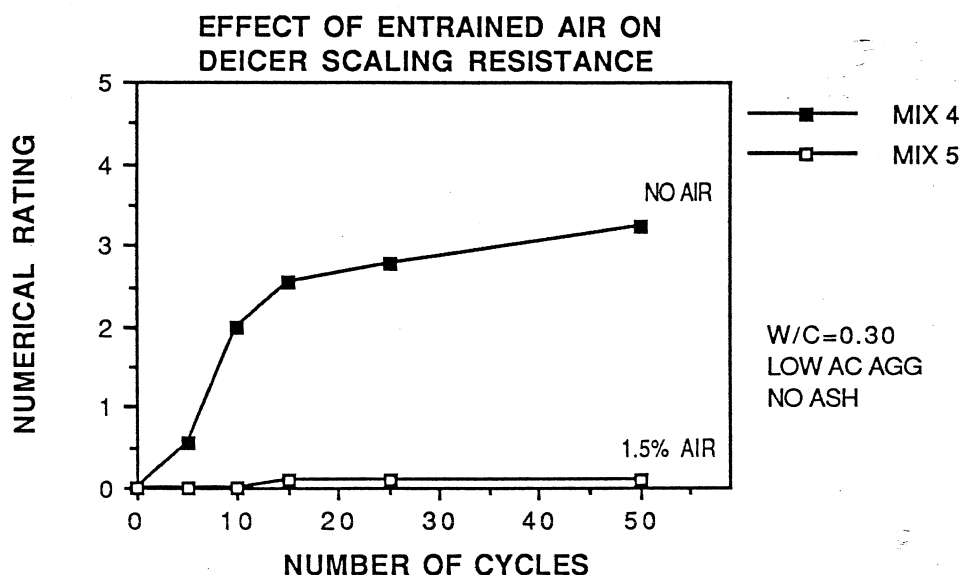


Figure 6.1 Effect of Engrained Air on Deicer Scaling Resistance

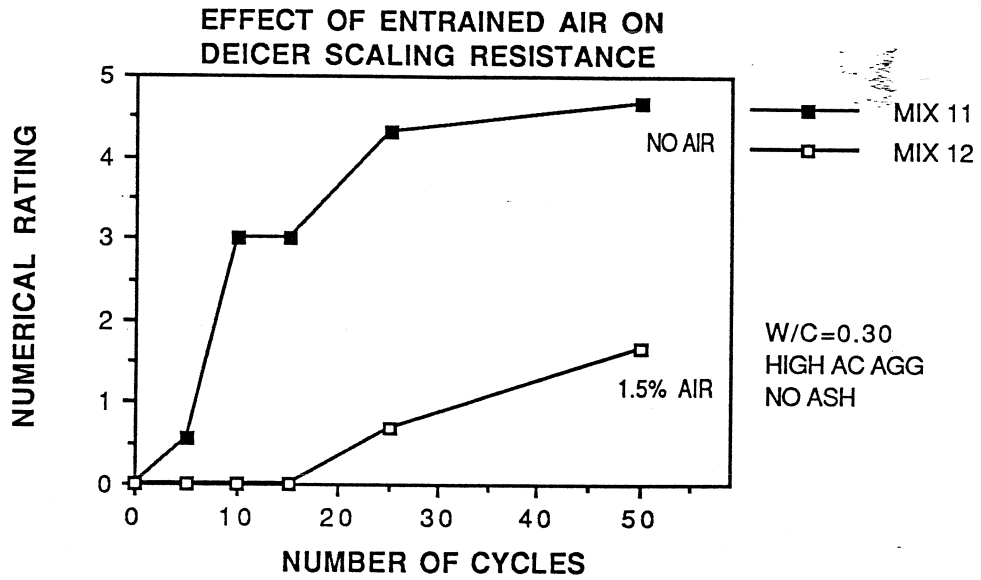


Figure 6.2 Effect of Engrained Air on Deicer Scaling Resistance

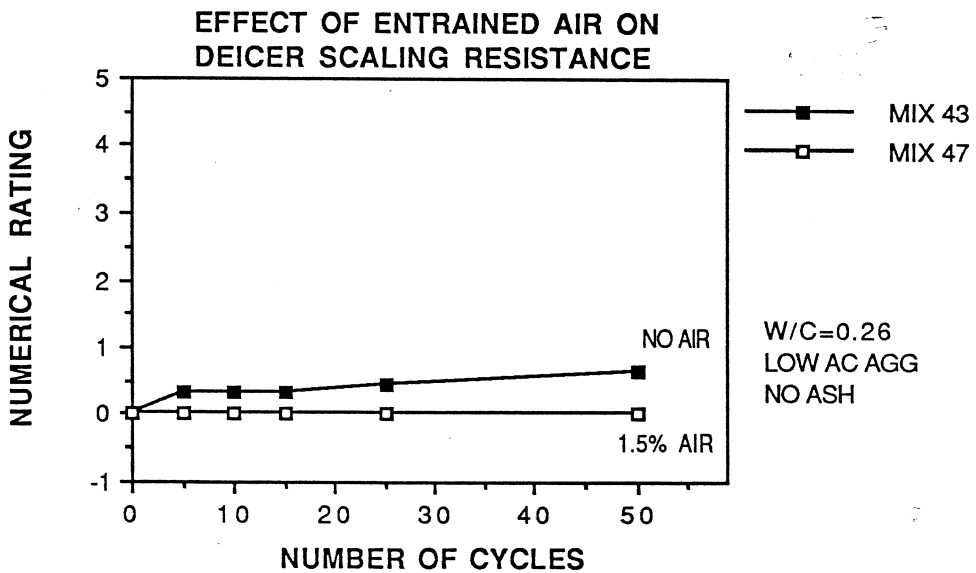


Figure 6.3 Effect of Engrained Air on Deicer Scaling Resistance

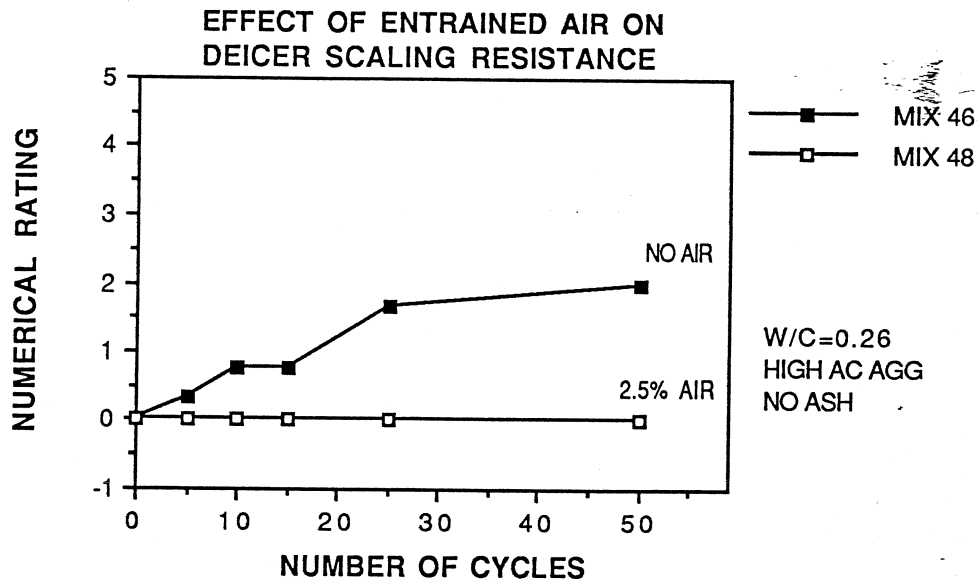


Figure 6.4 Effect of Engrained Air on Deicer Scaling Resistance

In Figures 6.5 and 6.6, the scaling performance of non-air entrained, 0.30 water/cement ratio mixtures containing fly ash is compared to the performance of identical mixtures containing a small amount of entrained air. In this comparison, the air entrained mixtures were more resistant to scaling in both cases. Figures 6.7 and 6.8 compare the scaling performance of air and non-air entrained fly ash mixtures when the water/cement ratio equals 0.26. Again the addition of a small amount of entrained air resulted in no scaling at all for either mixture tested.

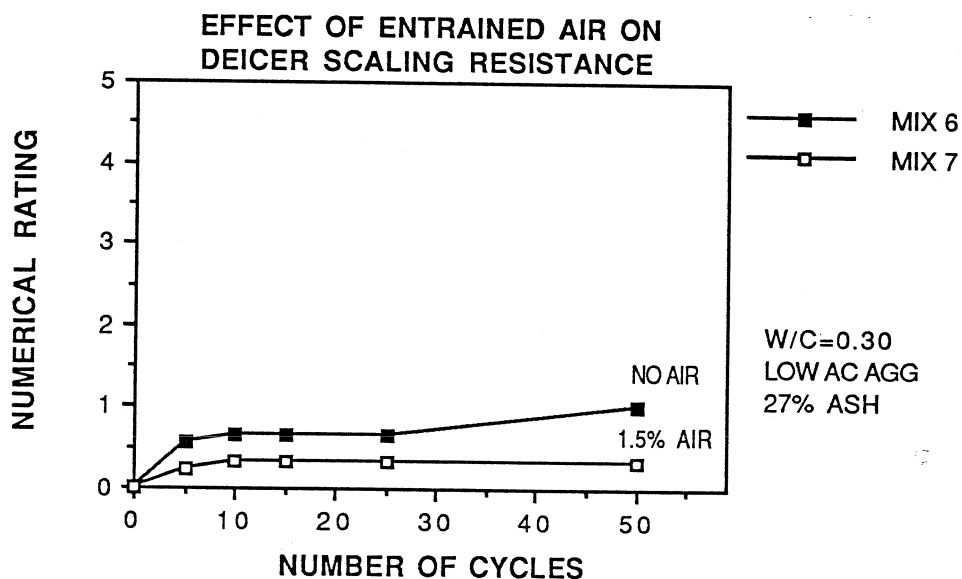


Figure 6.5 Effect of Entrained Air on Deicer Scaling Resistance

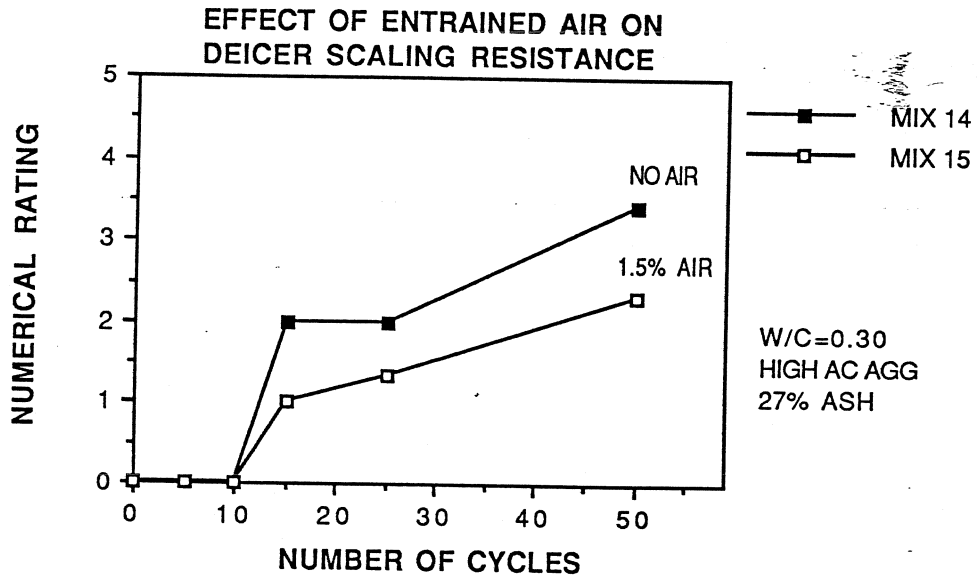


Figure 6.6 Effect of Entrained Air on Deicer Scaling Resistance

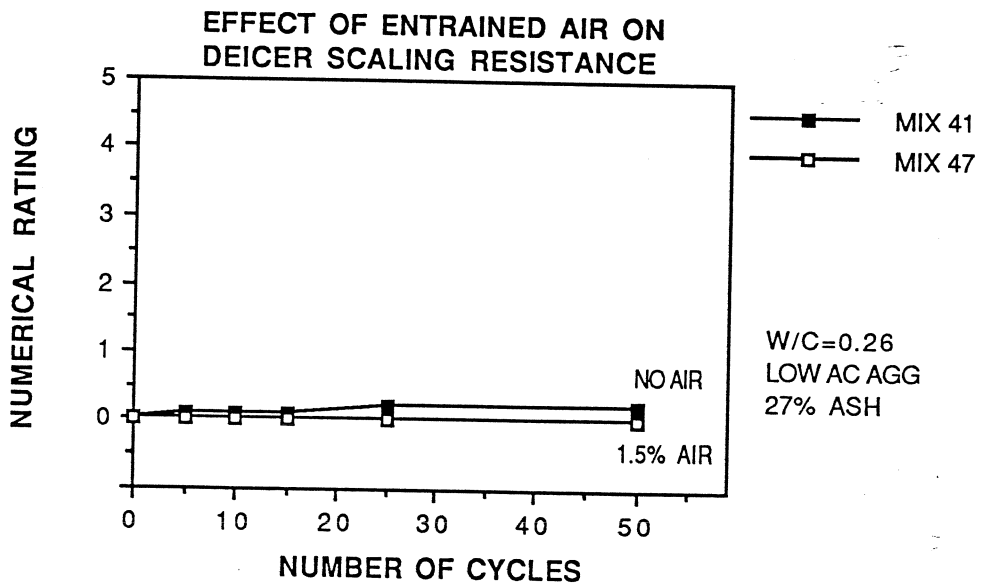


Figure 6.7 Effect of Entrained Air on Deicer Scaling Resistance

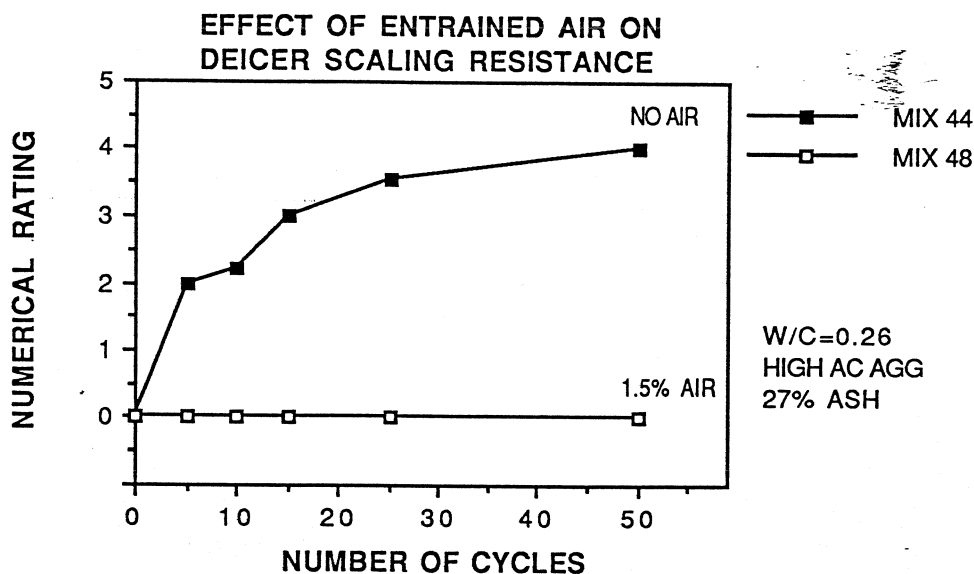


Figure 6.8 Effect of Entrained Air on Deicer Scaling Resistance

No graphs were made comparing the effect of entrained air on the scaling performance of the Phase III (silica fume) concrete because these mixtures were so resistant to scaling that little effect was observed when changing any of the parameters. The average visual rating for the 16 mixtures containing silica fume was less than 1 meaning that most of the silica fume specimens showed only very slight scaling over a small portion of their surface after 50 cycles. In every case where entrained air was added to a silica fume mixture, the scaling resistance either improved or remained essentially unchanged. In most cases, the surface condition improved from very slight scaling over a small portion of the specimen to no scaling at all.

In summary, the addition of entrained air to the high strength low water/cement ratio fly ash concrete mixtures used in this study improved the deicer scaling resistance. The improvement was noted in all mixtures regardless of fly ash content or coarse aggregate type. The Phase III mixtures containing silica fume were extremely resistant to scaling and did not scale sufficiently to detect a significant amount of improvement in scaling resistance when entrained air was added.

6.2.2 Effect of Water/Cement Ratio. Since scaling is primarily a physical process involving freezing of water applied to the concrete surface, air entrainment and permeability would be expected to have important roles in determining the concrete's resistance to deicer scaling. Lowering the water/cement ratio reduces freezable water and permeability and therefore, it was expected to have a positive effect on deicer scaling resistance. The effect of lowering the water/cement ratio on deicer scaling resistance was evaluated in a series of eight comparisons shown in Figures 6.9 and 6.10. The results show that for mixtures without

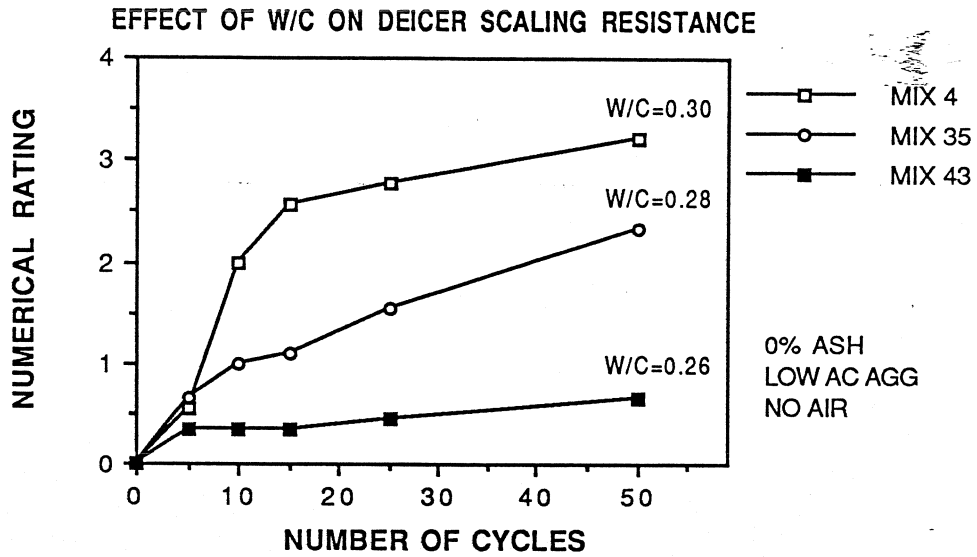


Figure 6.9 Effect of W/C Ratio on Deicer Scaling Resistance.

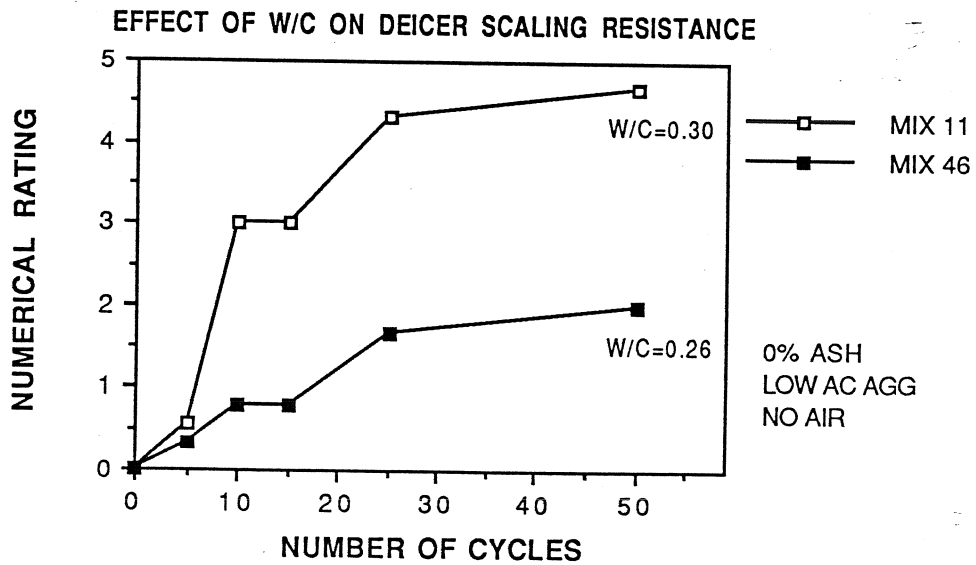


Figure 6.10 Effect of W/C Ratio on Deicer Scaling Resistance

entrained air or fly ash, reducing the water/cement ratio clearly improved the scaling resistance. When fly ash was added to the mixtures tested above, similar results were obtained using low absorption aggregate as shown in Figure 6.11 but Figure 6.12 shows that high scaling was observed in both mixtures when cast with the high absorption aggregate. This is due to a combination of high absorption capacity of the coarse aggregate and the higher permeability which consistently occurred in concrete containing this aggregate. Figures 6.13 through 6.16 compare the effect of reducing the water/cement ratio on air entrained mixtures. In each case, reducing the water/cement ratio resulted in a slight improvement in scaling resistance.

In summary, lowering the water/cement ratio resulted in improved deicer scaling resistance for the high strength mixtures tested in this program. For high absorption aggregate concrete mixtures however, the additional water held within the aggregate combined with the high permeability exhibited by these mixtures resulted in lower scaling resistance which the change in water/cement did not significantly improve.

6.2.3 Effect of Fly Ash. The addition of fly ash to normal strength concrete has been shown [] to improve scaling resistance because it increases cohesiveness of the mixture, reduces bleeding and segregation, and reacts with calcium hydroxide which reduces permeability. The effect of fly ash on the scaling resistance of the high strength concrete in this study was evaluated by comparing four pairs of non-air entrained mixtures from Phases I and II. The results are shown in Figures 6.17 to 6.20. In three out of four cases, the mixture containing fly ash scaled less than an identical non-fly ash mixture.

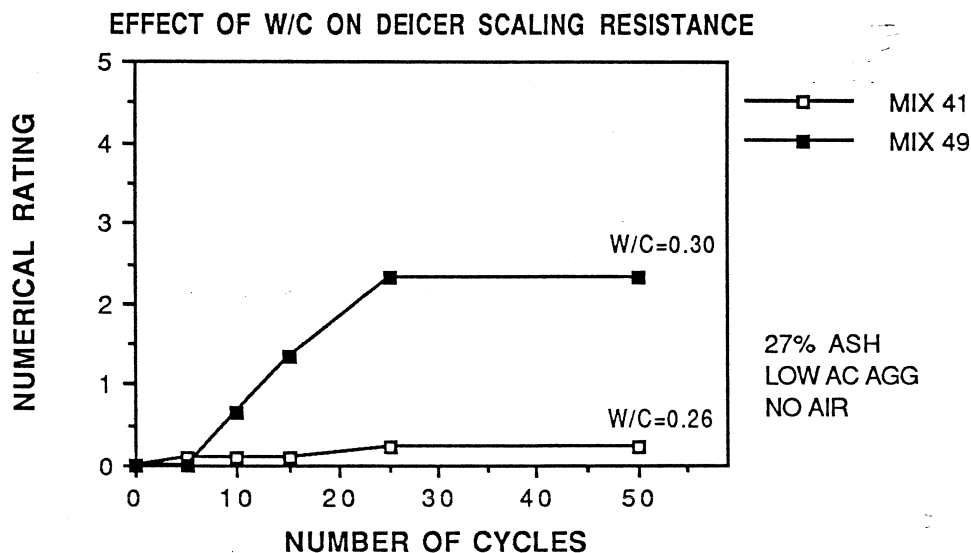


Figure 6.11 Effect of W/C Ratio on Deicer Scaling Resistance

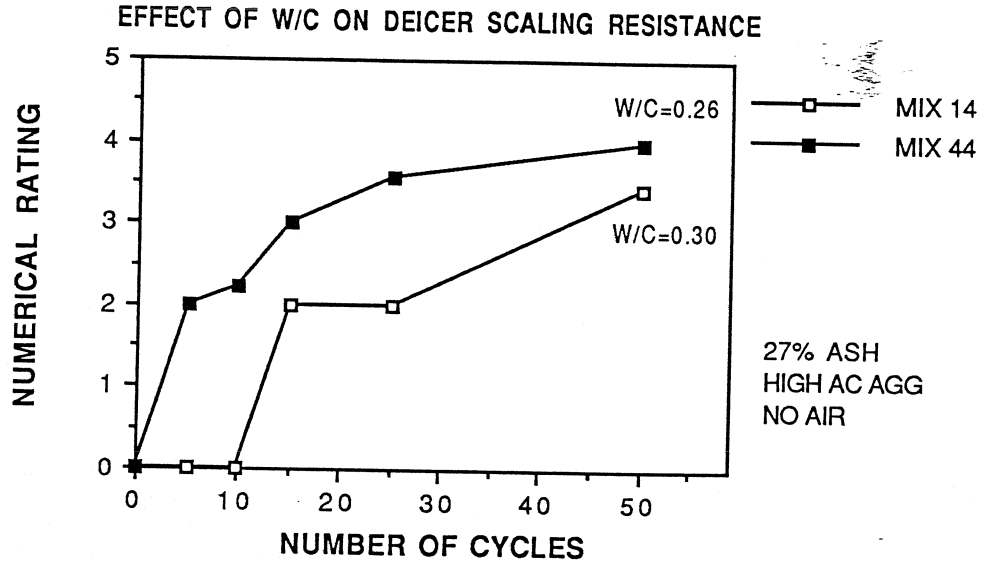


Figure 6.12 Effect of W/C Ratio on Deicer Scaling Resistance

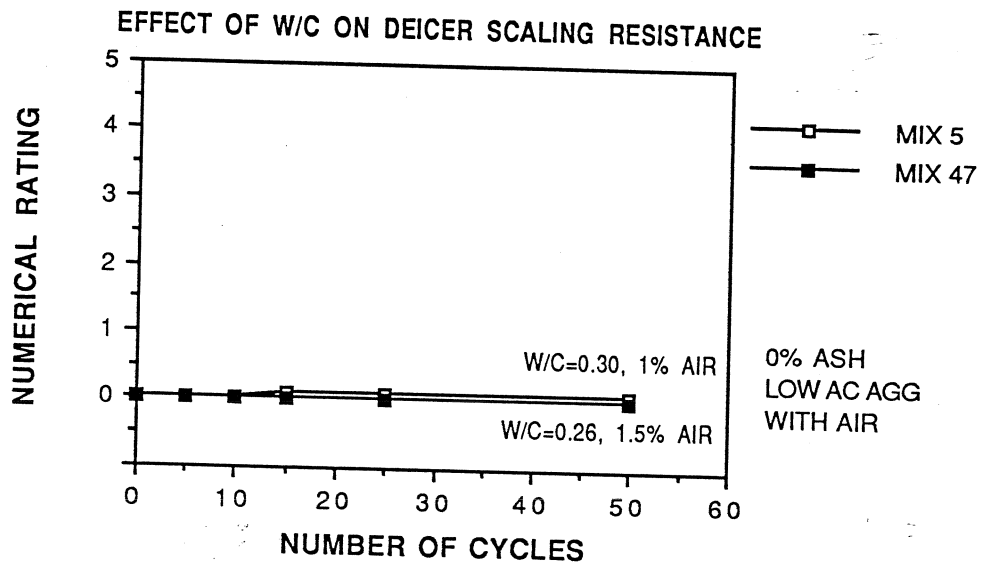


Figure 6.13 Effect of W/C Ratio on Deicer Scaling Resistance

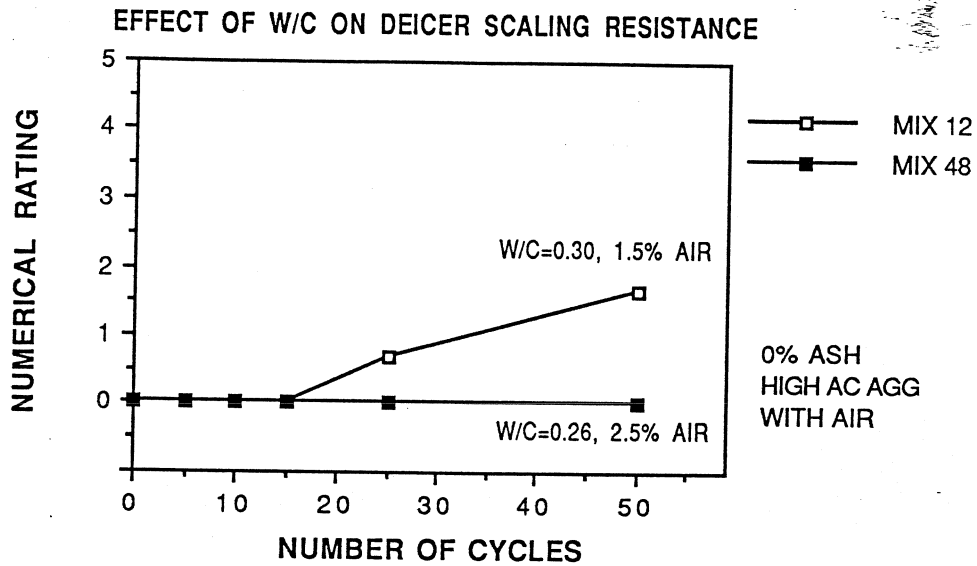


Figure 6.14 Effect of W/C Ratio on Deicer Scaling Resistance

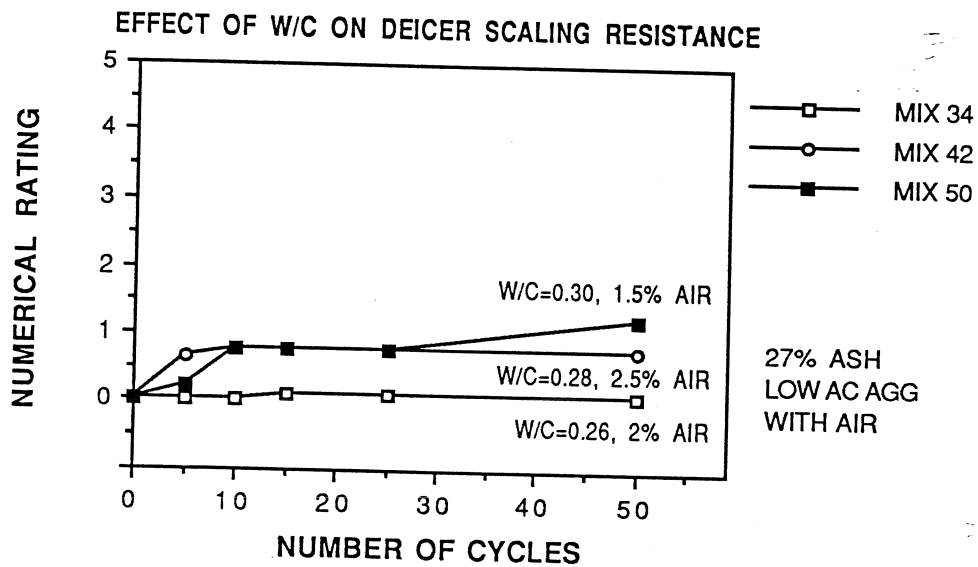


Figure 6.15 Effect of W/C Ratio on Deicer Scaling Resistance

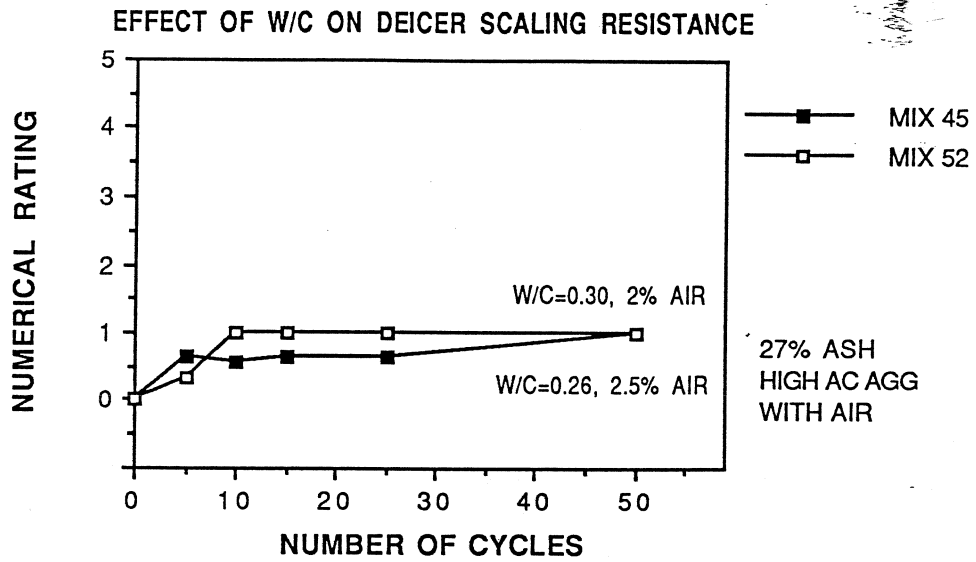


Figure 6.16 Effect of W/C Ratio on Deicer Scaling Resistance

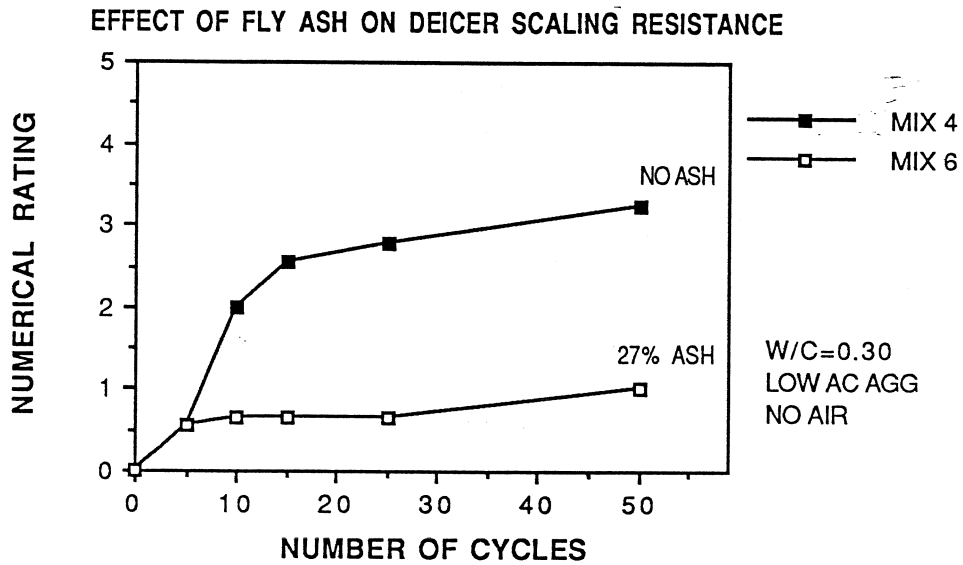


Figure 6.17 Effect of Fly Ash on Deicer Scaling Resistance

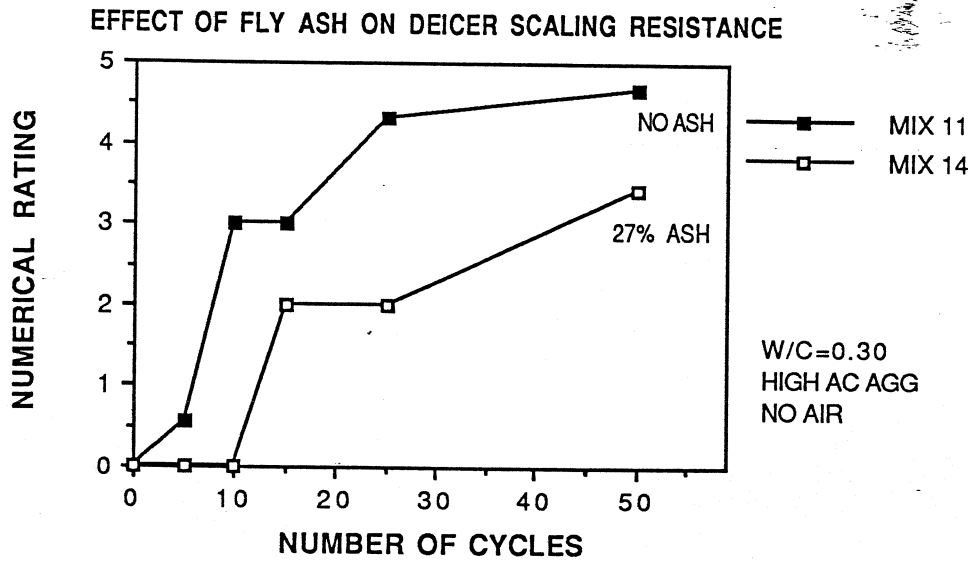


Figure 6.18 Effect of Fly Ash on Deicer Scaling Resistance

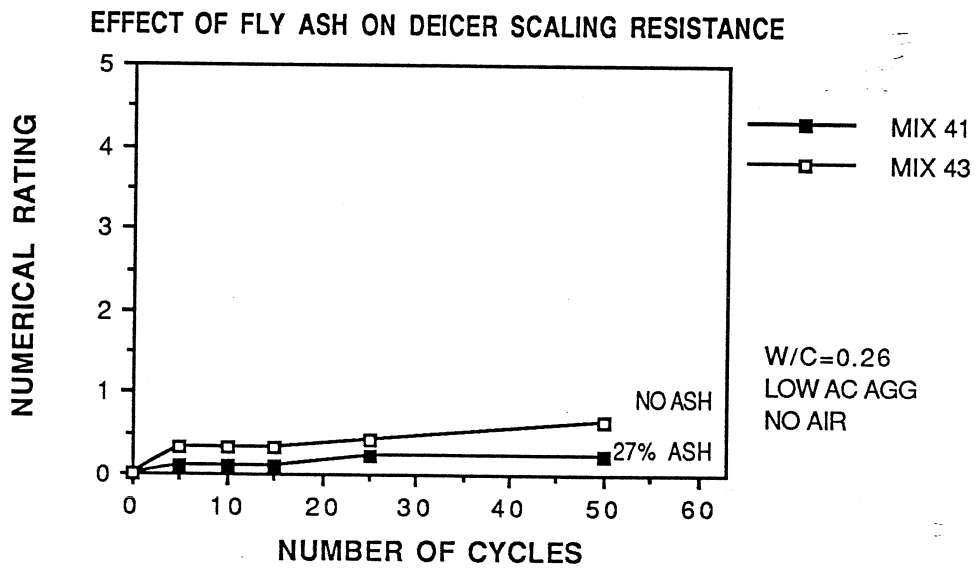


Figure 6.19 Effect of Fly Ash on Deicer Scaling Resistance

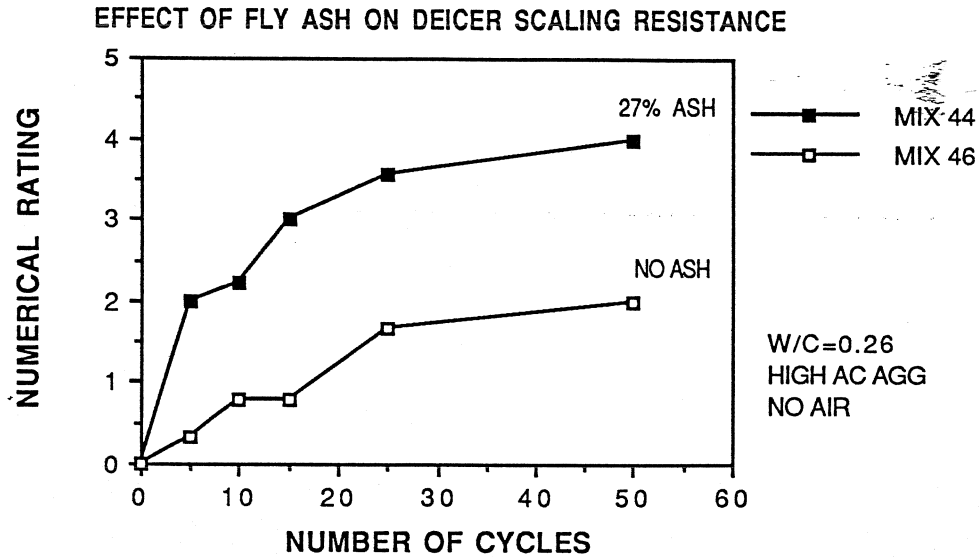


Figure 6.20 Effect of Fly Ash on Deicer Scaling Resistance

6.2.4 Effect of Coarse Aggregate. Figures 6.21 through 6.24 compare the effect that coarse aggregate absorption had on the scaling resistance of the non-air entrained high strength mixtures tested from Phases I and II. Similar to the permeability results obtained in Chapter 5, the mixtures cast with low absorption aggregate scaled much less than companion specimens made with high absorption aggregate. This is due to the higher permeabilities of the high absorption aggregate mixtures as discussed in Chapter 5 combined with the higher water content in the mixtures due to the absorption capacity of the coarse aggregate. This occurred in every case regardless of the water/cement ratio in both fly ash and non-fly ash mixtures. This trend continued when entrained air was added to the mixtures as shown in Figures 6.25 through 6.28. The data in Figures 6.26 and 6.28 indicate that if at least 2.5 percent entrained air is present, the high absorption aggregate mixture approaches the low absorption aggregate mixture in scaling resistance.

The superior deicer scaling resistance of the mixtures containing low absorption aggregate can be attributed in part to the permeability of the concrete. In Chapter 5 the data showed that the porosity of the high absorption aggregate resulted in consistently higher concrete permeability. These higher permeabilities allow greater ingress of the salt solution which in turn causes more scaling. Additionally, the higher absorption capacity means that there is more freezable water in the matrix which can freeze and damage the concrete. Whereas only 1.5% entrained air resulted in no scaling for low absorption concrete mixtures, it appears that entrained air contents of 2.5 percent or higher are necessary to overcome the scaling problems caused by the high absorption aggregate.

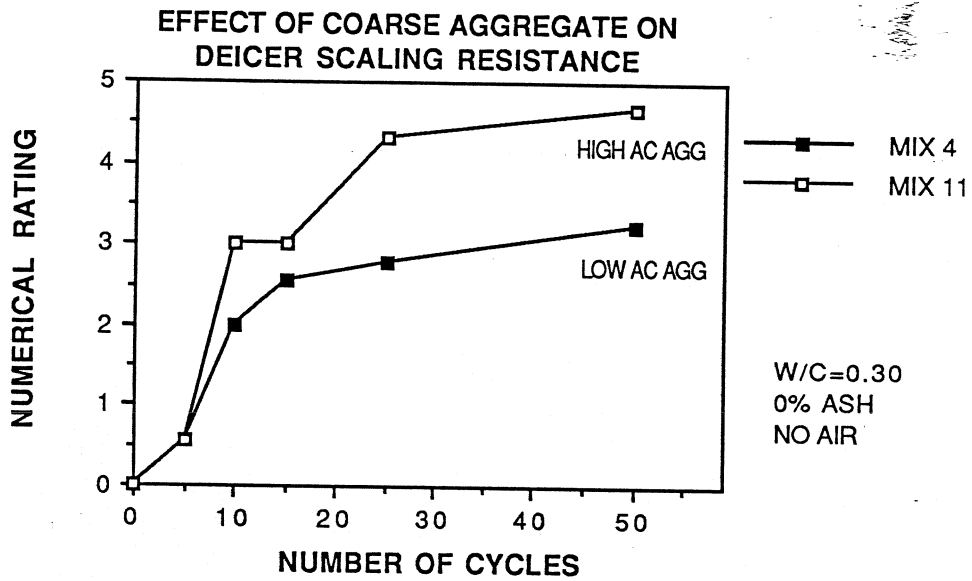


Figure 6.21 Effect of Coarse Aggregate on Scaling Resistance

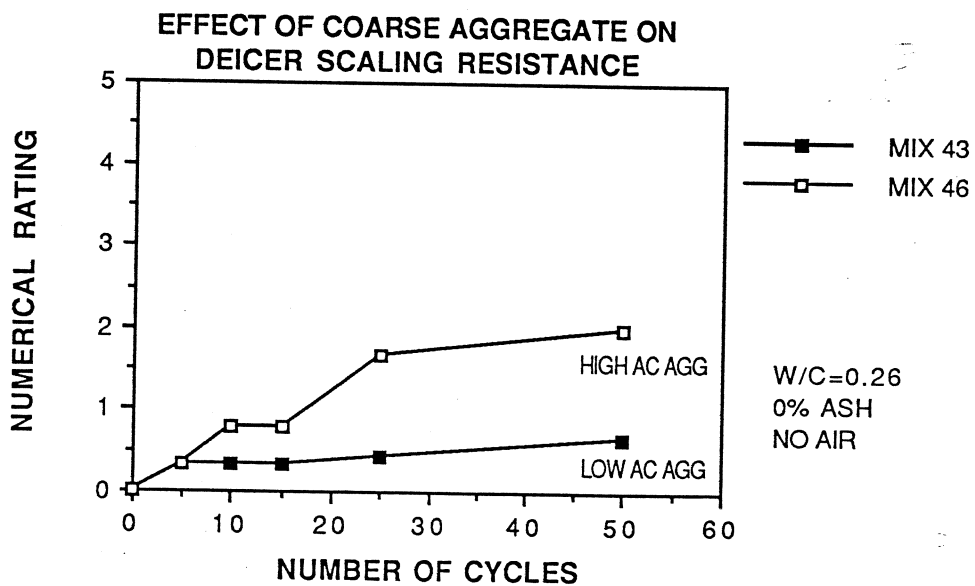


Figure 6.22 Effect of Coarse Aggregate on Scaling Resistance

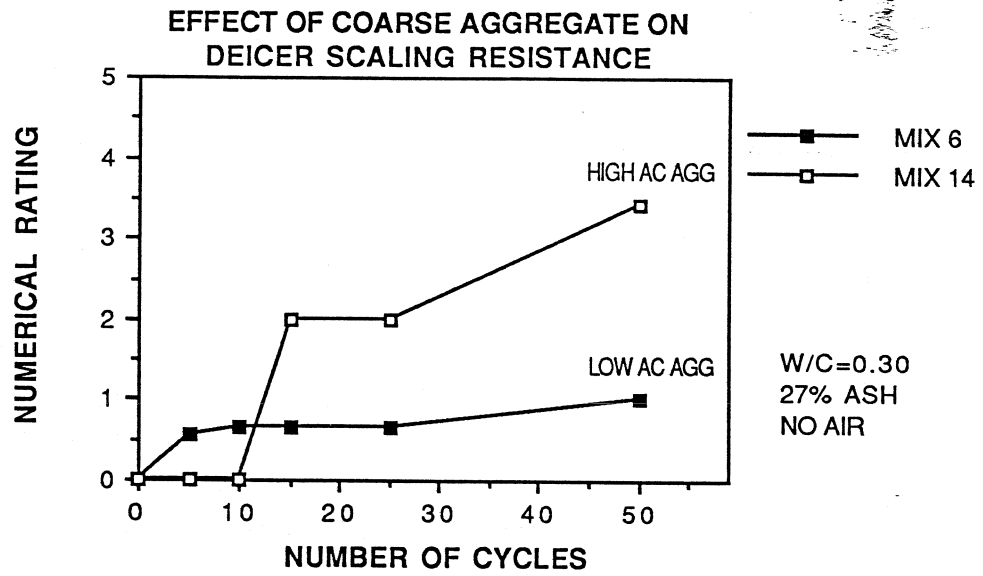


Figure 6.23 Effect of Coarse Aggregate on Scaling Resistance

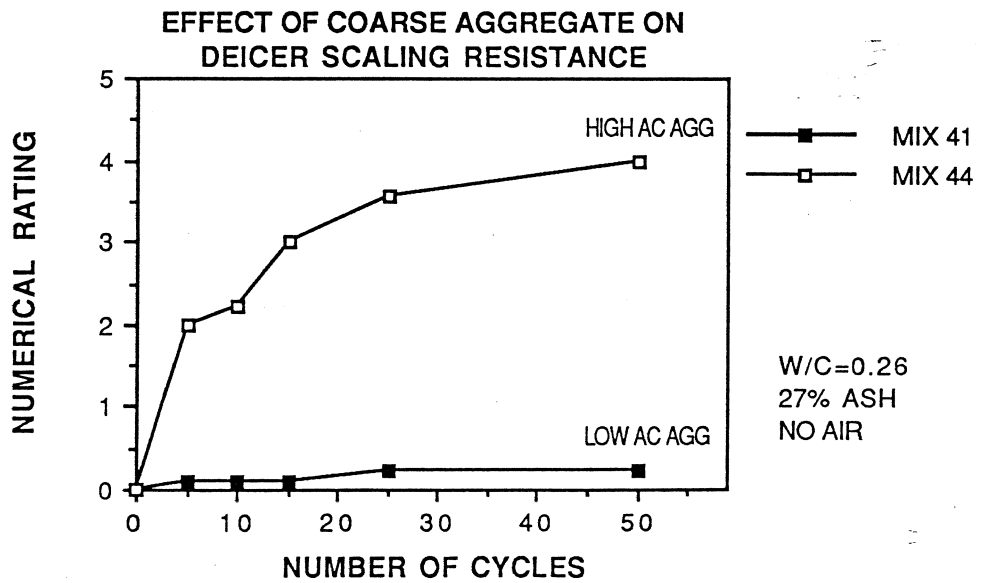


Figure 6.24 Effect of Coarse Aggregate on Scaling Resistance

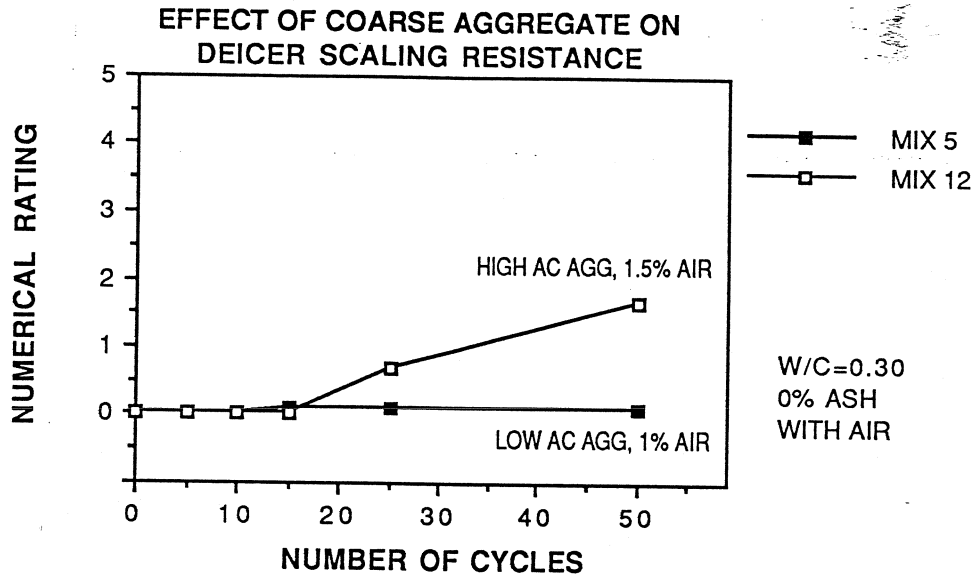


Figure 6.25 Effect of Coarse Aggregate on Scaling Resistance

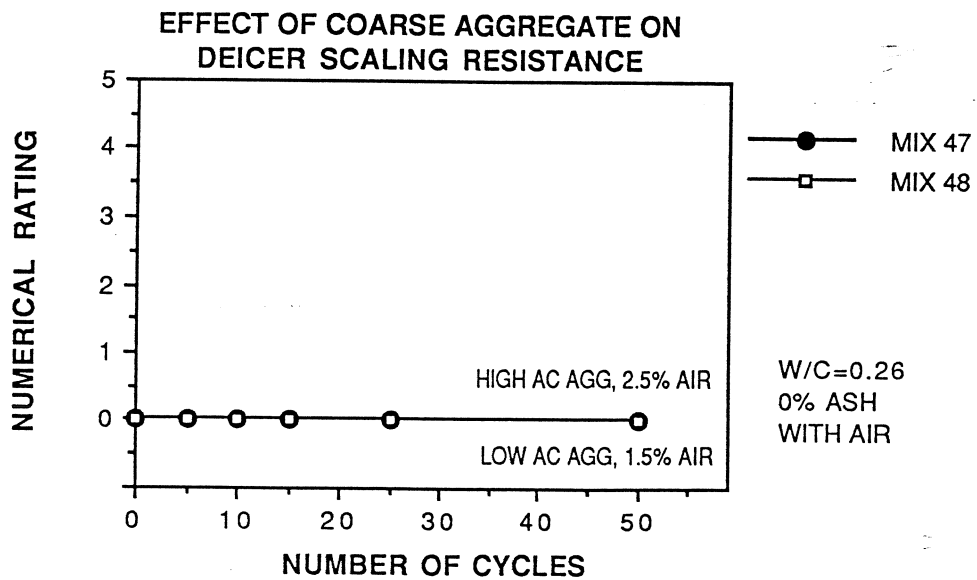


Figure 6.26 Effect of Coarse Aggregate on Scaling Resistance

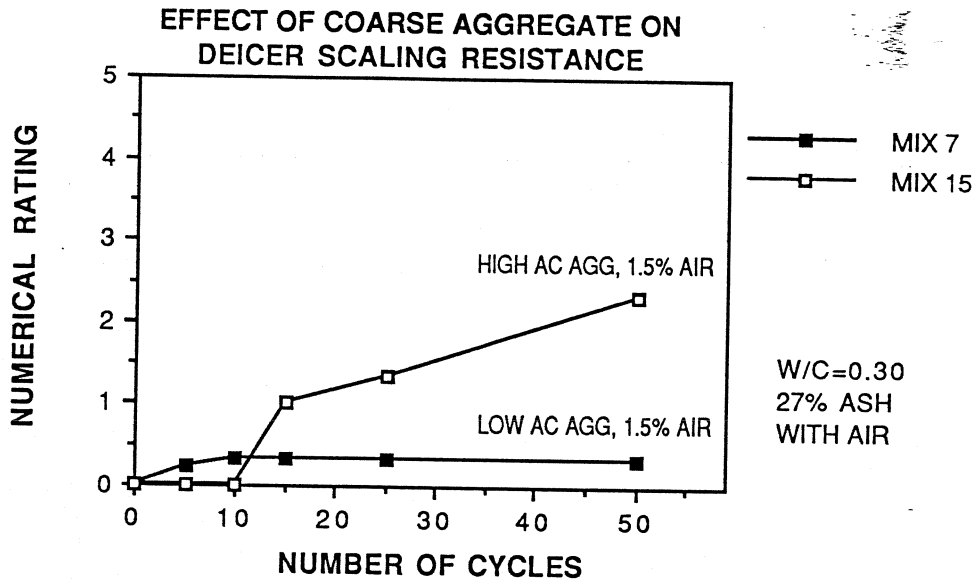


Figure 6.27 Effect of Coarse Aggregate on Scaling Resistance

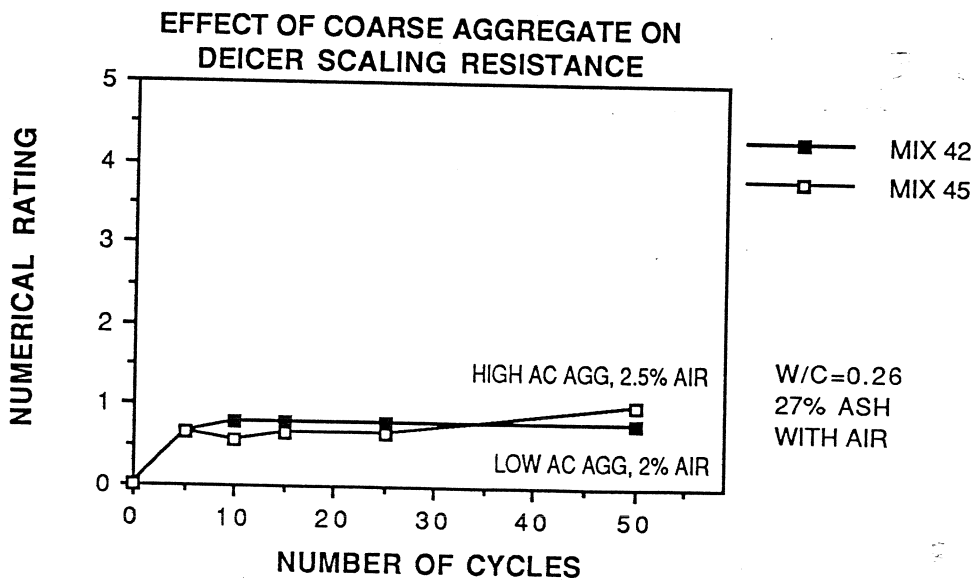


Figure 6.28 Effect of Coarse Aggregate on Scaling Resistance

6.2.5 Effect of Silica Fume. The addition of silica fume to the concrete in Phase III resulted in such high scaling resistance that the effect of the parameters examined earlier such as cement content, silica fume content, and coarse aggregate selection, were insignificant. Only 1 of 16 mixtures received a visual rating greater than 2, slight to moderate scaling, and only 3 others attained a rating of 1, very slight scaling. Adding entrained air to these mixtures did improve the scaling resistance however the improvement was slight because the initial resistance was so high. The results indicated that low water/cement ratio, silica fume concrete could be made resistant to deicer scaling without requiring entrained air.

6.2.6 Summary. The results of the deicer scaling tests conducted in this program show that at water/cement ratios of 0.30 and 0.26, the deicer scaling resistance is generally excellent with only isolated cases of moderate to severe scaling exhibited. Reducing the water/cement ratio improved the scaling resistance as did adding fly ash to the mixture. Mixtures containing high absorption aggregate scaled more than identical mixtures cast with low absorption aggregate due to the increased permeability of the high absorption aggregate mixtures. The addition of entrained air was the most effective method of improving the scaling resistance for the mixtures in Phases I and II. Mixtures containing high absorption coarse aggregate required more entrained air to prevent scaling than those cast with low absorption aggregate. Phase III mixtures containing silica fume did not scale after 50 cycles according to ASTM C 672 and showed exceptional scaling resistance without entrained air.

6.3 Chloride Ion Penetration Test Results

The specimens tested for scaling under ASTM C 672 were also sampled and tested to determine the amount and penetration of water soluble chlorides in the concrete at two depths. Each specimen was sampled by drilling holes to the prescribed depth and collecting the concrete dust. Two samples taken from three holes were collected from each specimen at each depth. The concrete dust was then prepared and tested for chloride content using a commercially-available test kit. The results of the chloride ion penetration tests are shown for all the mixtures tested in Table 6.2. The ACI limit for chloride content of reinforced concrete is 0.15% by weight of cement. For the high strength mixtures tested in this study, this limit is equivalent to 0.036% by weight of the concrete which is the parameter measured by the testing procedure.

As can be seen from the table, most of the concrete mixtures exhibited chloride contents far below this limit especially at the deeper level of 1-1/4 to 1-1/2 inches. One series of 10 mixtures in Phase I having a water/cement ratio of 0.30 and cast with high absorption coarse aggregate recorded extremely high chloride levels at both depths. The high porosity of this aggregate increased the amount of freezable water in the concrete. This same porosity also contributed to increased permeability of the these mixtures. These two factors resulted in increased scaling of these mixtures which led to the high chloride

Table 6.2 Chloride Ion Penetration Data for All Mixtures

Mixture Number	Mixture Data	Chloride Content (% by weight of concrete)	
		3/4" Depth	1-1/2" Depth
4	30A00LA0	0.014	0.014
5	30A00LA3	0.011	0.012
5A	30A00LA6	0.016	0.012
6	30A27LA0	0.012	0.013
7	30A27LA3	0.013	0.013
7A	30A27LA3	0.011	0.010
8	30A33LA0	0.015	0.013
9	30A33LA1	0.014	0.014
9A	30A33LA6	0.016	0.012
12	30A00HA1	0.272	0.018
13	30A00HA6	0.261	0.019
14	30C27HA0	0.175	0.038
15	30A27HA1	0.213	0.012
18	30A33HA1	0.210	0.039
19	30A33HA3	0.230	0.040
20	30A27HA0	0.165	0.040
21	30A27HA1	0.243	0.042
22	30A27HA4	0.152	0.040
23	30A33HA4	0.162	0.043
31	28A27LA0	0.029	0.015
32	28A33LA0	0.019	0.012
33	28A27LA6	0.014	0.012
34	28A27LA2	0.017	0.014
35	28A00LA0	0.014	0.012
41	26A27LA0	0.014	0.011
42	26A27LA2	0.013	0.012
43	26A00LA0	0.010	0.010
44	26A27HA0	0.010	0.007
45	26A27HA3	0.008	0.008
46	26A00HA0	0.007	0.005
47	26A00LA2	0.013	0.011
48	26A00HA3	0.007	0.005
49	30A27LA0	0.015	0.018
50	30A27LA2	0.011	0.011
52	30A27HA2	0.008	0.006
53	30A27HA0	0.007	0.006
54	28S7LA0	0.033	0.015
55	28S7LA3	0.012	0.010
56	28S7HA0	0.025	0.012
57	28S7HA3	0.005	0.004
58	28S10LA0	0.026	0.013
59	28S10LA3	0.014	0.012
60	28S10HA0	0.015	0.014
61	28S10HA3	0.012	0.008
62	28S7HA0	0.008	0.005
63	28S7HA3	0.009	0.005
64	28S7LA5	0.013	0.017
65	28S7LA0	0.015	0.014
66	28S10LA3	0.012	0.013
67	28S10LA0	0.018	0.014
68	28S10HA3	0.007	0.005
69	28S10HA0	0.008	0.006

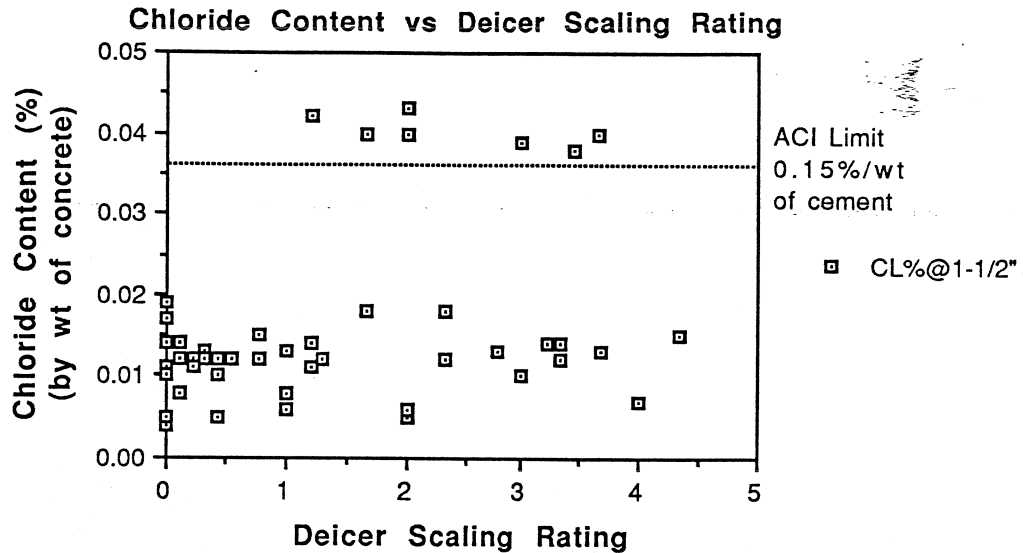


Figure 6.30 Chloride Ion Content vs Deicer Scaling Rating

consistently scaled less than companion mixtures containing high absorption coarse aggregate. The addition of silica fume in the proportions used in the study resulted in concrete which scaled very little regardless of the presence of air entrainment.

Most of the concrete mixtures tested exhibited extremely low chloride contents at both of the depths chosen with the exception of one 10 mixture series cast in Phase I using high absorption aggregate. These results are due to increased freezable water in the coarse aggregate of these mixtures and higher concrete permeability values which resulted in lower scaling resistance and correspondingly deeper penetration of chloride ions. There does not appear to be a significant correlation between the chloride content of a mixture determined upon completion of testing by ASTM C 672, and its visual rating assigned during the test.

CHAPTER V AIR-VOID SYSTEM ANALYSIS

7.1 Introduction

One of the main objectives of this study was to determine if entrained air was necessary in low water/cement ratio, low permeability, high strength concrete in order to render the concrete freeze-thaw resistant. A corollary to this objective was to determine if entrained air was found to be necessary, did current guidelines regarding required air content apply to these high strength materials or do new rules need to be formulated. All air content tests were measured in the plastic state by the volumetric method according to ASTM C 231 just prior to placing the concrete in the molds. Although performed precisely according to the standard, all fresh concrete air tests contain a degree of variability. There is always a possibility that the air content measured in the plastic state will not be the same as that locked into the hardened concrete. In order to validate the experimental test results, and thus ensure a correct basis for later conclusions, a selected number of mixtures were analyzed for air content of the hardened concrete.

In order to verify the accuracy of the fresh concrete air content tests reported in Chapter 4, nine mixtures were selected and analyzed for entrained air content by using the modified point-count method given in ASTM C 457 "Microscopical Determination of the Air Content and Parameters of the Air-Void System in Hardened Concrete." The specimens were prepared by grinding a slice from a 4-inch by 8-inch cylinder on a vibratory lapping table using successively finer grits of grinding powder until the air voids were clearly delineated. The samples were then analyzed by a registered professional petrographer.

7.2 Air-Void System Parameters

The three parameters commonly reported to describe the air-void system in concrete are spacing factor, specific surface, and number of voids per linear inch. These are shown in Table 7.1 along with their units of measure and minimum/maximum recommended values according to ASTM C 457. The spacing factor is the average distance between any point in the paste and the nearest entrained air bubble. Powers⁵⁶ determined from his work on

Table 7.1 Air-Void System Parameters

PARAMETER	UNITS	RECOMMENDED VALUES
Spacing Factor	inches (mm)	0.008 (0.02)
Specific Surface	sq. in/cu in. (mm)	400 - 600 (16 - 25)
Number of Voids per inch	each	1.5 - 2.0 x Air Content in %

freezing of water in concrete that if the water had to travel more than 0.01 inches before reaching an air bubble, it would generate sufficient pressure to rupture the paste structure. Consequently the maximum spacing factor is usually specified to be less than 0.008 inches in order to ensure durable concrete.

The second parameter is the specific surface of the air void system. The specific surface is the ratio of the surface area of the air bubbles divided by the volume of the bubbles. A large value of specific surface indicates a large number of small air voids which will provide more protection than a smaller number of larger voids. The recommended range of values of specific surface necessary to produce durable concrete is a minimum of 400-600 in²/in³. The final parameter which must be met is the minimum number of voids per linear inch of concrete. This parameter ensures an even distribution of voids throughout the concrete. The required number of voids per linear inch must be a minimum of 1.5 to 2 times the measured air content in percent.

7.3 Data and Results

Table 7.2 gives a summary of the entrained air data measured in both the fresh and hardened concrete for the mixtures analyzed along with the freeze-thaw test results. The table is divided into three groups: one non-air entrained mixture, one group with less than 3 percent entrained air and one with greater than 4 percent entrained air. It is clear from the table that non-air entrained concrete with a water/cement ratio equal to 0.30 is not durable since Mixture 11 recorded a very high spacing factor and as a result performed very poorly in the freeze-thaw test.

The group of mixtures which contained less than 3 percent entrained air exhibited irregular values of specific surface and spacing factor values considerably higher than 0.01 inches. The durability factors achieved were equally erratic, especially at the 7 day test age. The freeze-thaw performance improved with increased moist curing suggesting that as the amount of freezable water is reduced in the paste, larger spacing factors can be tolerated. The uncertainty involved in predicting durability is manifest in the performance of this group where Mixtures 12 and 18 possessed the highest of spacing factors in the group yet achieved the highest durability factors in the test. The data also show rather conclusively that approximately 3 to 4 percent entrained air is required in order for the concrete to consistently achieve satisfactory durability factors when tested according to ASTM C 666. This was achieved by Mixtures 13, 19, 22 and 23 whose average entrained air content was just over 4 percent.

7.4 Summary

A main objective of this program was to study whether the parameters governing freeze-thaw durability in concrete applied to high strength concrete or whether new values

Mixture Description	AIR-VOID SYSTEM DATA					DURABILITY FACTOR			
	Plastic Total Air Content (%)	Entrained Air Content (%)	Specific Surface (sq. in/cu. in)	Spacing Factor (in.)	Numbers of Voids per inch (ea)	Air Cured* 7 Days (%)	Moist Cured 7 Days (%)	Air Cured** 91 Days (%)	Moist Cured 91 Days (%)
NON-AIR ENTRAINED MIXTURES									
11-10A00HA0	2.00	1.2	224	0.044	0.6	8	8	19	n/a
POORLY AIR ENTRAINED MIXTURES									
12-10A00HA3	3.00	2.6	287	0.025	1.9	92	58	94	53
15-10A27HA3	3.00	1.1	681	0.015	1.8	47	29	86	61
18-10A33HA3	3.00	2.0	397	0.019	2.0	95	79	97	62
21-10A27HA3	2.75	1.4	529	0.016	1.9	46	43	93	76
ADEQUATELY AIR ENTRAINED MIXTURES									
13-10A00HA6	7.75	5.2	919	0.006	12	99	100	103	94
19-10A27HA6	6.00	4.1	523	0.011	5.3	102	N/A	104	93
22-10A27HA6	5.25	3.9	547	0.011	5.3	102	98	101	89
23-10A33HA6	5.75	4.3	823	0.007	8.9	103	99	104	68

needed to be applied. Since all air content tests were conducted in the fresh state, the possibility for error existed in interpreting test results from specimens tested in the hardened state. To validate this, nine mixtures were selected and their air-void parameters measured in the hardened state and compared to their fresh state measurements. These parameters were also evaluated in light of the mixture performance in the freeze-thaw test. The results show that at this water/cement ratio, non air entrained mixtures are not durable, mixtures with less than 3 percent entrained air exhibit erratic freeze-thaw performance, and those with greater than 4 percent entrained air attain high durability factors similar to normal strength concrete.

CHAPTER VIII

FREEZE-THAW TEST RESULTS AND ANALYSIS

8.1 Freeze-Thaw Testing

ASTM C 666 Procedure A was used to evaluate the freeze-thaw resistance of the high strength mixtures cast as part of this study. All mixtures were cured according to Table 4.5 with freeze-thaw testing commencing simultaneously with the permeability tests. This chapter presents the results obtained from the freeze-thaw tests conducted and analyzes these results to assess the effects of entrained air, water/cement ratio, curing, coarse aggregate absorption, and fly ash, silica fume, and cement content.

8.2 Effect of Air Entrainment

Phase I of the study involved 23 concrete mixtures having a water/cement ratio of 0.30 having a 91-day compressive strength of approximately 8000 psi. Figure 8.1 shows the freeze-thaw performance of these mixtures when tested at 7 days containing low absorption coarse aggregate and entrained air levels varying from 0 to 6 percent. When tested at 7 days, none of the non-air entrained mixtures achieved durability factors (DF) greater than 20 percent which is well below the ASTM C 666 minimum of 60 percent to be considered durable concrete. However, it should be noted that all mixtures which contained entrained air levels of 2 percent or higher achieved DF's near 100 percent. Companion specimens cast from the same mixtures were tested at 91 days of age and the performance is shown in Figure 8.2. There was little or no improvement in the performance of the non-air entrained, air cured specimens when tested at 91 days. This indicates that there is little benefit derived from increasing the moist curing period from 7 to 28 days and following with air curing until testing at 91 days. Ninety-one-day moist cured, non-air entrained specimens, however, showed a distinct improvement in durability achieving durability factors of 40, 50, and 80%. Data presented in Figure 8.2 also show that a minimum of 2 percent entrained air must be present in order to provide durable concrete.

Figures 8.3 and 8.4 show the freeze-thaw performance of the 0.30 water/cement ratio mixtures when cast with the high absorption coarse aggregate and tested at 7 and 91 days. As shown in Figure 8.3, at 7 days neither the air cured nor the moist cured non-air entrained specimens achieved durability factors greater than 20%. At 91 days of age, none of the non-air entrained specimens tested satisfactorily according to ASTM C 666 as shown in Figure 8.4. Figure 8.4 also shows a distinct loss of freeze-thaw resistance in the 91-day moist cured specimens made with high absorption coarse aggregate compared to the air cured companion specimens independent of the amount of entrained air. The results again showed that a minimum of 2 to 3 percent entrained air is required to provide durable concrete.

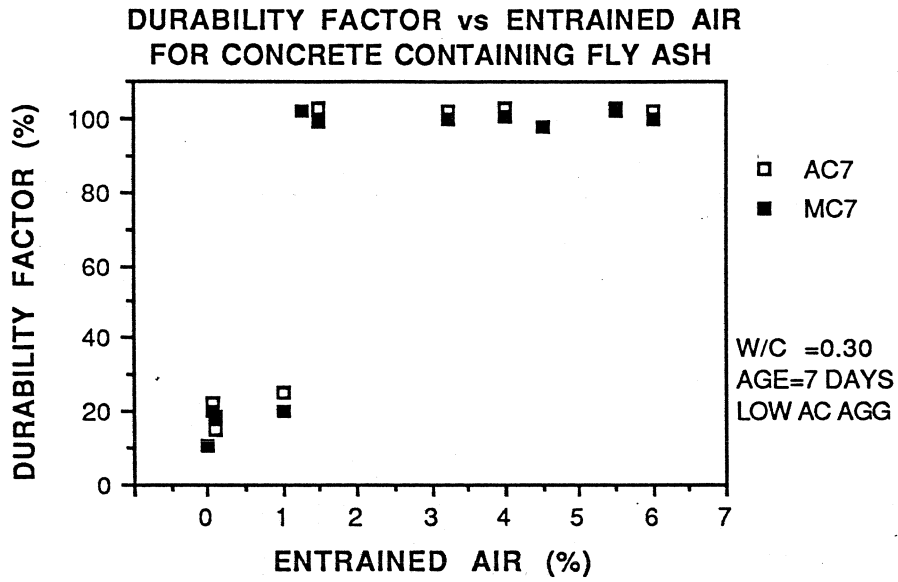


Figure 8.1 Durability Factor vs Entrained Air Content

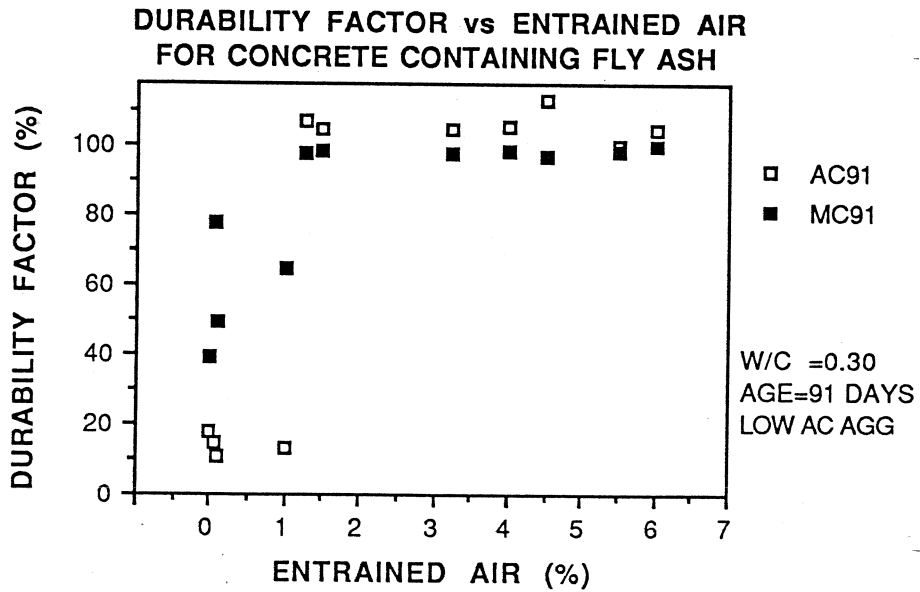


Figure 8.2 Durability Factor vs Entrained Air Content

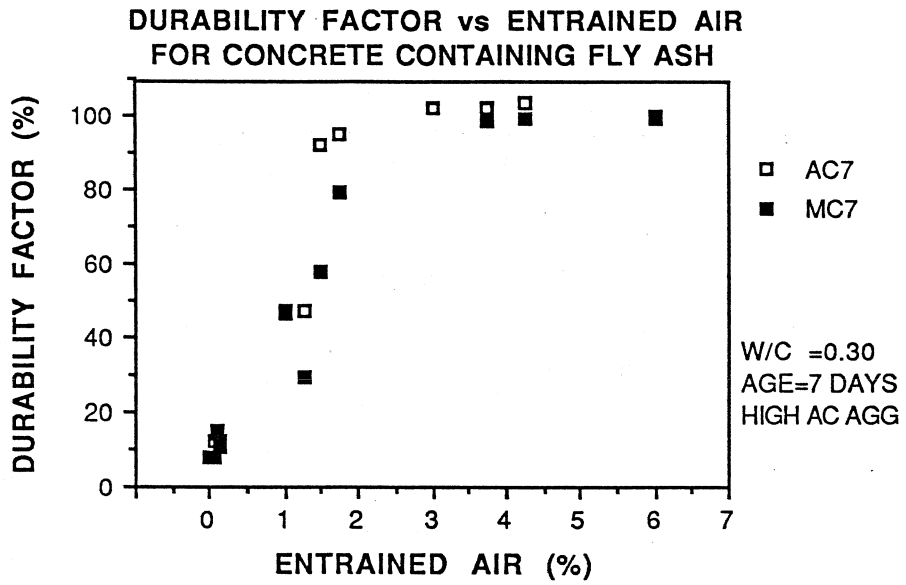


Figure 8.3 Durability Factor vs Entrained Air Content

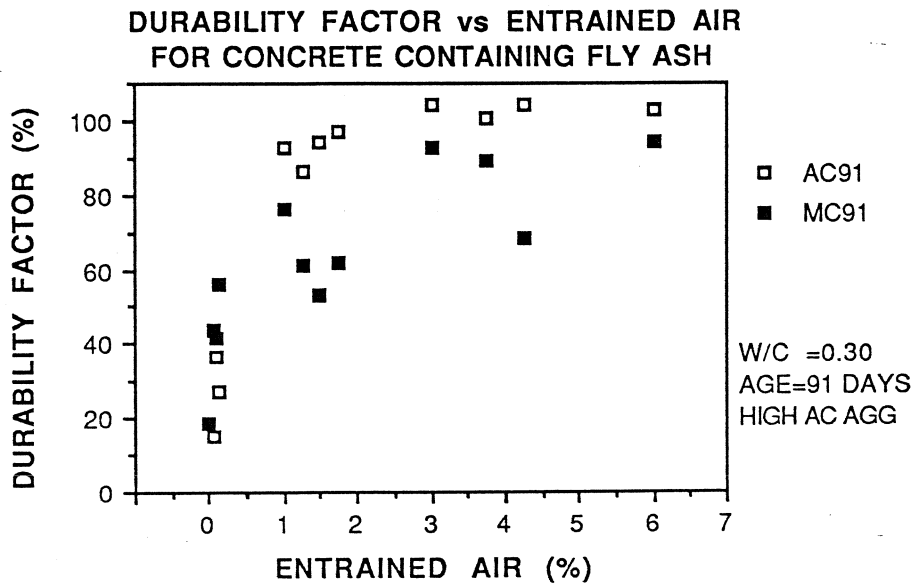


Figure 8.4 Durability Factor vs Entrained Air Content

The 8 mixtures cast in Phase II of the study were similar to those in Phase I except the water/cement ratio was lowered to 0.26. Since every concrete mixtures having six percent entrained air which was tested in Phase I achieved a high durability factor, mixtures in Phase II containing six percent entrained air were eliminated in order to concentrate on the testing of non-air entrained and three percent air entrained mixtures. Figures 8.5 through 8.8 show the results when the water/cement ratio was lowered to 0.26 for mixtures cast with both low and high absorption coarse aggregate and subjected to different curing conditions. Figures 8.5 and 8.6 shows that even at a water/cement ratio of 0.26, non-air entrained specimens are not freeze-thaw resistant at seven days of age regardless of curing method or coarse aggregate type. Both figures indicate the need for a minimum of 2 to 3 percent entrained air in order to achieve a durability factor of 60 percent according to ASTM C 666.

Figures 8.6 to 8.8 show that even at 91 days of age the non-air entrained, air cured specimens are not durable however the moist cured specimens are when made with low absorption coarse aggregate. Figures 8.7 and 8.8 both show that the air entrained mixtures made with high absorption coarse aggregate suffer distress due to the saturation level whereas low absorption coarse aggregate mixtures do not. Again it is clear that a level of air entrainment in the range of 2 to 3 percent is necessary to ensure freeze-thaw resistance especially if the concrete is exposed at early ages.

Phase III consisted of 16 mixtures containing silica fume contents of 7 and 10 percent by weight in addition to the cement. The silica fume concrete mixtures were evaluated for the effect of coarse aggregate absorption, cement content, and entrained air. Figures 8.9

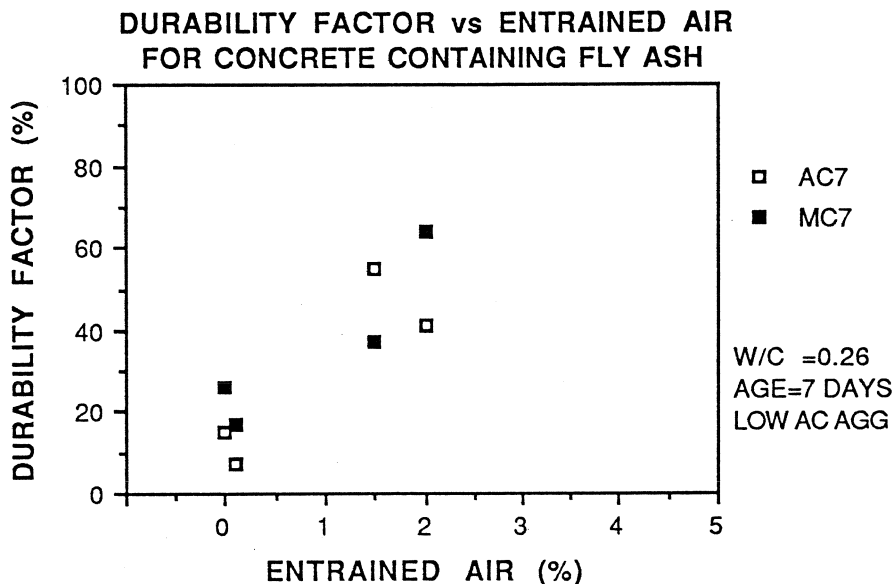


Figure 8.5 Durability Factor vs Entrained Air Content

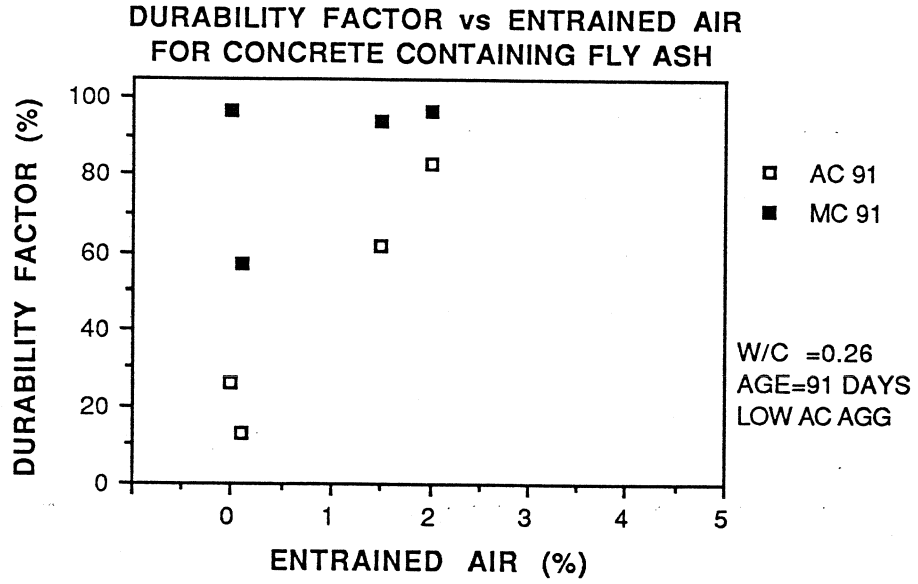


Figure 8.6 Durability Factor vs Entrained Air Content

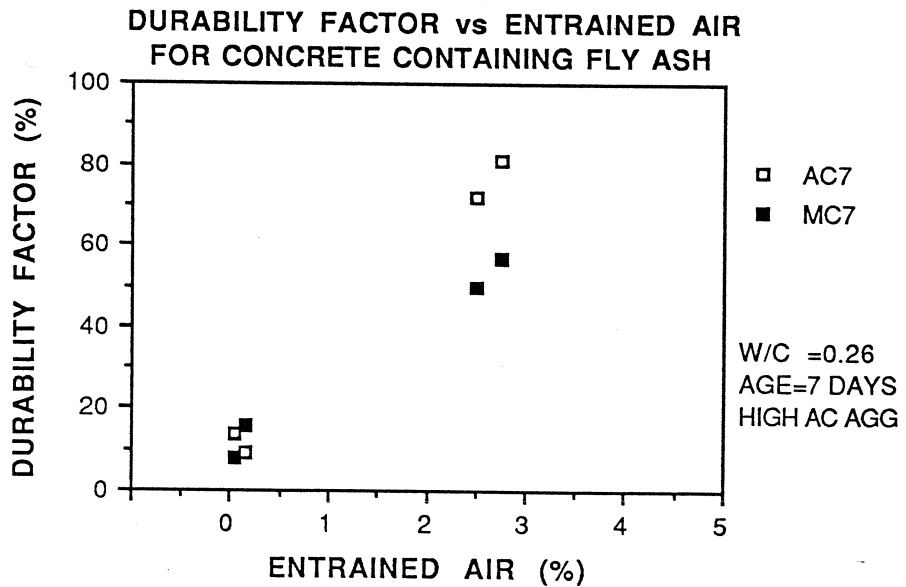


Figure 8.7 Durability Factor vs Entrained Air Content

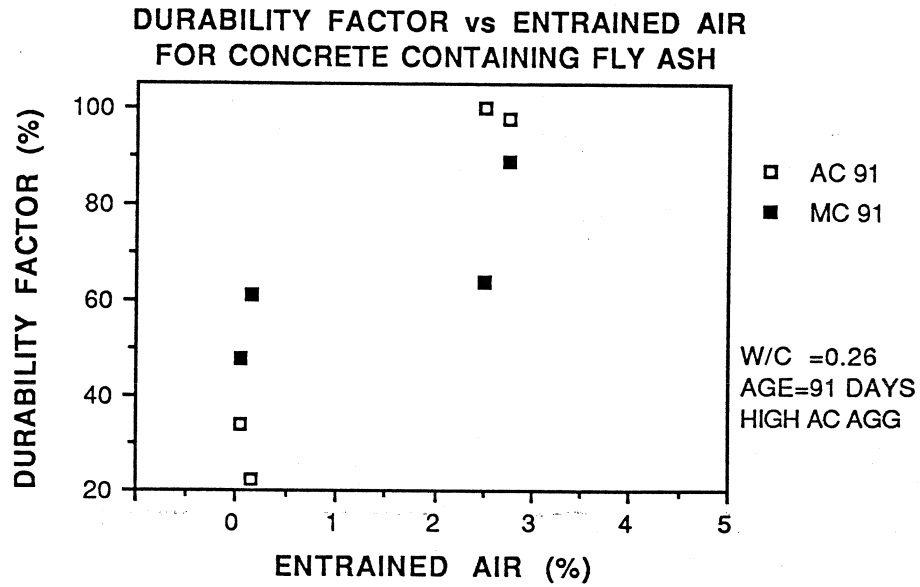


Figure 8.8 Durability Factor vs Entrained Air Content

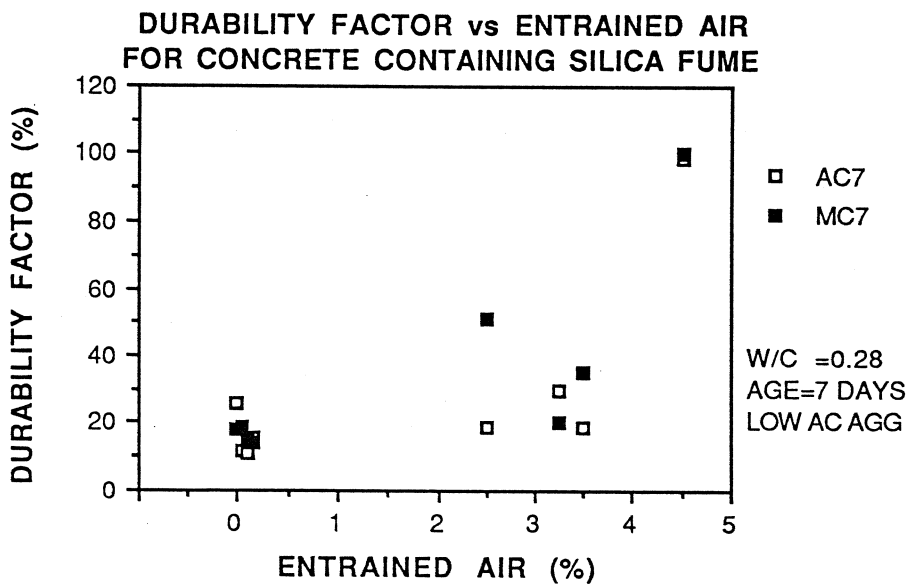


Figure 8.9 Durability Factor vs Entrained Air Content

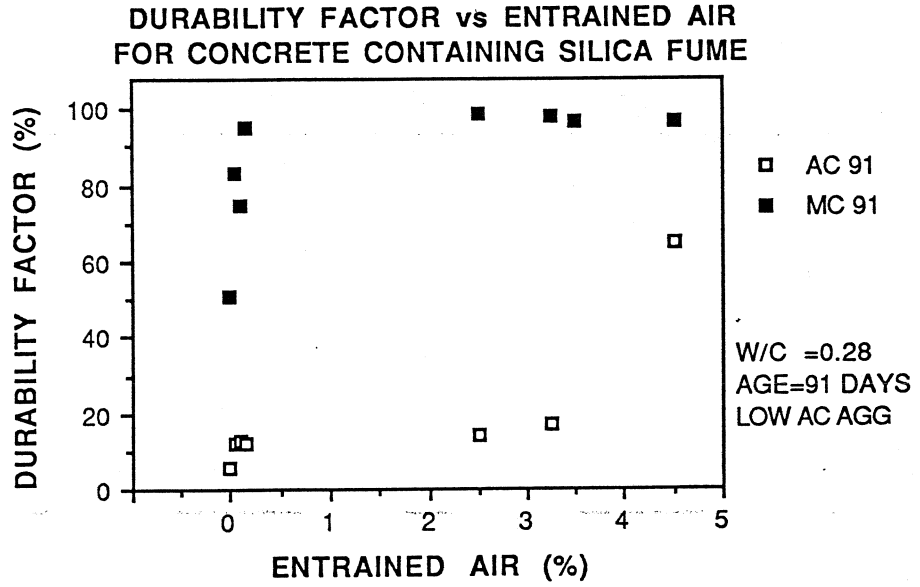


Figure 8.10 Durability Factor vs Entrained Air Content

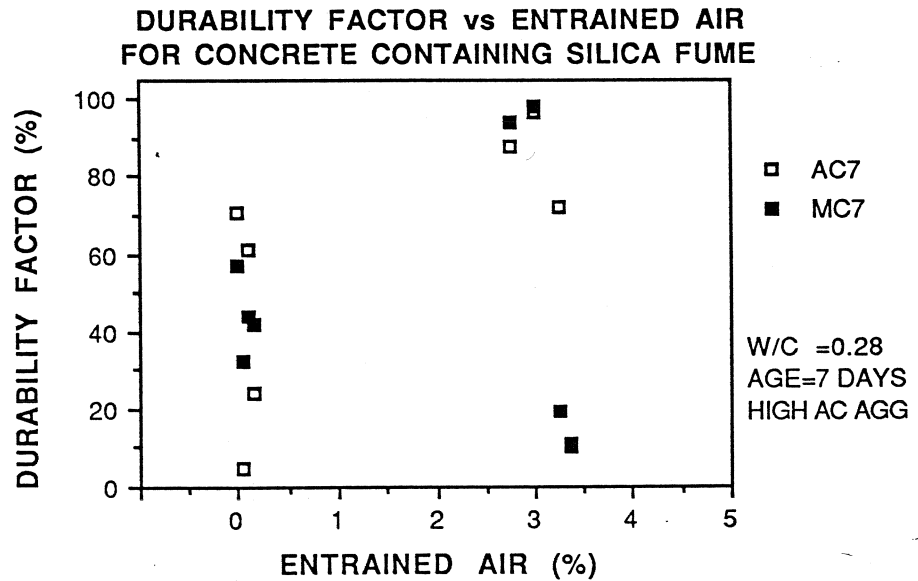


Figure 8.11 Durability Factor vs Entrained Air Content

through 8.12 show the durability factors for the silica fume mixtures plotted as a function of entrained air content for both aggregates at both test ages. Figure 8.9 shows that despite the extremely low permeability results recorded by these mixtures, their freeze-thaw resistance was poor even with over three percent entrained air. Only one mixture made with low absorption coarse aggregate was durable by ASTM 666 standards at 7 days of age and it required 4.5 percent to do so. When these mixtures were tested at 91 days, only the moist cured specimens recorded durable results.

Figure 8.11 shows the test results from the silica fume mixtures cast with high absorption aggregate tested at 7 days. Of note is the fact that the high absorption coarse aggregate whose porosity contributed to higher permeability readings and lower durability factors in the first two phases of the program combined with the cement/silica fume paste in Phase III to provide much higher durability factors than its low absorption companion specimens. Figure 8.12 shows that at 91 days the high absorption aggregate mixtures were much more durable than the low absorption aggregate mixtures.

It is interesting to note that the very property which makes silica fume concrete so attractive, its low permeability, also renders the concrete less durable when tested for freeze-thaw resistance. This fact was very evident from visual examination of many of the silica fume mixtures which exhibited serious cracking problems very early in the freeze-thaw test. This was a common problem among the silica fume specimens but did not occur in the fly ash mixtures. Equally interesting is the fact that the high absorption aggregate which was detrimental to the durability of the fly ash mixtures interacts with the cement/silica fume paste to provide relieve for the water as it freezes and provides a measure of frost resistance even without entrained air.

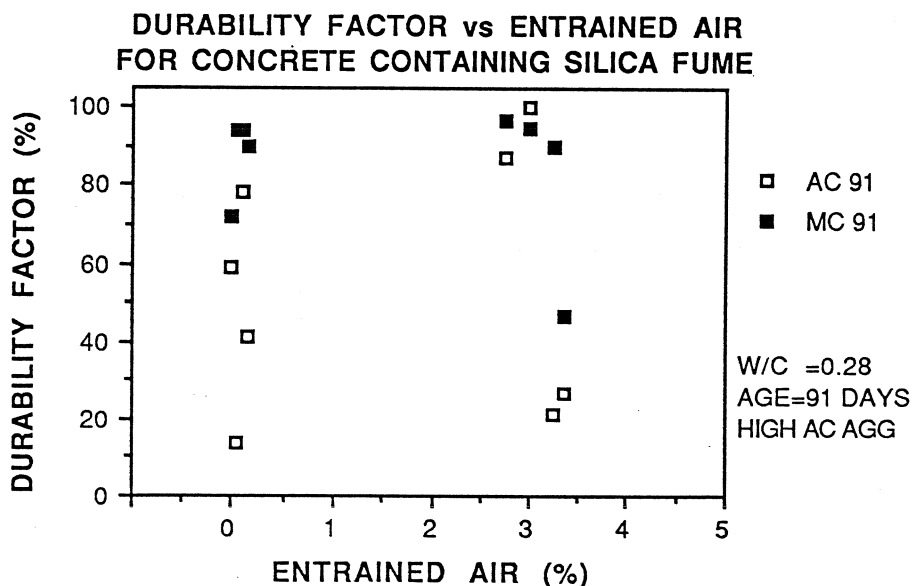


Figure 8.12 Durability Factor vs Entrained Air Content

8.3 Effect of Water/Cement Ratio

One primary hypothesis to be tested in this study was whether lowering the water/cement ratio significantly improved the freeze-thaw resistance of the concrete in the absence of entrained air. Accordingly, mixtures utilizing several combinations of fly ash and aggregates were compared in order to evaluate the effect of the change in water/cement ratio on the freeze-thaw resistance of concrete. Figure 8.13 shows the durability factors obtained from testing three mixtures containing 940 lb/cy of cement, no fly ash, low absorption coarse aggregate, no entrained air, and water/cement ratios of 0.30, 0.28 and 0.26, respectively. Only when moist cured for 91 days did lowering the water/cement ratio result in an improvement in durability performance. However, even with 92 days of moist curing, the highest durability factor achieved was 57 percent which is still below the ASTM C 666 minimum of 60 percent.

Figure 8.14 compares the freeze-thaw test results obtained for the 0.26 and 0.30 water/cement ratio mixtures made with the high absorption coarse aggregate. There was little improvement in durability for the 7-day test age due to the lower water/cement ratio. The improvement in durability factor achieved after 91 days of moist curing by the 0.26 mixture over the 0.30 mixture was more significant with the high absorption aggregate than with the low absorption aggregate. However the highest DF achieved was 61 percent which barely meets the ASTM minimum of 60 percent. A main conclusion drawn from this data is that for high strength concrete mixtures without fly ash, lowering the water/cement ratio from 0.30 to 0.26 is not sufficient to consistently produce durable concrete when tested according to ASTM C 666, even when moist cured for 91 days.

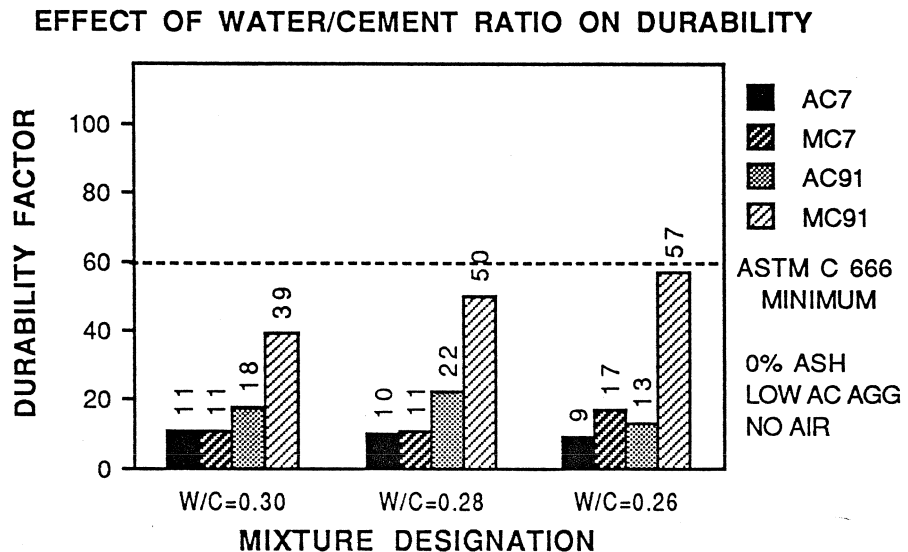


Figure 8.13 Effect of Water/Cement Ratio on Durability

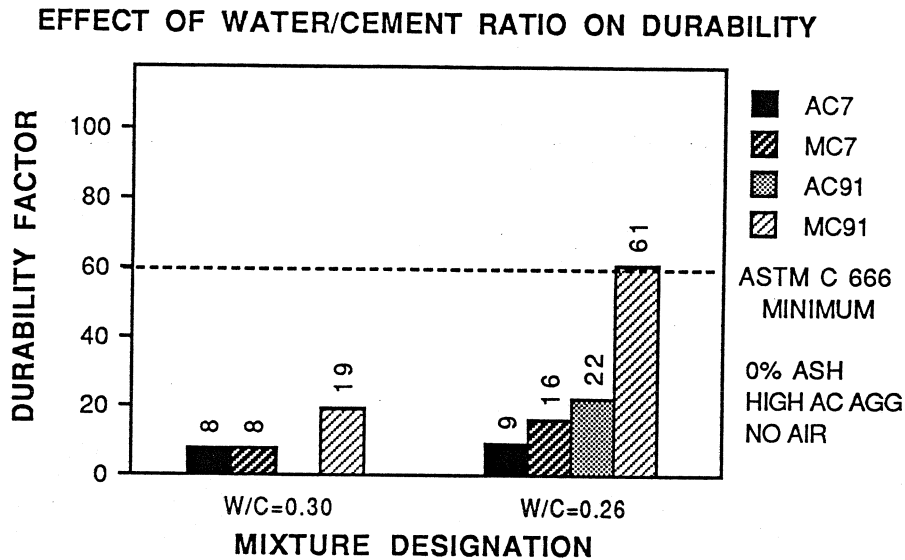


Figure 8.14 Effect of Water/Cement Ratio on Durability

The effect of lowering the water/cement ratio on mixtures containing fly ash was also evaluated. The mixtures tested above were duplicated while substituting fly ash for 27 percent of the portland cement by weight. These mixtures were cast with water/cement ratios of 0.30, 0.28, and 0.26 with both coarse aggregates and no air entrainment. Figures 8.15 and 8.16 show how the freeze-thaw resistance varied with water/cement ratio for the fly ash mixtures cast with the low absorption and high absorption aggregates, respectively. The data showed that for fly ash mixtures, lowering the water/cement ratio resulted in only slight improvements in the freeze-thaw resistance for specimens moist cured up to 28 days. Only the 91 day moist cured, low absorption coarse aggregate specimens exceeded the minimum satisfactory durability factor of 60 percent where lowering the water/cement ratio on these specimens raised the DF from 78 to 97 percent. None of the 91-day moist cured fly ash specimens, made with high absorption coarse aggregate, achieved a durability factor of 60 percent.

Figures 8.17 and 8.18 show the performance of the 0 percent fly ash mixtures cast using both aggregates and a small amount of air entrainment. In general, for marginal amounts of air entrainment, reducing the water/cement ratio resulted in improved freeze-thaw resistance. In Figure 8.17 it can be seen that 1 percent entrained air in the 0.30 water/cement ratio mixture did not produce durable specimens whereas 1.5 percent in the 0.26 water/cement ratio mixture did. Figure 8.18 showed that when 2 to 3 percent entrained air was present, lowering the water/cement ratio improved the DF's of the concrete. Both

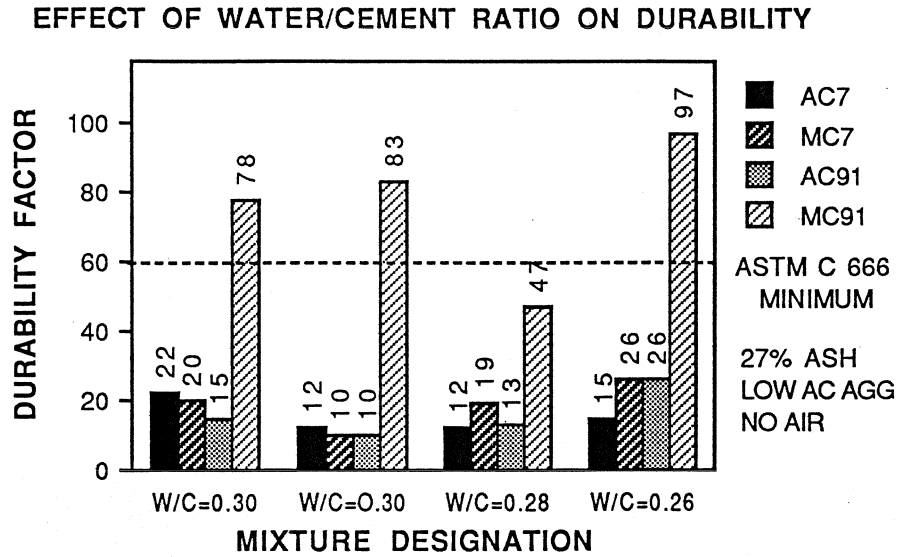


Figure 8.15 Effect of Water/Cement Ratio on Durability

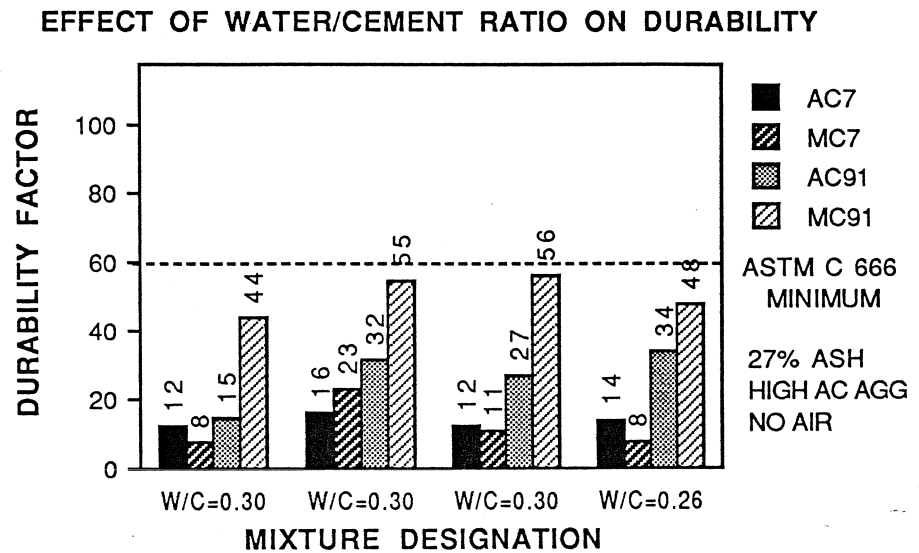


Figure 8.16 Effect of Water/Cement Ratio on Durability

EFFECT OF WATER/CEMENT RATIO ON DURABILITY

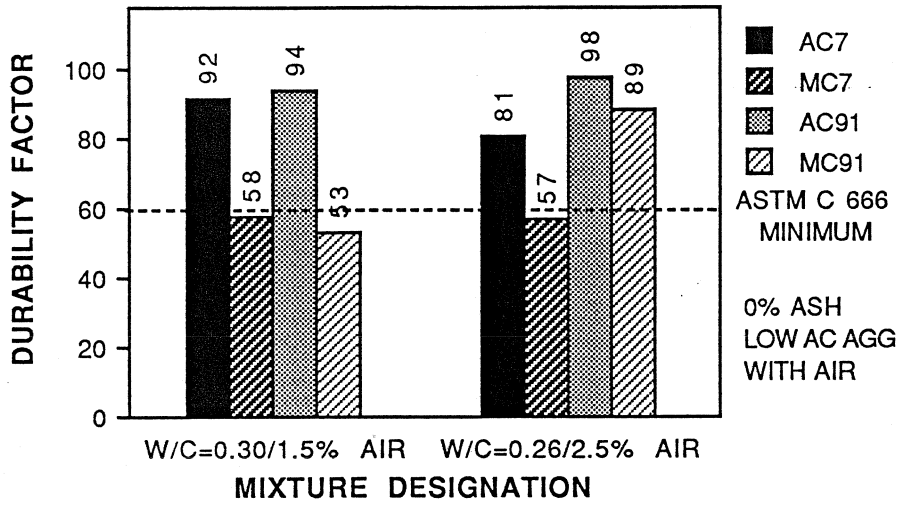


Figure 8.17 Effect of Water/Cement Ratio on Durability

EFFECT OF WATER/CEMENT RATIO ON DURABILITY

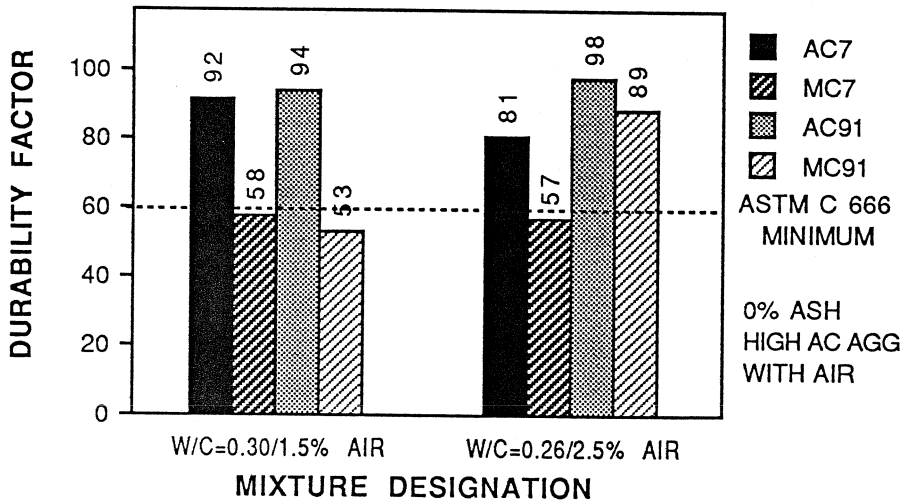


Figure 8.18 Effect of Water/Cement Ratio on Durability

figures showed the effect of aggregate saturation in that the 7 day air cured specimens were more durable than those receiving 7 days full moist curing. Figures 8.19 and 8.20 compare the durability factors achieved by the 27 percent fly ash mixtures with both aggregates when a small amount of air entrainment was added. When 2 to 3 percent entrained air is present in mixtures containing fly ahs, lowering the water/cement ratio results in improved durability factors.

In summary, it is clear that while lowering the water/cement ratio is helpful in improving the durability of high strength concrete, by itself it cannot be relied upon to consistently provide freeze-thaw resistant concrete.

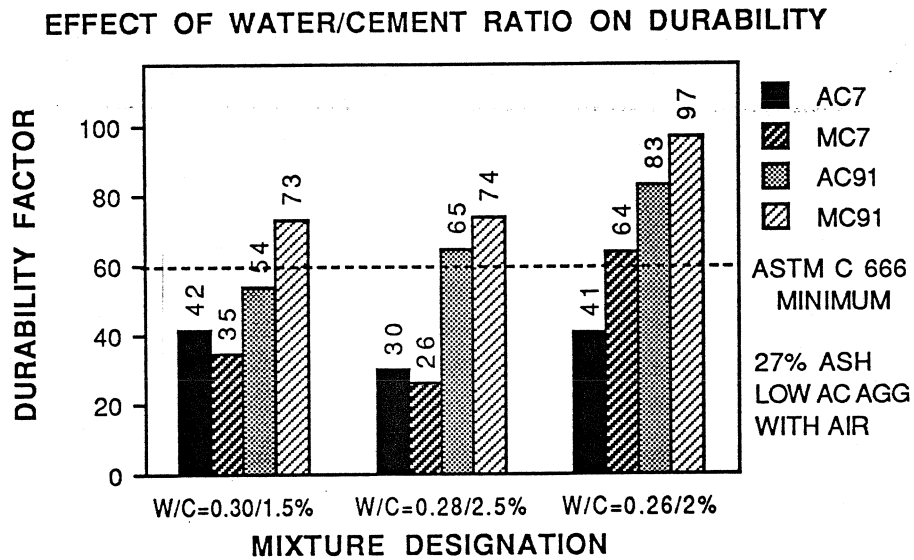


Figure 8.19 Effect of Water/Cement Ratio on Durability

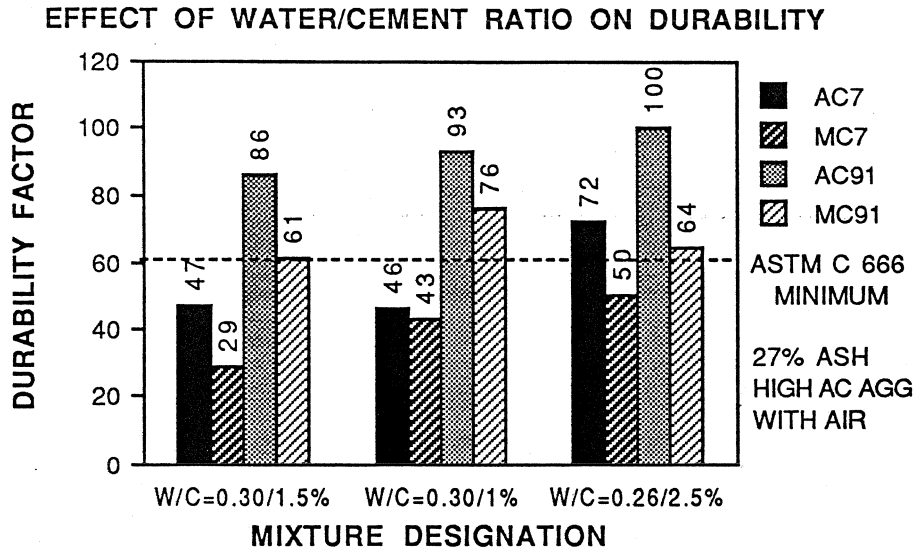


Figure 8.20 Effect of Water/Cement Ratio on Durability

8.4 Effect of Curing

In order to accurately measure the effect of the curing conditions on the freeze-thaw durability of the mixtures tested, a common baseline was needed. The baseline selected was the durability factor (DF) that each mixture achieved at 7 days of age under air curing. This curing condition provided 4 days of moist curing followed by 3 days of air curing prior to testing. All durability factor measurements for each mixture were then compared to the mixture's baseline DF and the relative change recorded. With this method, non-air entrained and air entrained mixtures could be compared without the entrained air overshadowing the effect of the curing.

The data showing the effect of curing on the mixtures cast in Phases I and II are shown in Table 8.1. The data was subdivided into three groups based upon entrained air content and the average durability factor at 7 days under air curing was calculated for each category. The "non-air entrained" group consisted of 16 mixtures cast without entrained air. The next group consisted of mixtures with approximately 3 percent entrained air or less. The final group had entrained air contents greater than 3 percent which achieved Durability Factors near 100 percent for all curing conditions.

Table 8.1 Effect of Curing on Durability of Phase I/II Mixes.

Mixture Designation	Baseline DF (Average DFAC7)	Change in Durability Factor		
		MC7	AC91	MC91
Non-Air Entrained	13%	2%	7%	40%
Less than 3% Air	55%	-11%	19%	25%
Greater than 3% Air	102%	-1%	2%	-8%
All Mixtures	52%	-3%	9%	21%

It is clear from the data in Table 8.1 that for the non-air entrained Phase I and II mixtures tested in this study, extending the moist curing period did not increase the durability factor significantly. Only after 91 days of moist curing did a substantial increase in durability factor occur. For those mixtures with less than 3 percent air entrainment, extending the moist curing period to 28 days increased the average DF by 19 percent from 55 to 74 percent. Further moist curing for a full 91 days only increased the DF by an average of 6 percent so moist curing past 28 days is not effective. In conclusion, if entrained air is not present, no amount of moist curing up to 91 days will make the concrete durable when tested according to ASTM C 666. If less than 3 percent entrained air is present, 28 days of moist curing and some drying period is necessary to make the concrete durable.

Table 8.2 Effect of Curing on Durability of Silica Fume Mixtures.

Mixture Designation	Baseline DF (Average DFAC7)	Change in Durability Factor		
		MC7	AC91	MC91
Non-Air Entrained	28%	2%	1%	54%
Less than 3% Air	33%	7%	-4%	50%
Greater than 3% Air	95%	2%	-12%	1%
All Mixtures	30%	5%	-1%	52%

Table 8.2 shows similar results for the silica fume mixtures cast in Phase III of the study. In this table, 8 non-air entrained mixtures, 5 mixtures with less than 3%, and 3 mixtures with greater than 3 percent entrained air were examined for the effect of curing on the durability factor. For the non-air entrained silica fume mixtures, the average baseline DF was 28 percent which was higher than the 13 percent attained by the fly ash mixtures. Despite these higher initial durability factors, extending the moist curing period for the silica fume mixtures without entrained air did not produce durable concrete until a full 91 days of moist curing had been applied. It could be concluded that moist curing non-air entrained silica fume concrete beyond 4 days will not provide durability in lieu of air entrainment unless it is provided for 91 days.

The average durability factor for the 7-day air cured silica fume mixtures with less than 3 percent entrained air was only slightly higher than the non-air entrained mixtures at 33 percent. Extending the moist curing period to 28 days for these mixtures did not raise the durability factor as much as it did for the fly ash mixtures. This result was unexpected and must be the result of the decreased permeability of the silica fume concrete. As with the non-air entrained specimens, when the air entrained silica fume mixtures were given 91 days of moist curing, either all the freezable water had hydrated or it was being held in such small cavities that it couldn't freeze and this rendered the concrete durable.

In summary, the high strength mixtures tested in this study failed to produce durable concrete on a consistent basis regardless of water/cement ratio or mineral admixture unless more than 3 percent entrained air was present. While extending the moist curing period improved the durability factor of non-air entrained mixtures, a full 91 days of moist curing was required to even approach the ASTM C 666 minimum of 60 percent. Fly ash mixtures with between 2 and 3 percent entrained air usually required 28 days of moist curing followed

by air curing in order to attain a DF greater than 60 percent and similarly air entrained silica fume mixtures needed 91 days of moist curing to be judged durable by ASTM C 666.

8.5 Effect of Coarse Aggregate

The absorption capacity and pore size distribution of the coarse aggregate was expected to play a significant role in the freeze-thaw resistance of the concrete mixes tested. Several studies reviewed in Chapter 3^{13, 25, 66} confirmed the fact that if the coarse aggregate has high absorption capacity and a medium to fine pore distribution, the chance of freeze-thaw damage to concrete made with this type of aggregate is greatly increased. This is because the aggregate will readily absorb water available to the concrete and, if frozen in the saturated state, will either fracture due to the pressure from expansion or push unfrozen water out of the aggregate into the surrounding paste and stress the matrix in this manner.

Figures 8.21 and 8.22 compare the durability performance of identical mixtures at water/cement ratios of 0.30 and 0.26 without fly ash or entrained air having different coarse aggregates. In Figure 8.21, with a water/cement ratio equal to 0.30, the low absorption coarse aggregate mixture was slightly more frost resistant than its high absorption coarse aggregate counterpart. However, neither of the mixtures tested satisfactorily according to ASTM C 666. When the water/cement ratio was lowered to 0.26, Figure 8.22 shows the performance was about equal regardless of the coarse aggregate used. Figures 8.23 and 8.24 compare the non-air entrained fly ash mixtures at both water/cement ratios for each of the coarse aggregate types. In every case but one the low absorption coarse aggregate mixtures

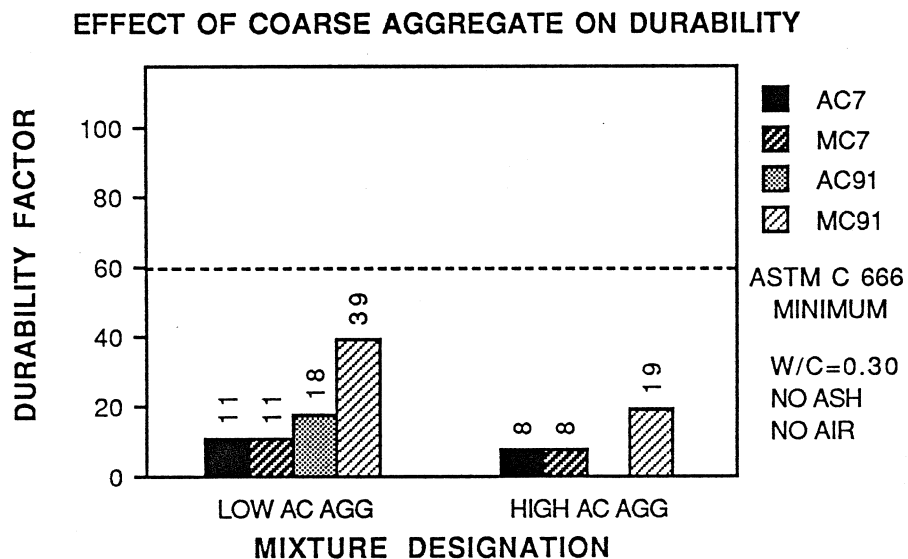


Figure 8.21 Effect of Coarse Aggregate on Durability

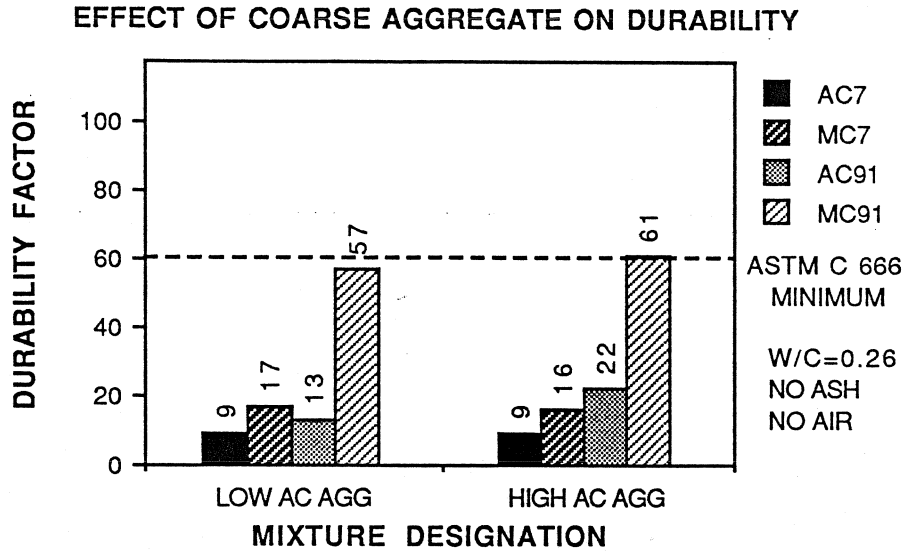


Figure 8.22 Effect of Coarse Aggregate on Durability

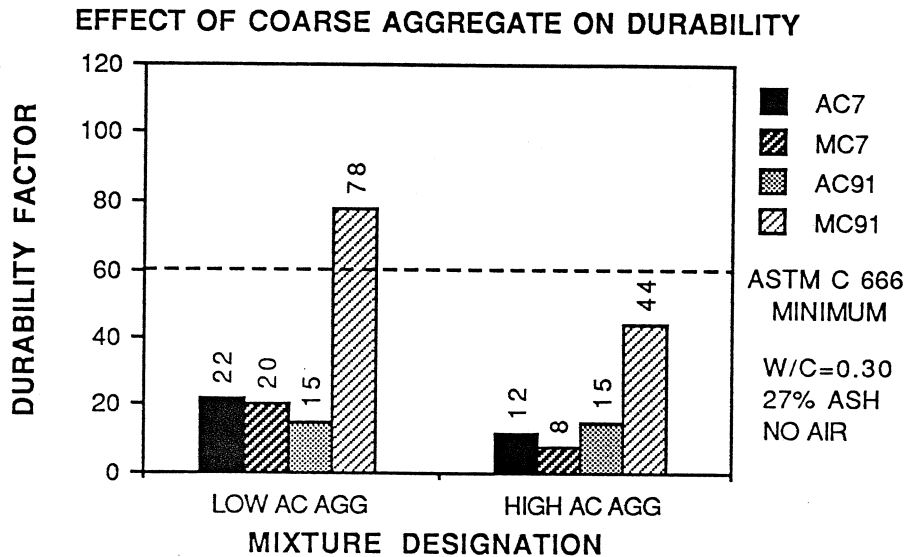


Figure 8.23 Effect of Coarse Aggregate on Durability

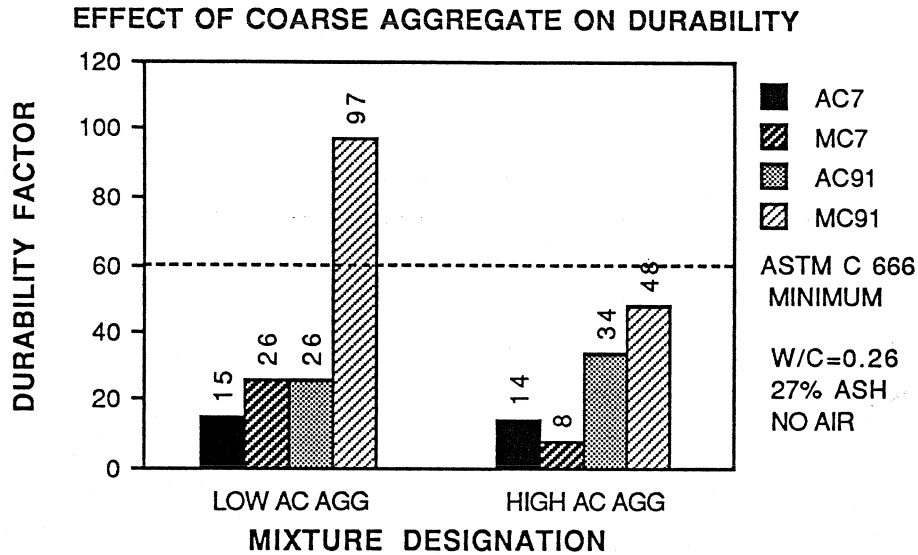


Figure 8.24 Effect of Coarse Aggregate on Durability

achieved slightly higher durability factors than the mixtures containing the high absorption coarse aggregate. In general, for the non-air entrained concrete with or without fly ash, the coarse aggregate absorption made little difference in the concrete's durability.

When comparing the effect of coarse aggregate absorption on freeze-thaw resistance of air entrained mixtures, the amount of air entrainment usually overshadowed the effect of the aggregate absorption. Figures 8.25 through 8.28 show that for similar air contents, the low absorption coarse aggregate mixture usually had higher durability factors. When analyzing the test results for the air entrained mixtures with high absorption aggregate, the 91-day air cured specimens, which had been moist cured for 28 days and air cured for 63 days, consistently achieved higher durability factors than companion specimens which had received a full 91 days moist curing. This did not occur in the air entrained mixtures containing low absorption coarse aggregate nor was it found in any of the non-air entrained mixtures regardless of coarse aggregate type. This would indicate that the 63 days of air curing dried the specimens below the critical saturation level and this, combined with a small amount of air entrainment, enabled the specimens to achieve a higher durability factor.

In summary, coarse aggregate absorption had a minor effect on the freeze-thaw resistance of the high strength fly ash concrete mixtures tested in this study. The use of high absorption aggregate tended to lower the durability performance of the mixtures both with and without air entrainment when compared to identical mixtures cast with low absorption aggregate. The high absorption mixtures also experienced distress due to saturation of the coarse aggregate when moist cured continuously until tested.

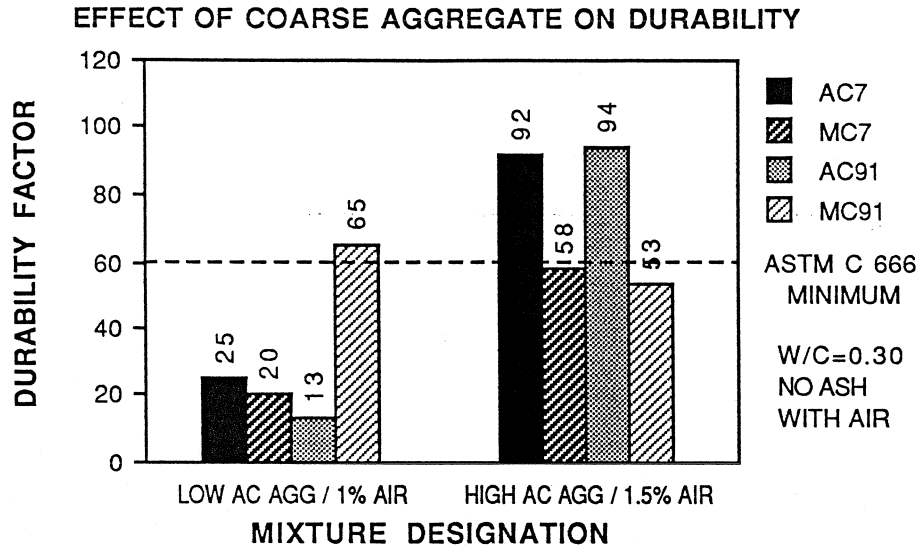


Figure 8.25 Effect of Coarse Aggregate on Durability

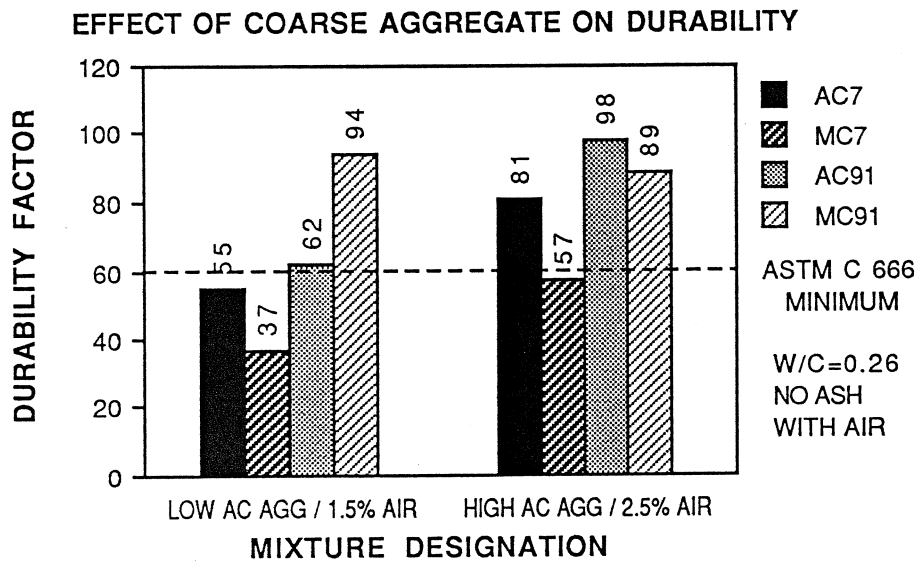


Figure 8.26 Effect of Coarse Aggregate on Durability

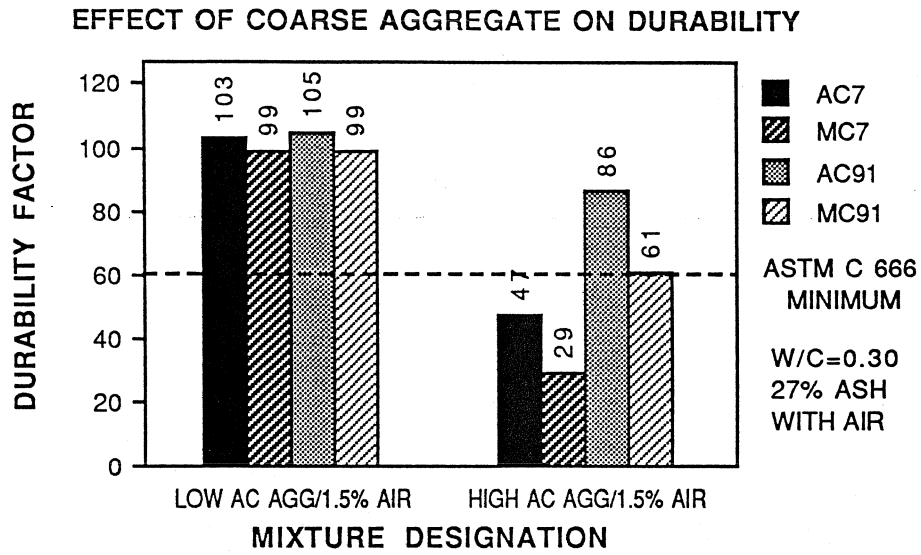


Figure 8.27 Effect of Coarse Aggregate on Durability

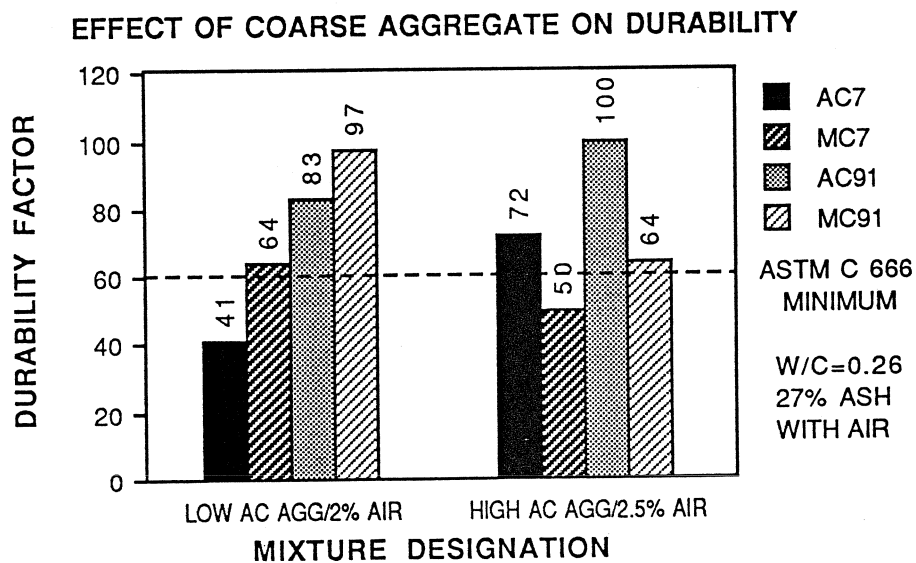


Figure 8.28 Effect of Coarse Aggregate on Durability

8.6 Effect of Fly Ash

The test results were also compared to evaluate the effect of use of fly ash had on the freeze-thaw resistance of non-air entrained mixtures. Previous research^{9,31} on normal strength concrete has shown that the addition of fly ash has little effect on the freeze-thaw resistance of concrete except to raise the required dosage level of air entraining agent necessary to create an adequate air void system. Fly ash was investigated in this study due to its effect on reducing permeability which was observed in Chapter 5. It was felt that the pozzolanic effect of the fly ash would reduce the capillary porosity especially at later ages and this could result in frost protection if the remaining water could be made unfreezable due to physical adsorptive forces.

The test results are shown in Figures 8.29 through 8.32. In 30 out of 36 cases the use of fly ash resulted in increased durability factors when compared to identically cured non-air entrained mixtures without fly ash. In most cases, however, the increase was small and did not result in satisfactory DF's according to ASTM C 666. Only at the 91-day moist cured condition where the pozzolanic reaction was more prevalent did the fly ash produce substantial increases in durability and even this did not occur in all cases. The effect of fly ash on air entrained mixtures was also examined, but not graphed because the results showed no clear effect that could be attributed to the presence of the ash in the mixtures.

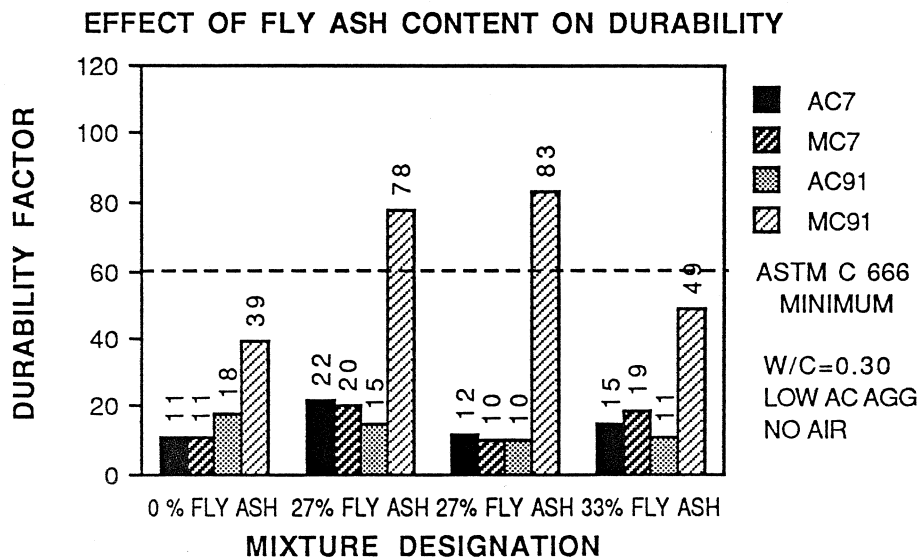


Figure 8.29 Effect of Fly Ash Content on Durability

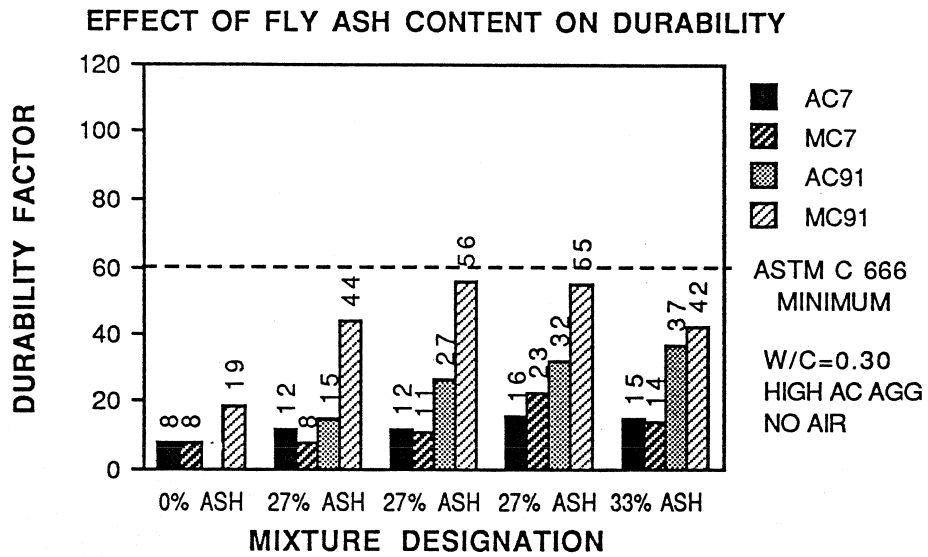


Figure 8.30 Effect of Fly Ash Content on Durability

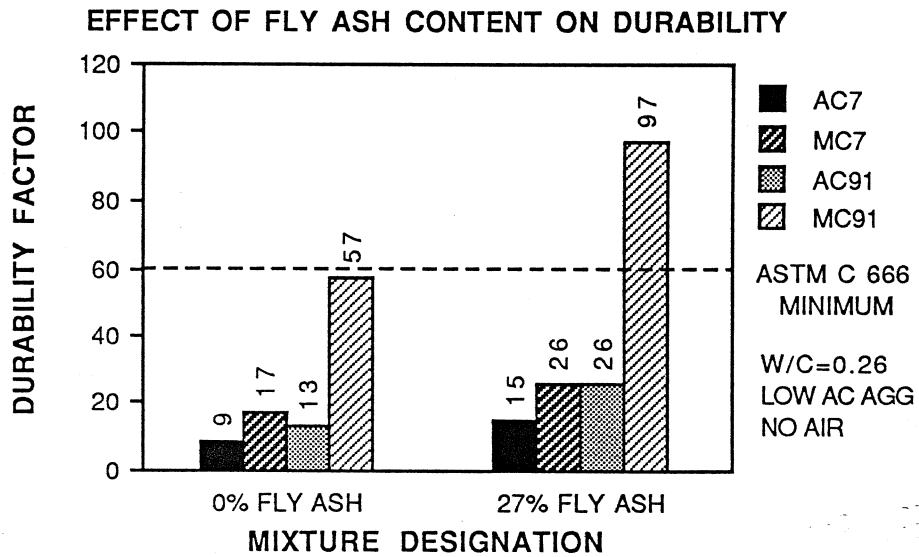


Figure 8.31 Effect of Fly Ash Content on Durability

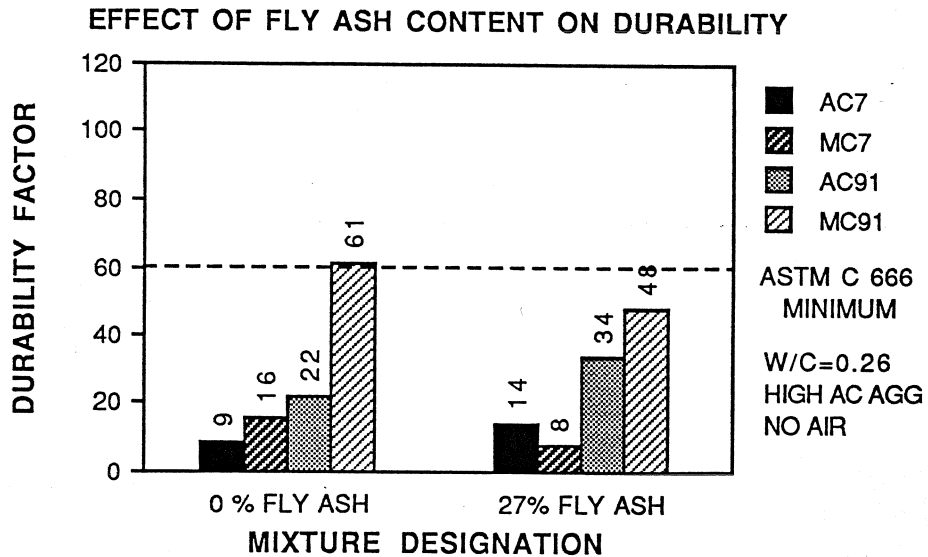


Figure 8.32 Effect of Fly Ash Content on Durability

In conclusion, the use of fly ash as a cement replacement for the high strength mixtures tested in this study resulted in only slightly improved durability factors. The use of fly ash could not be relied upon to provide freeze-thaw resistance in the absence of air entrainment. Air entrained fly ash mixtures were not consistently more durable than non-fly ash mixtures with similar air contents.

8.7 Effect of Silica Fume

Phase III of the program studied the effect of silica fume on the freeze-thaw resistance of high strength concrete both with and without air entrainment. Silica fume contributes to strength and durability in two ways: pozzolanic activity and the fineness effect. Because of its high SiO_2 content, silica fume is extremely reactive with the calcium hydroxide ($\text{Ca}(\text{OH})_2$), which is created during the cement hydration process, and combines with it to produce calcium silicate hydrate (C-S-H). Due to its small size, the silica fume particles fit in the voids between the hydrated cement grains in the paste and, upon combination with the calcium hydroxide, fill these capillary voids with more C-S-H which increases the strength and reduces the permeability.

In the literature review presented in Chapter III, it was noted that dosage levels of silica fume greater than 15 percent by weight of cement consistently produced less durable concrete when tested for freeze-thaw resistance than concrete containing 5 to 10 percent silica fume. This has been attributed to increased pressure within the paste caused by the decreased permeability due to the presence of the silica fume. Accordingly, the addition of

silica fume at rates of 7 and 10 percent by weight of cement were used in this study and compared to evaluate the effect on concrete durability. The water/cementitious material ratio, $W/(C+SF)$, was kept constant throughout this phase at 0.28 by weight and mixtures were cast with both types of coarse aggregate and with and without entrained air. No fly ash was used in this phase of the study.

8.7.1. Effect of Silica Fume Content. A total of eight 10-sack mixtures were cast in the first half of Phase II and how their freeze-thaw performance varied with silica fume content is shown in Figures 8.33 through 8.36. Figures 8.37 through 8.40 compare the freeze-thaw resistance of eight additional 8-sack mixtures subsequently cast and evaluated in the same manner. The results show that the silica fume content had no significant effect on non-air entrained concrete durability at either cement level. When air entrainment was added, its presence completely obscured the effect of silica fume content. The combination of high absorption aggregate with 7 percent silica fume resulted in higher than expected durability factors in two non-air entrained mixtures shown in Figures 8.34 and 8.38. This may be due more to the aggregate than to the silica fume percentage.

8.7.2 Effect of Cement Content. Because of the increased amount of fines in the mixtures due to the presence of the silica fume, it was desired to determine if the cement could be reduced without lowering freeze-thaw performance or raising the concrete's permeability. The data shown in the previous eight graphs was regraphed in Figures 8.41 through 8.48 in order to compare the effect of cement content on the freeze-thaw resistance of the silica fume mixtures. This could result in substantial cost savings in material if performance did not suffer at the lower cement content. Figures 8.41 through 8.44 show

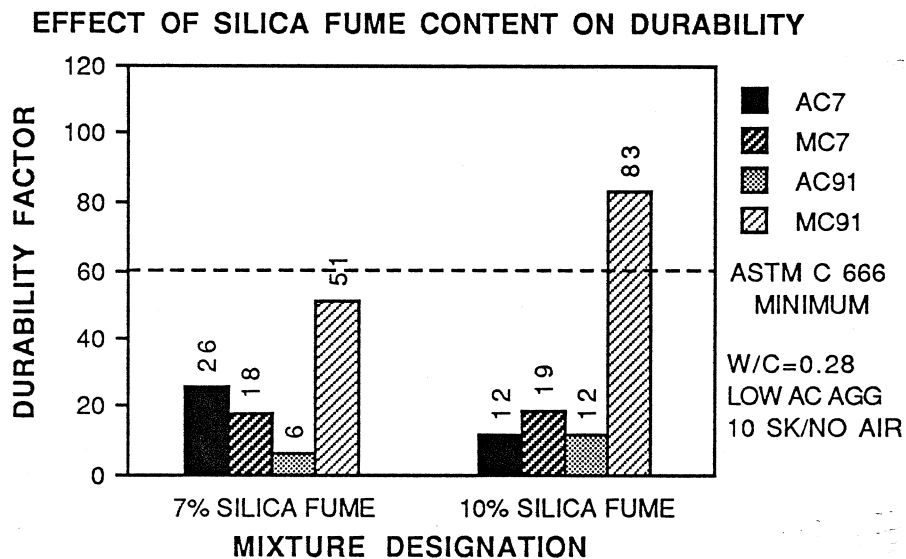


Figure 8.33 Effect of Silica Fume Content on Durability

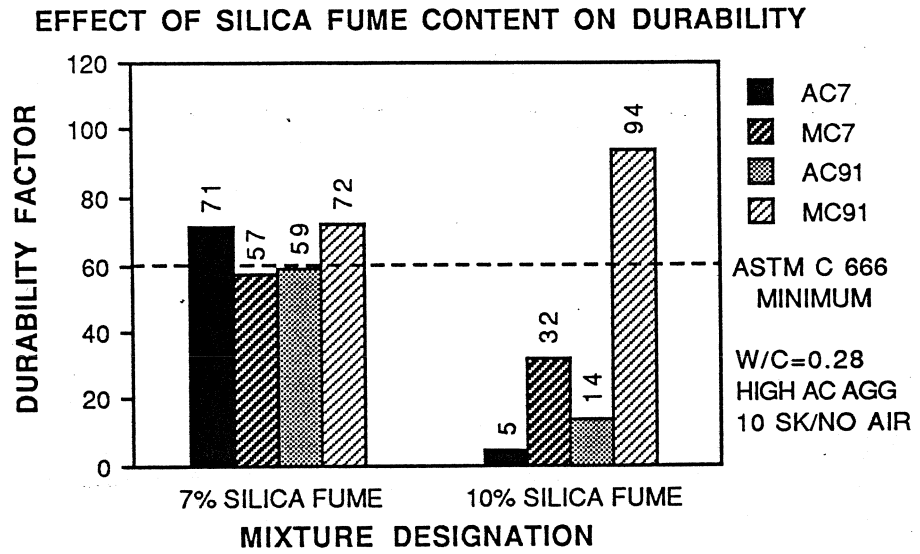


Figure 8.34 Effect of Silica Fume Content on Durability.

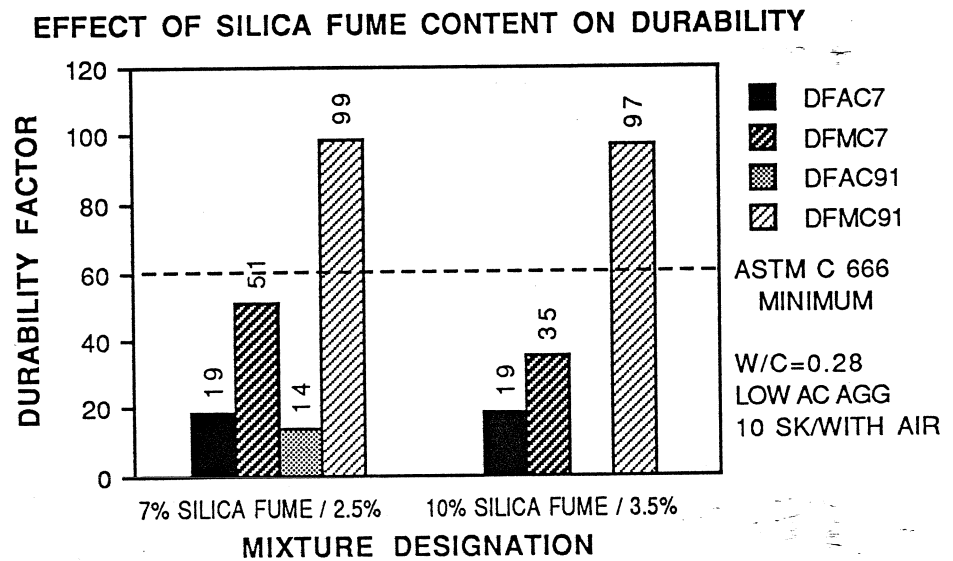


Figure 8.35 Effect of Silica Fume Content on Durability

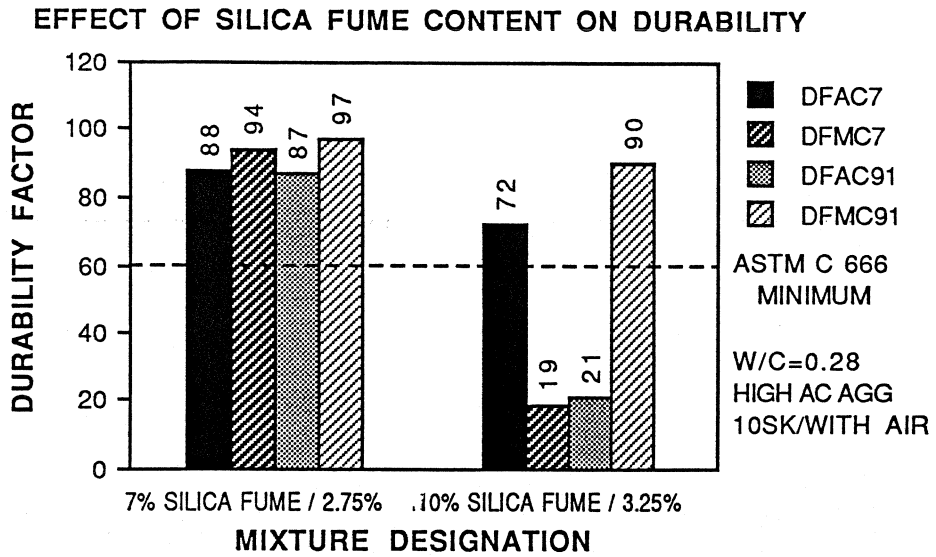


Figure 8.36 Effect of Silica Fume Content on Durability

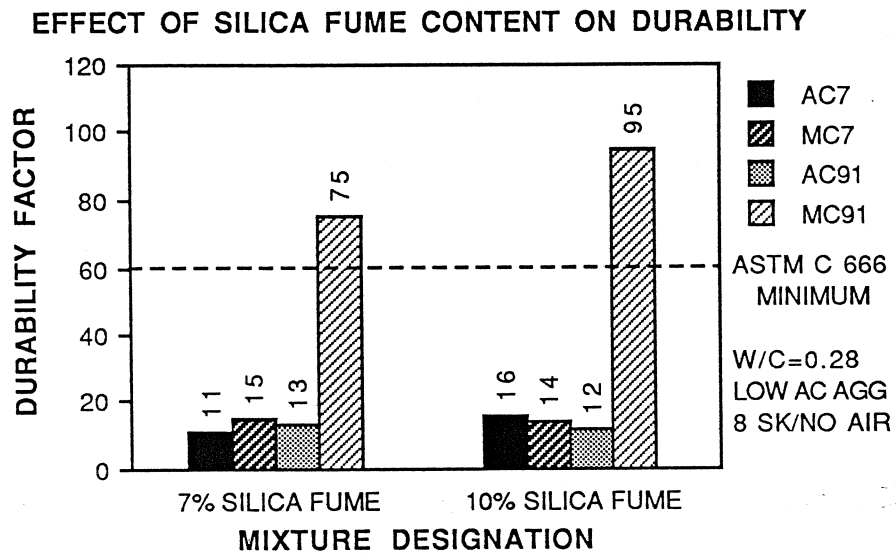


Figure 8.37 Effect of Silica Fume Content on Durability

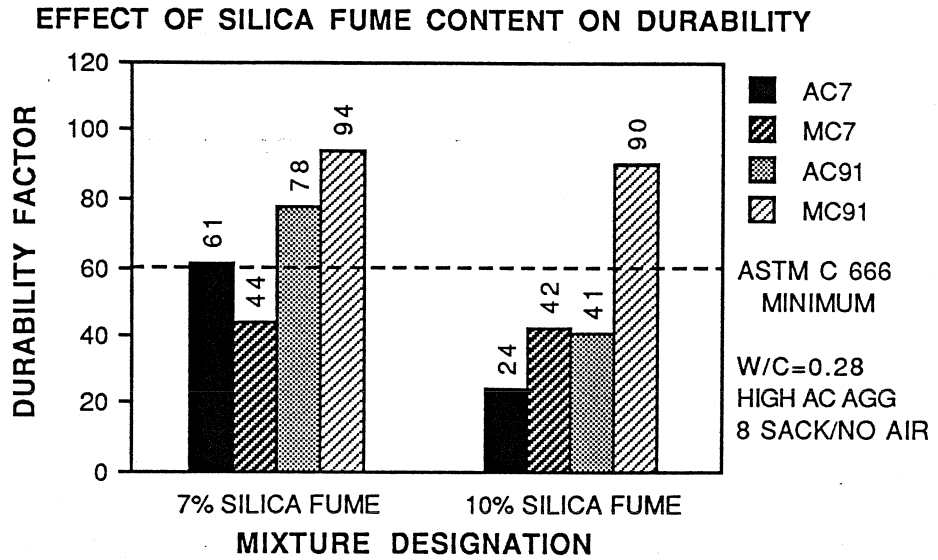


Figure 8.38 Effect of Silica Fume Content on Durability

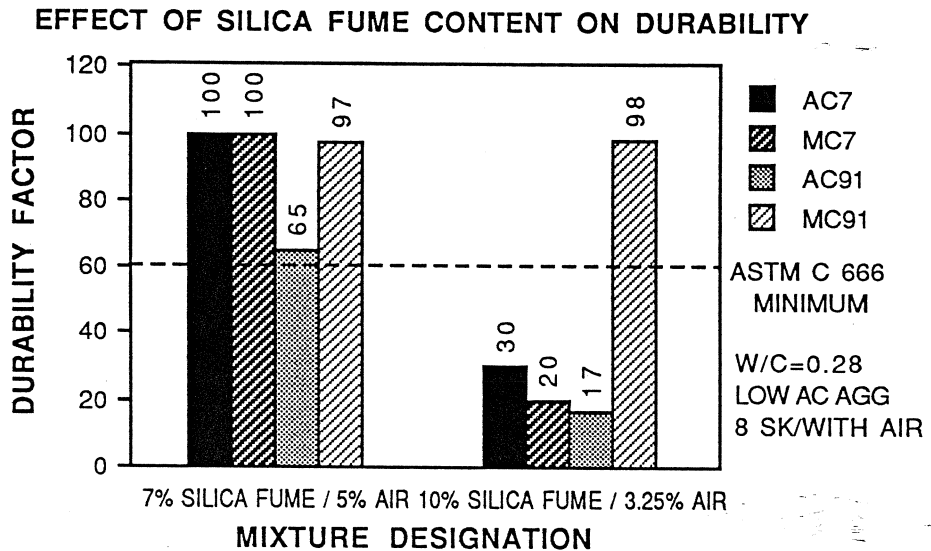


Figure 8.39 Effect of Silica Fume Content on Durability

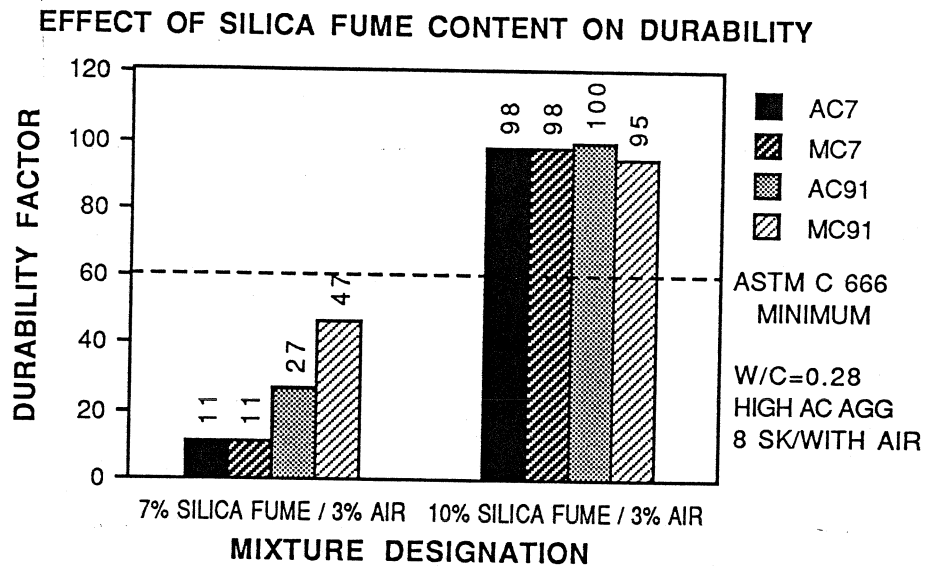


Figure 8.40 Effect of Silica Fume Content on Durability

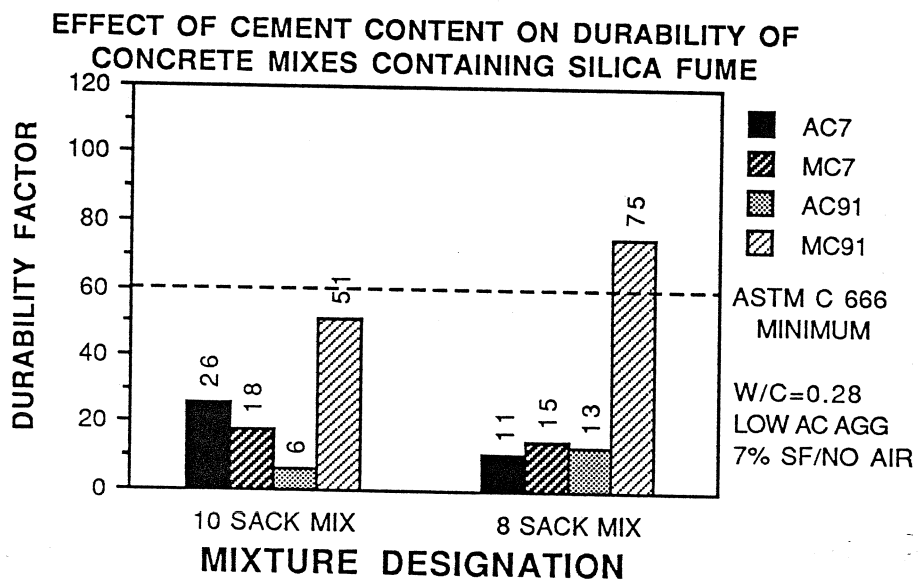


Figure 8.41 Effect of Cement Content on Durability

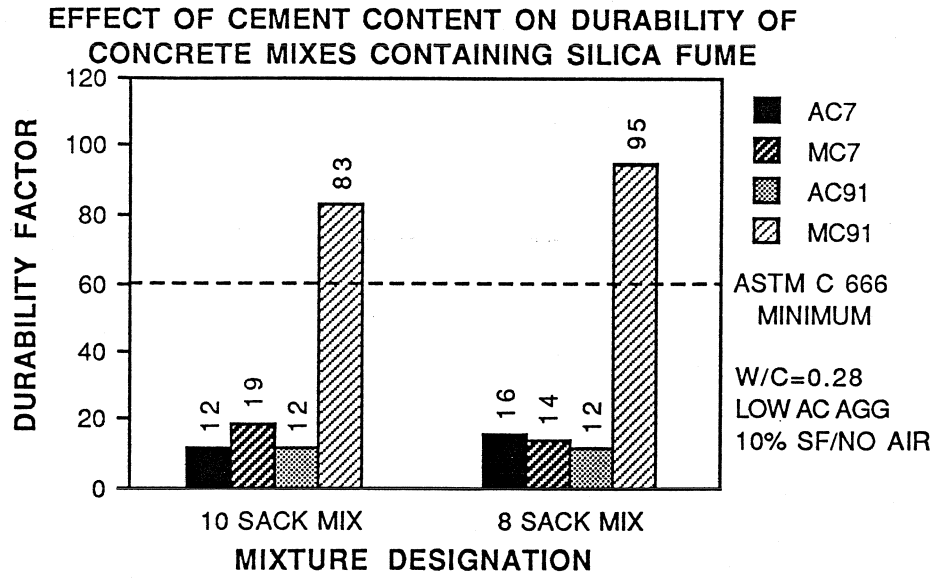


Figure 8.42 Effect of Cement Content on Durability

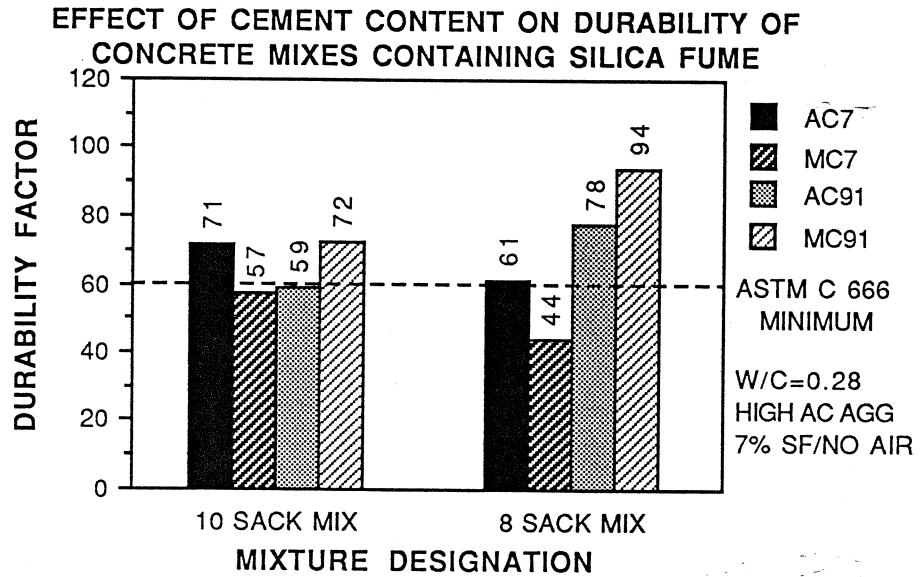


Figure 8.43 Effect of Cement Content on Durability

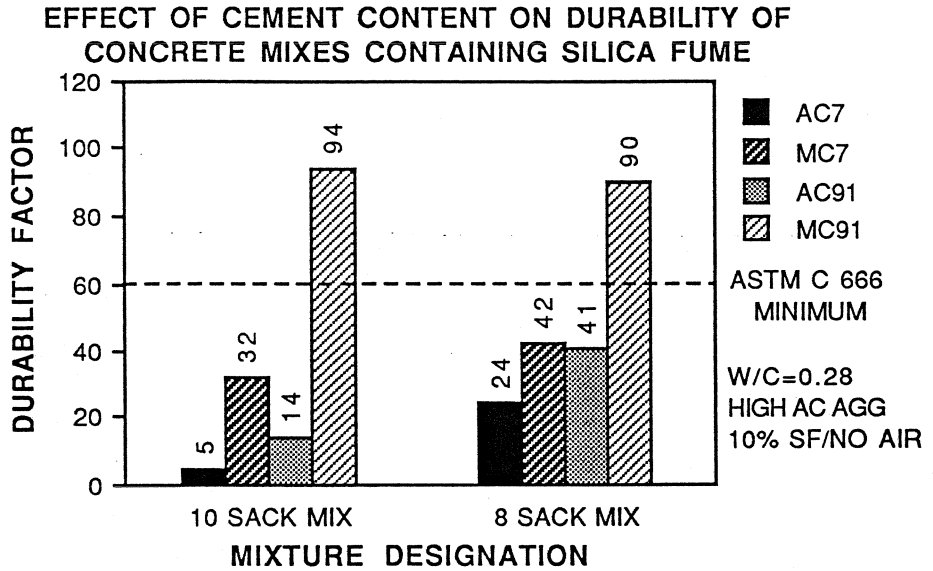


Figure 8.44 Effect of Cement Content on Durability

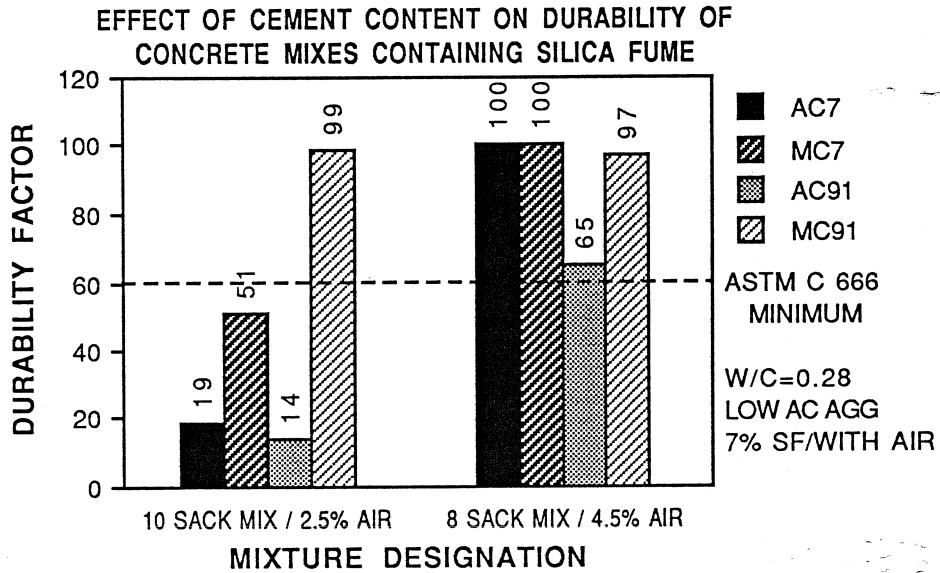


Figure 8.45 Effect of Cement Content on Durability

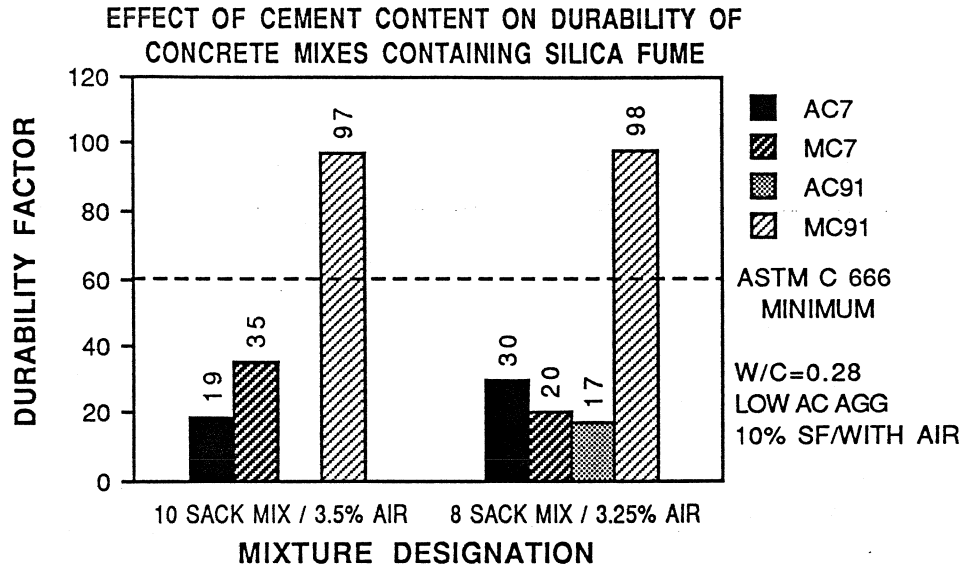


Figure 8.46 Effect of Cement Content on Durability

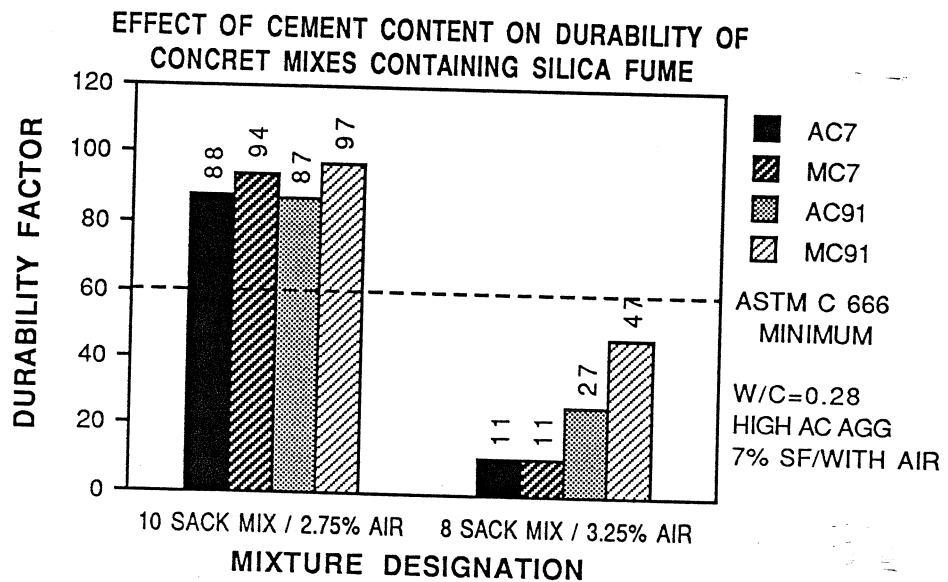


Figure 8.47 Effect of Cement Content on Durability

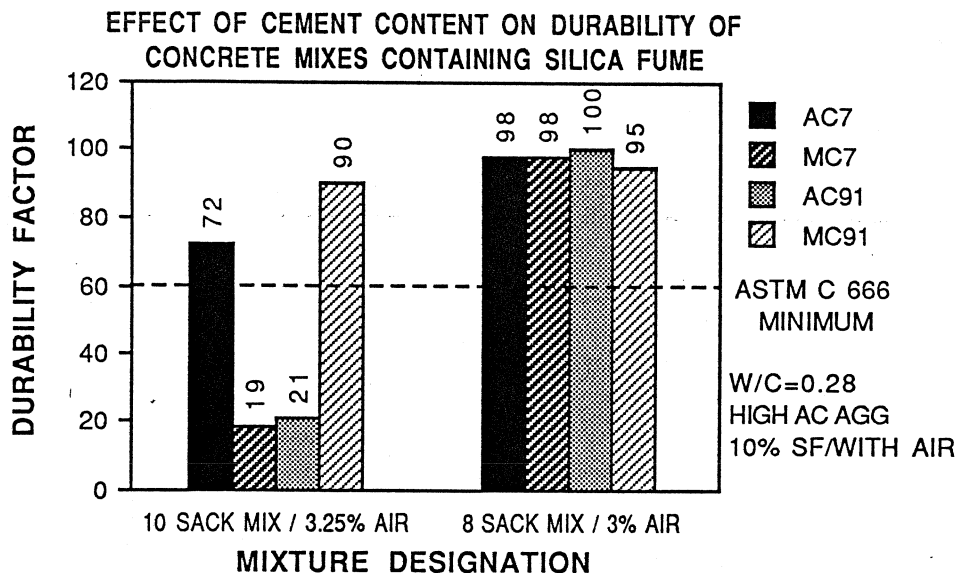


Figure 8.48 Effect of Cement Content on Durability

that neither the 7 nor the 10 percent non-air entrained silica fume mixtures were sensitive to cement content when cast with either coarse aggregate. When the air entrained silica fume mixtures were examined to evaluate the effect of cement content, this effect was completely obscured by the air entrainment.

8.7.3 Effect of Air Entrainment. The presence of air entrainment proved to be the governing factor when comparing the durability performance of all the silica fume mixtures regardless of cement or silica fume content. As shown in Figure 8.35, entraining small amounts of air in the 10-sack, low absorption coarse aggregate silica fume mixtures resulted in only slight improvements in their durability factors over those shown in Figure 8.33 for identical non-air entrained mixtures. Only the 91-day moist cured specimens from each silica fume mixture in both graphs attained a DF greater than 60 percent. These results were surprising when compared to the effect a small amount of entrained air had on the durability factors of the fly ash mixtures tested in Phases I and II. This is probably due to the increased density of the silica fume mixtures as evidenced by the very low values of permeability discussed in Chapter 5. This leads to the conclusion that perhaps the air content levels and associated spacing factors which provide durability for fly ash concrete does not provide the same margin of improvement for silica fume concrete because of its reduced porosity.

8.7.4 Effect of Coarse Aggregate. In analyzing the results from the fly ash mixtures tested in Phase I and II, it was found that the concrete cast with low absorption aggregate consistently achieved higher durability factors and lower permeability values than identical mixtures made with high absorption aggregate. This is attributed to the higher porosity of the high absorption coarse aggregate and the inability of the concrete made with this

aggregate to control external sources of water and prevent saturation. A review of the 8-sack non-air entrained silica fume concrete mixtures in Figure 8.38 shows that the one made with the high absorption aggregate achieved higher durability factors than an identical mixture cast with low absorption aggregate. This trend was not observed, however, in the 10-sack mixtures as shown in Figure 8.42. A review of Figures 8.35, 36, 39 and 40 validates the data shown in Figures 8.11 and 8.12 showing that air entrained silica fume concrete mixtures cast with the high absorption coarse aggregate consistently performed more durably than identical mixtures containing low absorption aggregate.

It can be concluded that the same aggregate property that hinders concrete performance when using fly ash, high porosity, becomes a positive feature when this aggregate is combined with the very impermeable silica fume paste. The porosity of the coarse aggregate appears to provide the same function as does air entrainment to some degree. Of note is the fact that better performance was obtained with the 7 percent silica fume content than with the 10 percent level indicating that the decreased permeability caused by the silica fume counteracted the positive effect of the porous aggregate. The data clearly shows that the presence of the high absorption coarse aggregate alone cannot be relied upon to provide durability in lieu of air entrainment. However, it seems to assist the air void system in providing relief for the very impermeable silica fume paste.

8.8 Summary

The data clearly show that a minimum of 2 to 3 percent entrained air is necessary in order to produce fly ash concrete with water/cement ratios in the 0.26 to 0.30 range which can consistently achieve durability factors greater than 60 when tested according to ASTM C 666 Procedure A. This air entrainment value may be 4 percent or higher for silica fume concrete at this water/cement ratio because of the very dense paste produced. Reducing the water/cement ratio was not a significant factor in improving the durability of the concrete mixtures and did not result in any mixtures attaining acceptable durability factors unless the mixture was moist cured for 91 days. Moist curing up to 28 days produced little improvement in durability and on many occasions resulted in lower durability factors.

In most cases, fly ash concrete mixtures produced using low absorption aggregate were more durable than companion mixtures made with high absorption aggregate. High absorption aggregate fly ash mixtures with adequate air entrainment frequently experienced losses in durability factor due to saturation of the coarse aggregate when moist cured continuously until testing. The air cured specimens from these mixtures consistently tested more durable than companion specimens receiving full moist curing. Low absorption aggregate fly ash mixtures experienced no such aggregate saturation effects. The effect of fly ash on the durability of the mixtures was beneficial but not significant.

The addition of silica fume generally improved the durability of the high strength concrete mixtures tested; however, none of the non-air entrained silica fume mixtures were

durable until moist cured for 91 days. Equal amounts of air entrainment appear to be less effective at improving the durability of silica fume concrete than fly ash concrete because of the increased density and reduced porosity inherent in the cement/silica fume paste. Thus, it appears that higher amounts of air entrainment as measured in the fresh state may be necessary to ensure durability. The effect of silica fume and cement contents on durability were negligible compared to the effect of air entrainment. High absorption aggregate silica fume concrete mixtures performed in a more durable manner than identical mixtures containing low absorption aggregate.

CHAPTER IX SUMMARY AND CONCLUSIONS

9.1 Summary

The use of high strength concrete is becoming more common each year. Concrete strength levels which were considered extraordinary 10 years ago are now commonplace. As designers become more familiar with its properties, and producers develop experience with the production procedures involved, usage of high strength concrete is certain to grow. While most high strength concrete has thus far been limited to building structures, more applications are now being considered in the transportation area as well. Most applications in the transportation area involve the material being exposed to the environment and thus has raised questions about the durability of high strength concrete. One of the questions which needs to be addressed is the durability of high strength concrete exposed to freezing environments.

The reason for this concern is that the standard practice for rendering concrete freeze-thaw resistant is the use of entrained air. Air entrainment reduces the strength of concrete and could negate some of the advantage of using high strength concrete. Consequently many feel that air entrainment is not necessary in high strength concrete due to its high strength, low water/cement ratio and low permeability. The rationale provided for this is that there is very little internal water in the hardened concrete available to freeze and the low permeability will prevent saturation from the environment once the member is in service. Research completed on the subject has been contradictory in support of this premise.

The purpose of this dissertation was to address the use of high strength concrete in cold weather environments and assess its durability in that environment both with and without entrained air. One main goal was to establish guidelines and make recommendations to designers and engineers regarding how to specify high strength concrete in the field so as to ensure it remains durable throughout its intended service life.

The study was divided into three phases totaling over 50 different mixtures. Phases I and II investigated the durability of high strength concrete containing high calcium fly ash meeting the requirements of ASTM Class C (TSDHPT Type B) with respective water/cement ratios of 0.30 and 0.26. The 91-day compressive strength of the concretes tested in Phases I and II was approximately 8,000 and 10,000 psi respectively. In Phase III concrete containing condensed silica fume with a water/cement ratio equal to 0.28 and a 91-day compressive strength of 11,000 to 12,000 psi was cast and tested. In Phases I and II, fly ash content, coarse aggregate type, the amount and type of curing, and the entrained air content were varied in order to evaluate their effect on concrete durability. In Phase III, cement and silica fume content were varied in addition to the variables evaluated in Phases I and II. Concrete was tested for compressive strength, resistance to freezing and thawing,

deicer scaling resistance, chloride ion permeability, and resistance to chloride ion penetration. A selected group of mixtures was also subjected to a microscopical air-void analysis of hardened concrete by a professional petrographer.

9.2 Conclusions

Based upon the study described herein, the following conclusions can be drawn.

1. In order to render high strength concrete freeze-thaw resistant when tested according to ASTM C 666, the concrete must be air entrained.
2. When designing high strength concrete containing high calcium fly ash with a water/cement ratio in the range of 0.26 to 0.30, a minimum of 3 percent entrained air is necessary to ensure durable performance when tested according to ASTM C 666.
3. The use of entrained air was far more effective at improving the freeze-thaw resistance of high strength concrete than all other methods used in this study such as lowering the water/cement ratio, extending the moist curing period, and adding pozzolans such as fly ash or silica fume
4. The use of high absorption coarse aggregate increases the permeability of high strength concrete both with and without fly ash compared to identical concrete containing low absorption aggregate. This results in reduced freeze-thaw resistance due to saturation of the aggregate during the test.
5. The use of high calcium fly ash in high strength concrete results in reduced chloride ion permeability compared to concrete without fly ash especially at later ages.
6. Extended moist curing reduces the permeability and improves the freeze-thaw resistance of high strength concrete, however, moist curing alone cannot be relied upon to render non-air entrained fly ash concrete durable when tested according to ASTM C 666.
7. The deicer scaling resistance of high strength fly ash concrete is improved by the addition of 1.5 to 3 percent entrained air. Use of high absorption coarse aggregate reduces scaling resistance due to the presence of more freezable water in the aggregate and the increased permeability of the concrete.
8. High strength concrete containing silica fume with a water/cement ratio equal to 0.28 requires a minimum of 4 percent entrained air to perform adequately when tested according to ASTM C 666. This is attributed to the need for entrained air to offset

the increased internal stresses in the concrete during freezing due to the reduced permeability of the cement paste.

9. The use of entrained air is clearly the most efficient method of improving the freeze-thaw resistance of high strength concrete containing silica fume.
10. Silica fume concrete having a water/cement ratio of 0.28 could be made freeze-thaw resistant through additional moist curing if the moist curing was extended for 91 days.
11. The use of high absorption coarse aggregate in concrete containing silica fume results in higher durability performance compared to identical concrete containing low absorption aggregate.
12. The addition of silica fume to high strength concrete greatly reduces the chloride ion permeability to levels several times lower than that achievable with fly ash mixtures of comparable water/cement ratio.
13. The high strength silica fume concrete tested in this study did not scale when tested according to ASTM C 672.

9.3 Recommendations for Application

The following recommendations are suggested to assist in implementing the conclusions made in this study.

1. Ensure that any high strength concrete specified include a minimum of 3 percent entrained air if the member will be exposed to freezing temperatures.
2. When possible, choose the lowest absorption capacity coarse aggregate available for use in high strength fly ash concrete subjected to freezing temperatures.
3. Extend the moist curing period as long as possible on any high strength concrete in order to improve its durability.
4. Specify a minimum of 4 percent entrained air on any high strength concrete containing silica fume that is exposed to freezing temperatures.
5. Specify high absorption coarse aggregate in combination with silica fume to improve the freeze-thaw resistance.

9.4 Recommendations for Future Research

The following recommendations are made regarding areas requiring further research.

1. Investigate the durability of high strength concrete at water/cement ratios of 0.20 to 0.24 to determine if all freezable water in the concrete can be eliminated within normal curing times.
2. Investigate more fully the interaction between the high absorption coarse aggregate and the cement/silica fume paste to determine how it helps produce freeze-thaw resistant concrete.

APPENDIX A
MIXTURE PROPORTIONS

MIXTURE PROPORTIONS

MIXTURE NUMBER	CEMENT TYPE	ROCK TYPE	CEMENT LBS	FLY ASH LBS	S. FUME LBS.	ROCK LBS.	SAND LBS.	WATER LBS.	W/C+P
4	II	LOW AC	940	0	0	1752	1122	295	0.31
5	II	LOW AC	956	0	0	1785	1083	286	0.30
5A	II	LOW AC	920	0	0	1718	1026	274	0.30
6	II	LOW AC	693	222	0	1774	1205	253	0.28
7	II	LOW AC	701	225	0	1793	1102	266	0.29
7A	II	LOW AC	683	219	0	1743	1071	269	0.30
7B	II	LOW AC	676	217	0	1731	1064	260	0.29
8	II	LOW AC	633	271	0	1766	1148	279	0.31
9	II	LOW AC	637	273	0	1777	1051	290	0.32
9A	II	LOW AC	598	256	0	1668	987	262	0.31
9B	II	LOW AC	611	262	0	1704	1010	270	0.31
9C	II	LOW AC	628	269	0	1751	1036	275	0.31
9D	II	LOW AC	628	269	0	1751	1036	275	0.31
11	II	HIGH AC	940	0	0	1529	1124	263	0.28
12	II	HIGH AC	951	0	0	1546	1078	279	0.29
13	II	HIGH AC	939	0	0	1514	1055	278	0.30
14	II	HIGH AC	699	225	0	1560	1216	265	0.29
15	II	HIGH AC	681	219	0	1520	1185	259	0.29
17	II	HIGH AC	632	271	0	1535	1196	261	0.29
18	II	HIGH AC	627	269	0	1524	1187	259	0.29
19	II	HIGH AC	679	219	0	1520	1184	259	0.29
20	II	HIGH AC	699	225	0	1560	1216	265	0.29
21	II	HIGH AC	682	219	0	1520	1185	259	0.29
22	II	HIGH AC	676	217	0	1507	1175	256	0.29
23	II	HIGH AC	671	216	0	1501	1170	255	0.29
31	II	LOW AC	686	220	0	1755	1192	250	0.28
32	II	LOW AC	640	273	0	1776	1153	252	0.28
33	II	LOW AC	650	208	0	1663	1131	237	0.28
34	II	LOW AC	672	215	0	1720	1169	245	0.28
35	II	LOW AC	958	0	0	1788	1144	258	0.27
41	II	LOW AC	686	220	0	1966	1048	235	0.26
42	II	LOW AC	676	217	0	1936	1032	232	0.26
43	II	LOW AC	1013	0	0	1956	924	274	0.27
44	II	HIGH AC	687	220	0	1736	1050	236	0.26
45	II	HIGH AC	690	220	0	1824	924	237	0.26
46	II	HIGH AC	1000	0	0	1809	907	260	0.26
47	II	LOW AC	953	0	0	1990	942	248	0.26
48	II	HIGH AC	940	0	0	1813	909	244	0.26
49	II	LOW AC	684	218	0	1958	970	270	0.30
50	II	LOW AC	677	215	0	1940	960	268	0.30
52	II	HIGH AC	671	214	0	1775	890	265	0.30
53	II	HIGH AC	671	214	0	1775	951	265	0.30
54	II	LOW AC	905	0	65	1890	890	270	0.28
55	II	LOW AC	878	0	63	1835	908	262	0.28
56	II	HIGH AC	880	0	63	1700	910	263	0.28
57	II	HIGH AC	887	0	64	1710	800	265	0.28
58	II	LOW AC	886	0	88	1851	872	274	0.28
59	II	LOW AC	874	0	87	1825	860	270	0.28
60	II	HIGH AC	862	0	86	1663	891	267	0.28
61	II	HIGH AC	852	0	85	1643	880	264	0.28
62	II	HIGH AC	701	0	54	1890	1010	211	0.28
63	II	HIGH AC	693	0	53	1866	1000	208	0.28
64	II	LOW AC	677	0	52	2026	975	204	0.28
65	II	LOW AC	707	0	54	2115	1018	213	0.28
66	II	LOW AC	720	0	72	2013	1000	221	0.28
67	II	LOW AC	730	0	73	2040	1010	224	0.28
68	II	HIGH AC	703	0	70	1785	973	216	0.28
69	II	HIGH AC	720	0	72	1830	997	222	0.28

APPENDIX B
FRESH CONCRETE PROPERTIES

FRESH CONCRETE PROPERTIES

MIXTURE NUMBER	MIXTURE DESIGNATION	CONCRETE TEMPERATURE (°F)	1ST SLUMP (Inches)	2ND SLUMP (Inches)	TOTAL AIR CONTENT (%)
4	4-30A00LA0	82°F	0.25	10	0.00
5	5-30A00LA1	88°F	0.5	6.25	2.50
5A	5A-30A00LA5	82°F	0.75	9	7.00
6	6-30A27LA0	88°F	0	7	2.00
7	7-30A27LA1	86°F	0	4	3.00
7A	7A-30A27LA3	94°F	1.5	7.75	5.25
8	8-30A33LA0	84°F	0	7	2.00
9A	9-30A33LA1	87°F	0	7	3.25
9B	9A-30A33LA6	87°F	2.5	7.5	8.00
9D	9D-30A33LA4	84°F	1	7	6.00
11	11-30A00HA0	84°F	0.75	6.5	2.00
12	12-30A00HA1	73°F	2.5	7.5	3.00
13	13-30A00HA4	77°F	1	6	5.75
14	14-30C27HA0	69°F	1	5.5	1.75
15	15-30A27HA1	70°F	1	6	3.00
17	17-30A33HA0	78°F	0.5	4.5	n/a
18	18-30A33HA1	n/a	1	5.75	3.00
19	19-30A33HA3	72°F	0.5	4.5	4.50
20	20-30A27HA0	74°F	0.75	6.5	n/a
21	21-30A27HA1	68°F	0.75	6	2.75
22	22-30A27HA4	65°F	1	7	5.25
23	23-30A33HA4	62°F	3	7.75	5.75
31	31-28A27LA0	76°F	1.50	9	2.00
32	32-28A33LA0	80°F	1.5	8.75	1.50
33	33-28A27LA6	86°F	0.25	8.5	7.50
34	34-28A27LA2	81°F	0.5	7.5	4.00
35	35-28A00LA0	79°F	0.5	9.75	1.50
41	41-26A27LA0	90°F	0.5	7	n/a
42	42-26A27LA2	90°F	0.25	8	3.50
43	43-26A00LA0	87°F	0	8.5	1.25
44	44-26A27HA0	84°F	1	9	0.00
45	45-26A27HA2	89°F	0.25	9	4.00
46	46-26A00HA0	85°F	1	9.75	n/a
47	47-26A00LA2	86°F	0.25	9	3.00
48	48-26A00HA3	n/a	0	9	4.00
49	49-30A27LA0	87°F	3	9	n/a
50	50-30A27LA2	89°F	4	8.5	3.00
52	52-30A27HA2	85°F	4	8.5	3.50
53	53-30A27HA0	84°F	3.25	9	n/a
54	54-30S7LA0	82°F	1.75	8	n/a
55	55-30S7LA3	82°F	0.25	8.75	4.00
56	56-30S7HA0	80°F	1	9	n/a
57	57-30S7HA3	82°F	1.5	8	4.25
58	58-28S10LA0	89°F	2	8	n/a
59	59-28S10LA2	88°F	1	9	3.50
60	60-28S10HA0	86°F	1	8.5	n/a
61	61-28S10HA3	82°F	1	8	3.25
62	62-28S7HA0	80°F	0.5	9.5	1.50
63	63-28S7HA2	84°F	2.5	10	3.25
64	64-28S7LA5	80°F	0	9.5	6.50
65	65-28S7LA0	n/a	0	9.5	n/a
66	66-28S10LA3	83°F	1.5	9.5	4.50
67	67-28S10LA0	n/a	1	10	n/a
68	68-28S10HA3	76°F	0.5	9.5	4.50
69	69-28S10HA0	79°F	n/a	9	n/a

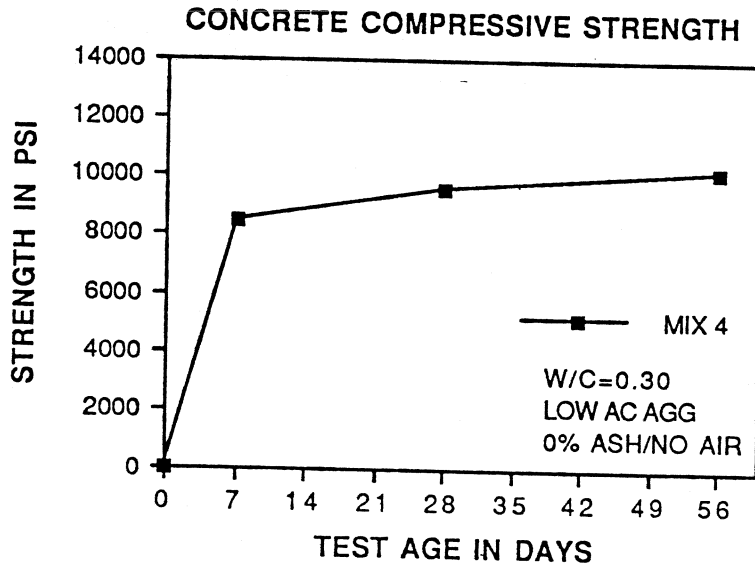
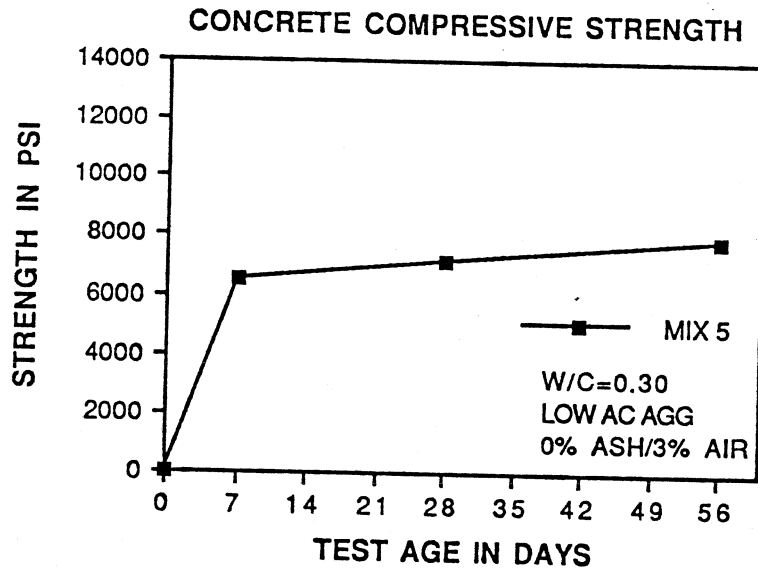
APPENDIX C
CONCRETE COMPRESSIVE STRENGTH DATA

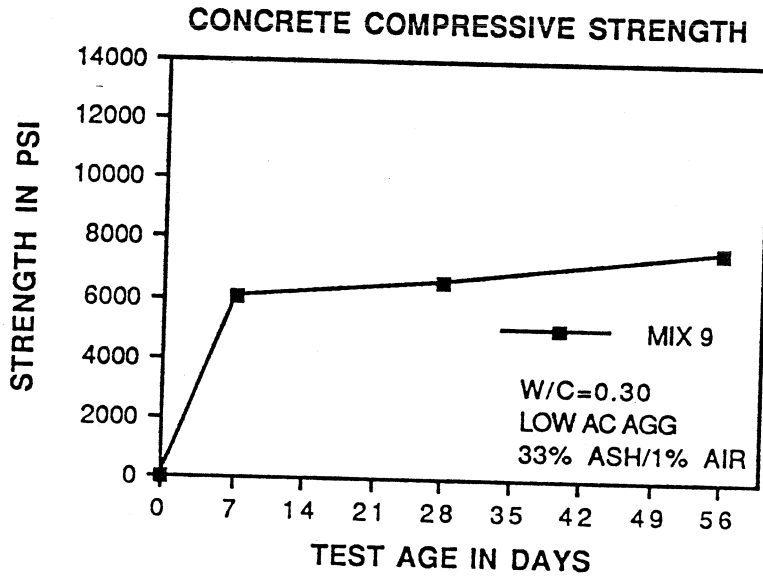
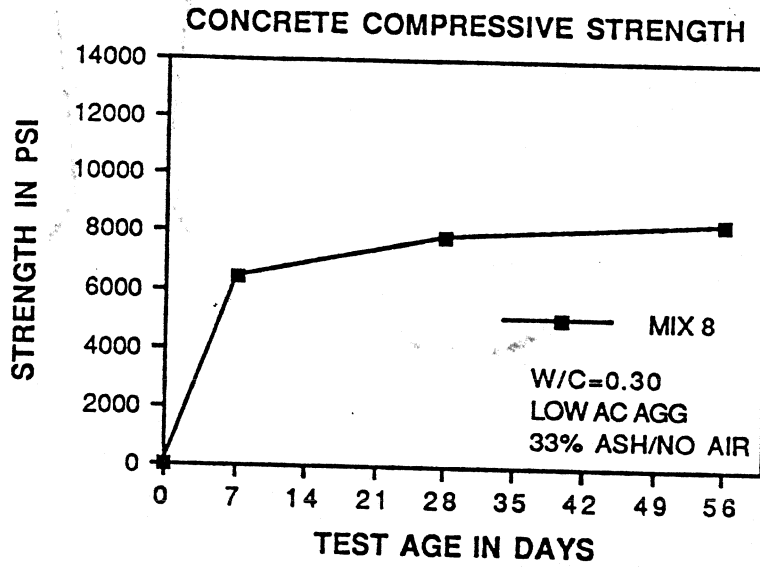
COMPRESSIVE STRENGTH TEST RESULTS

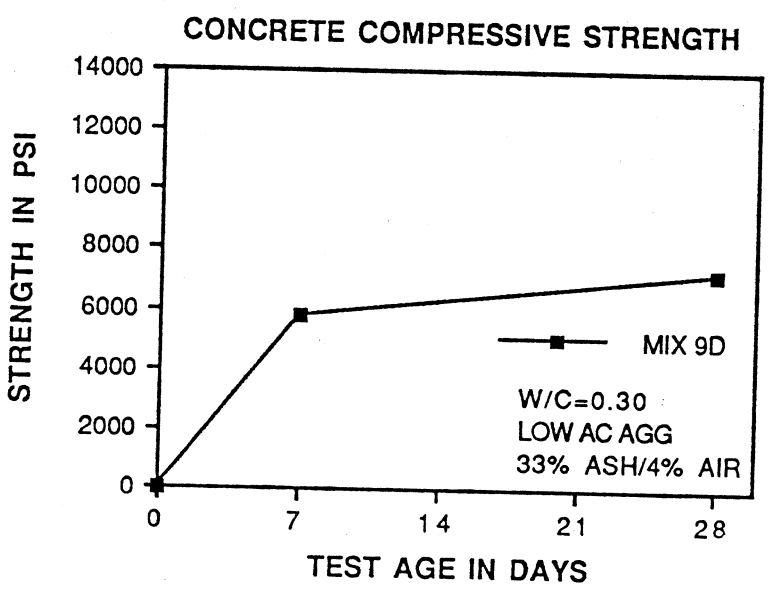
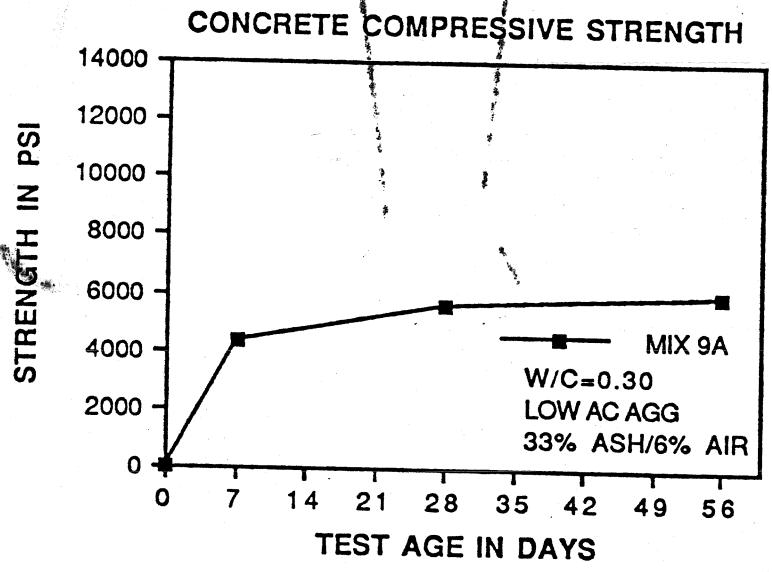
MIXTURE NUMBER	MIXTURE DESIGNATION	7 DAY STRENGTH (psi)	28 DAY STRENGTH (psi)	91 DAY STRENGTH (psi)	STRENGTH LOSS % / (% air)
4	4-30A00LA0	8520	9590	10200*	non-air entrained
5	5-30A00LA3	6500	7130	7900*	9
5A	5A-30A00LA6	**	6200	6690*	7.1
6	6-30A27LA0	6230	7720	8030*	non-air entrained
7	7-30A27LA3	6630	7670	8170*	1.7
7A	7A-30A27LA3	5740	6920	7470*	2.1
8	8-30A33LA0	6410	7880	8400*	non-air entrained
9A	9-30A33LA1	6070	6620	7690 *	
9B	9A-30A33LA6	4350	5560	5960*	6.76
9D	9D-30A33LA4	5810	7230	**	2.06
11	11-30A00HA0	6700	7590	8100*	non-air entrained
12	12-30A00HA1	6240	7260	7770*	4.07
13	13-30A00HA6	4900	5790	6250*	6.09
14	14-30C27HA0	7080	8370	**	non-air entrained
15	15-30A27HA1	7300	8350	8490*	0.2
17	17-30A33HA0	8300	9050	9980*	non-air entrained
18	18-30A33HA1	7400	8660	9230*	7.5
19	19-30A33HA3	7210	8640	8800*	3.94
20	20-30A27HA0	7510	8790	9190*	non-air entrained
21	21-30A27HA1	7070	8330	8900*	3.16
22	22-30A27HA4	6480	8060	8530*	2.4
23	23-30A33HA4	6300	7930	8730*	3.13
31	31-28A27LA0	6670	8190	9300	non-air entrained
32	32-28A33LA0	6620	7940	9120	non-air entrained
33	33-28A27LA6	6920	8340	9810	
34	34-28A27LA2	6560	7850	8520	4.2
35	35-28A00LA0	7260	7870	8500	non-air entrained
41	41-26A27LA0	7150	8530	9380	non-air entrained
42	42-26A27LA2	7630	8810	9860	
43	43-26A00LA0	7950	8990	10200	non-air entrained
44	44-26A27HA0	8630	10550	11510	non-air entrained
45	45-26A27HA3	8720	10110	11230	1.2
46	46-26A00HA0	7910	9140	10090	non-air entrained
47	47-26A00LA2	7210	8270	9630	3.7
48	48-26A00HA3	8130	9150	10530	
49	49-30A27LA0	6720	7990	9190	non-air entrained
50	50-30A27LA2	5730	7000	7950	9
52	52-30A27HA2	7270	9080	9960	7.5
53	53-30A27HA0	8210	9910	11220	non-air entrained
54	54-30S7LA0	8470	9380	9950	non-air entrained
55	55-30S7LA3	9940	11030	11300	
56	56-30S7HA0	11470	12730	13080	non-air entrained
57	57-30S7HA3	10200	11500	11530	5.27
58	58-28S10LA0	9510	10570	11120	non-air entrained
59	59-28S10LA3	9550	10460	10660	2.76
60	60-28S10HA0	10890	12380	12370	non-air entrained
61	61-28S10HA3	11150	12650	12680	
62	62-28S7HA0	10280	11980	12090	non-air entrained
63	63-28S7HA3	9030	10980	11020	4.63
64	64-28S7LA5	9140	11100	11250	2.8
65	65-28S7LA0	10900	12500	12900	non-air entrained
66	66-28S10LA3	9200	10760	11550	4.11
67	67-28S10LA0	11200	12790	12650	non-air entrained
68	68-28S10HA3	10500	12220	12470	1.54
69	69-28S10HA0	11420	12930	12970	non-air entrained

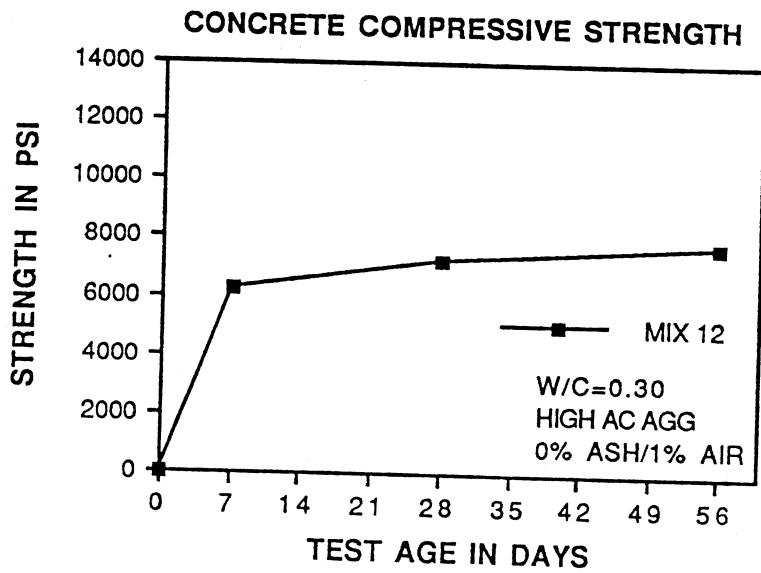
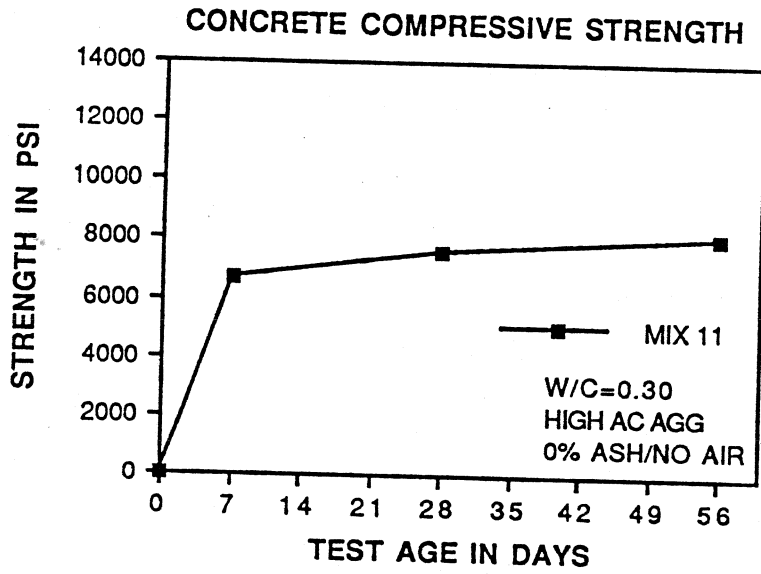
* Denotes 56 day strength

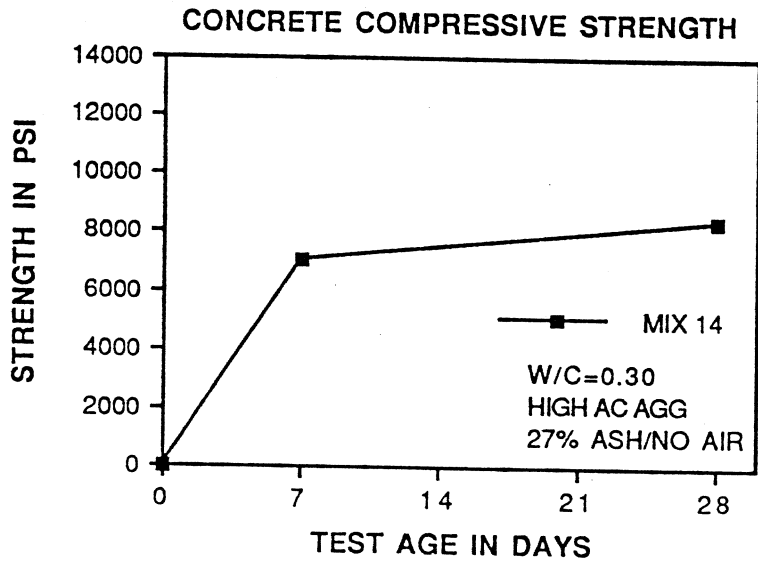
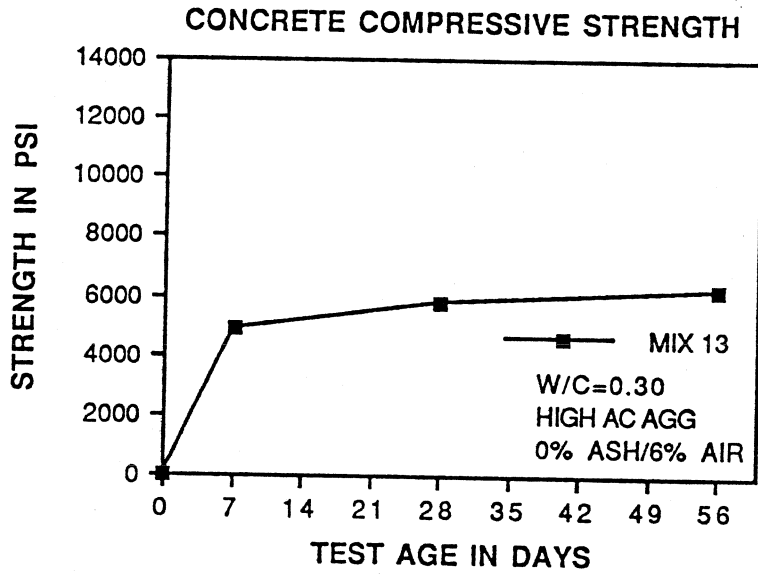
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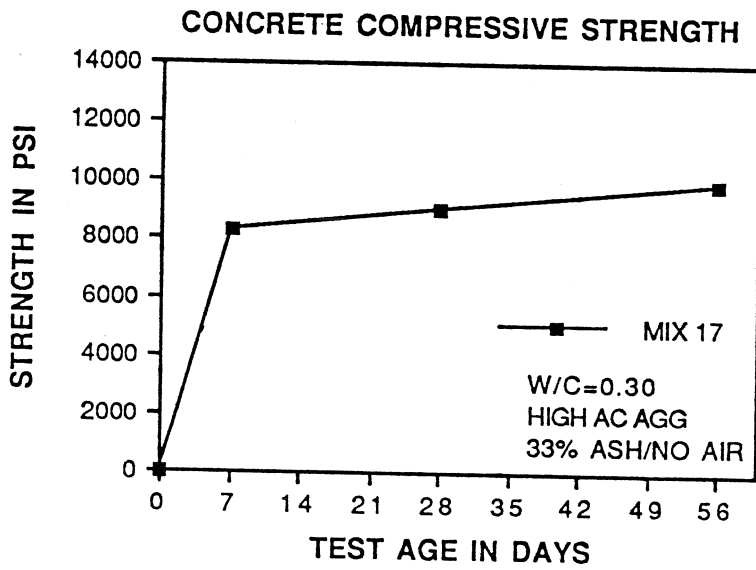
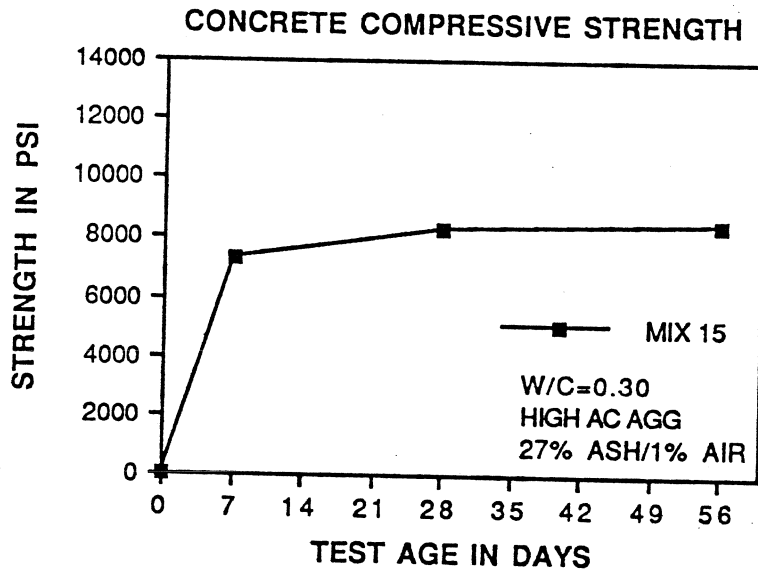


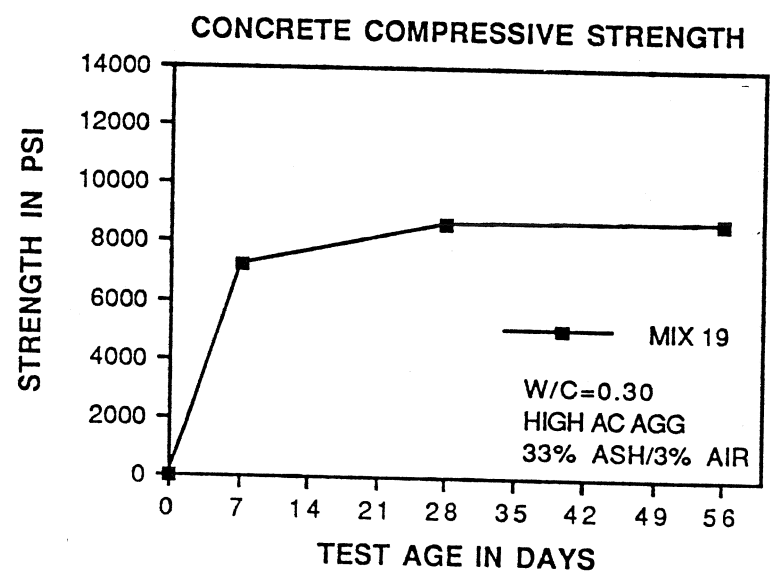
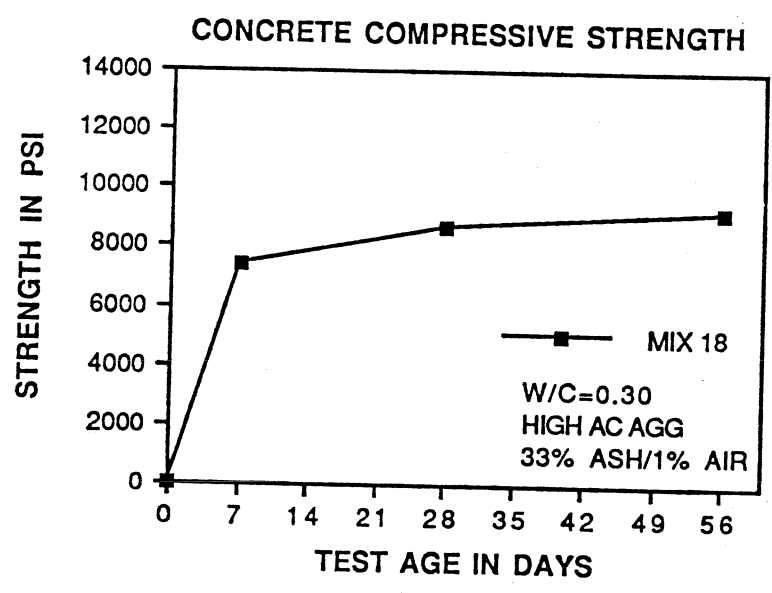


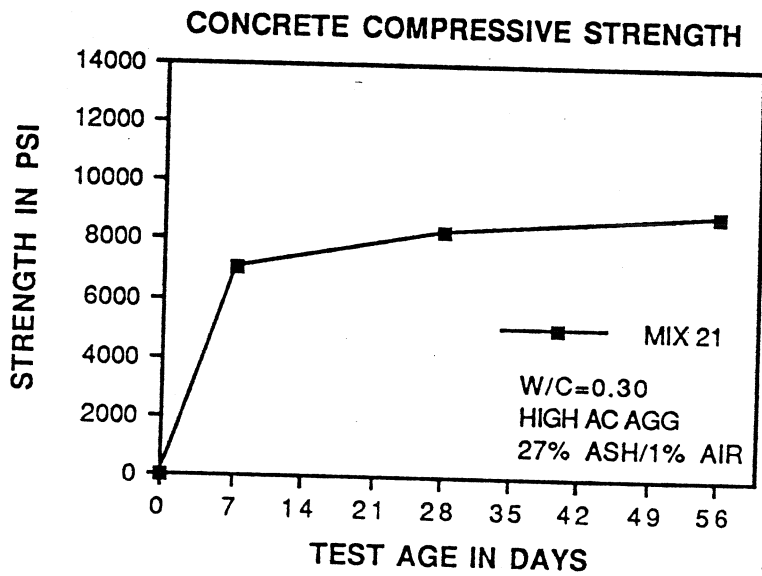
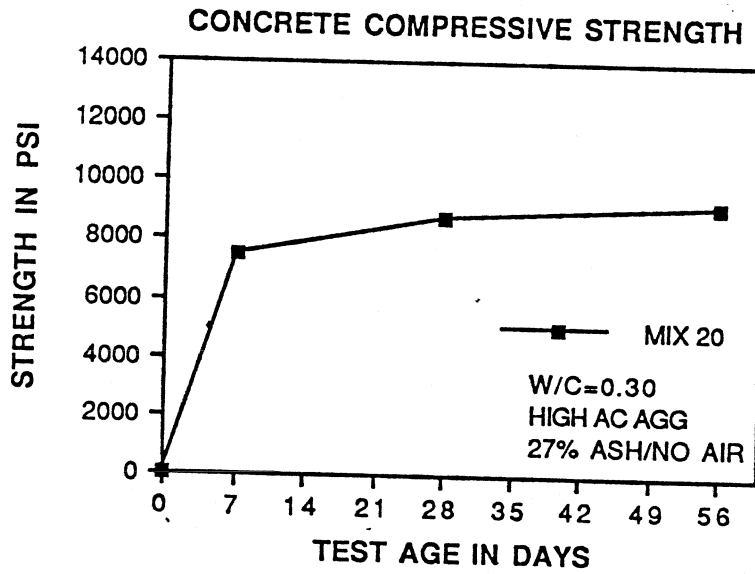


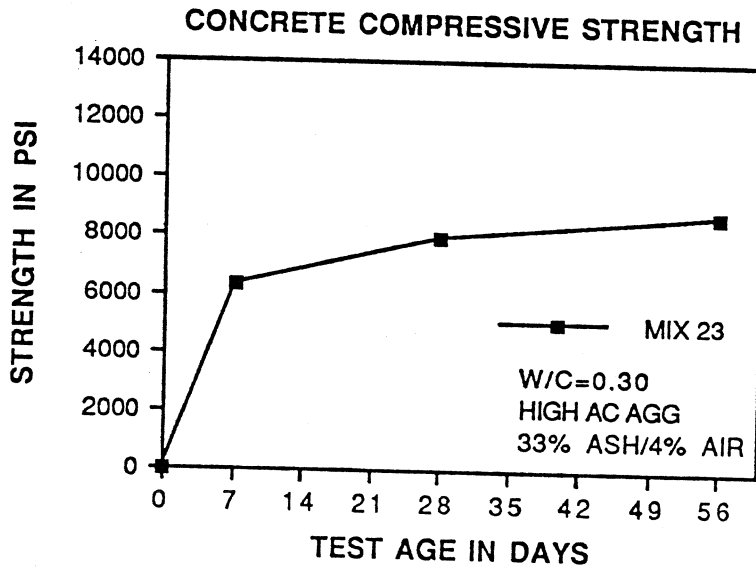
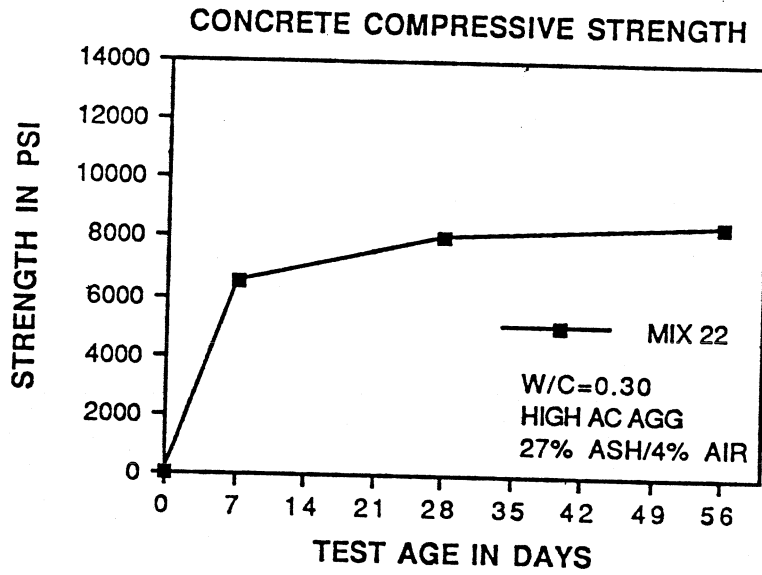


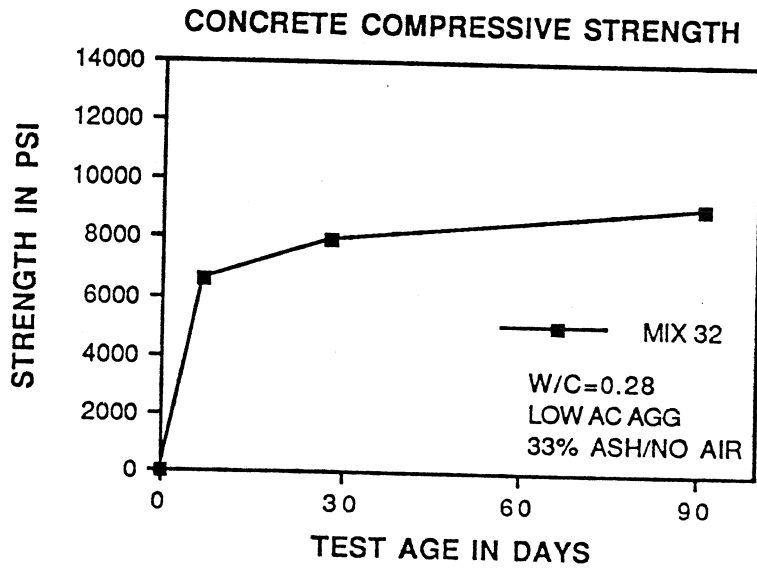
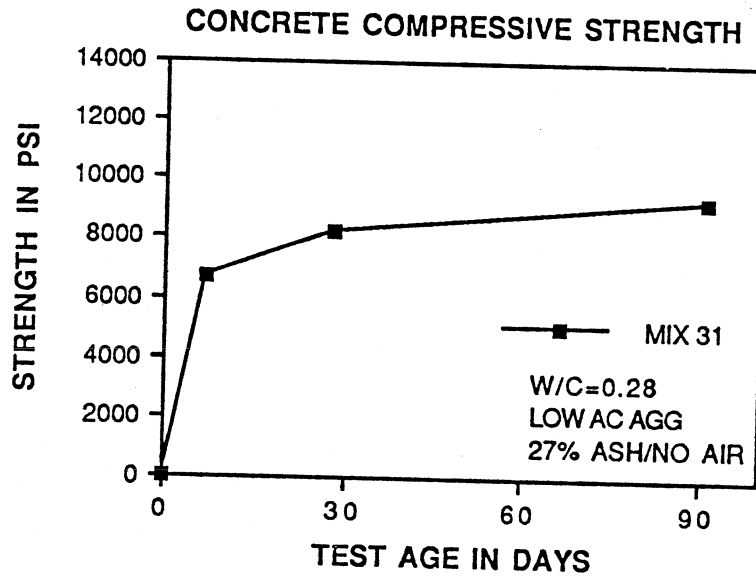


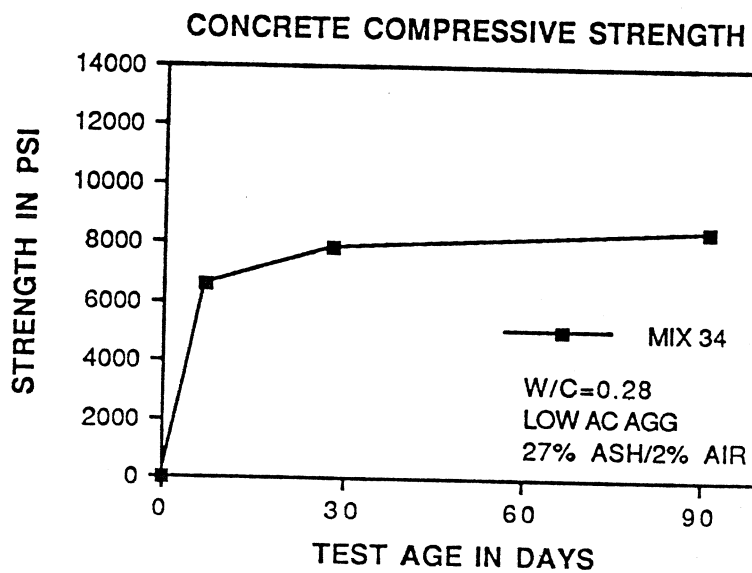
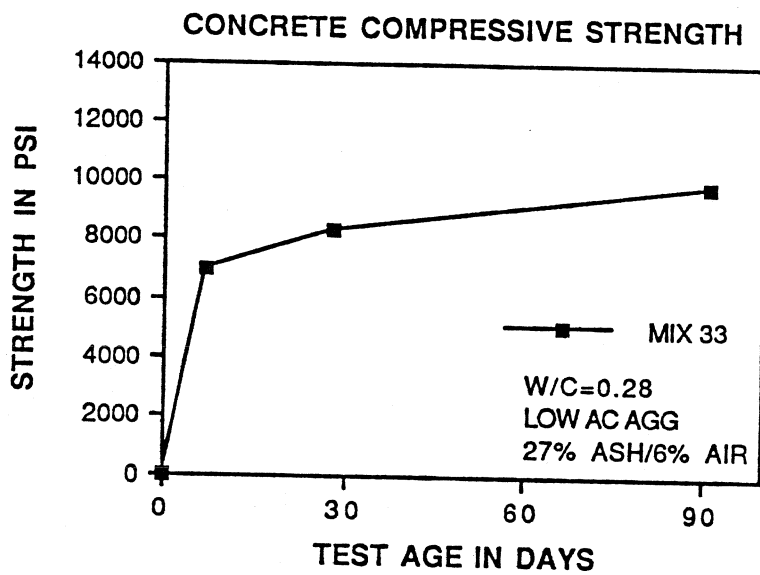


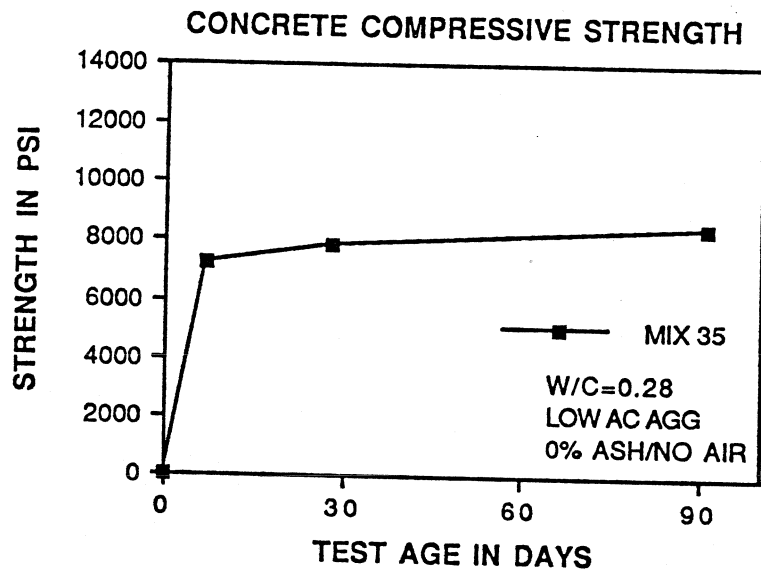


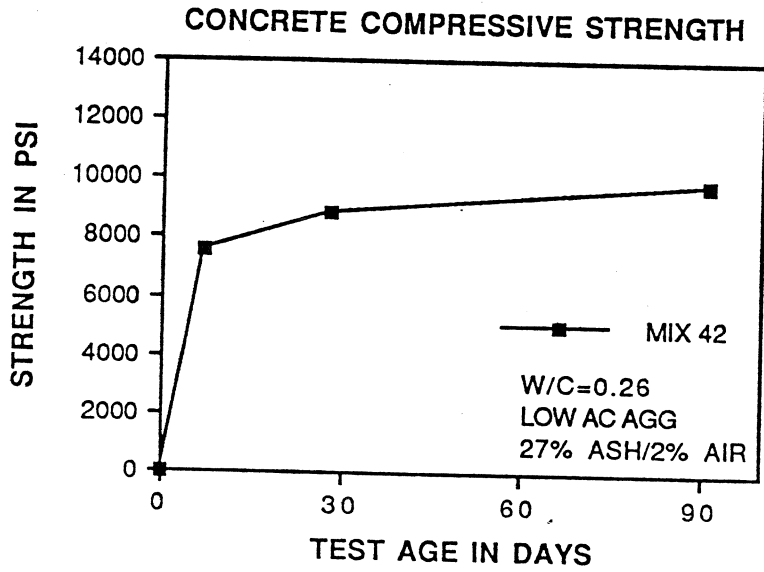
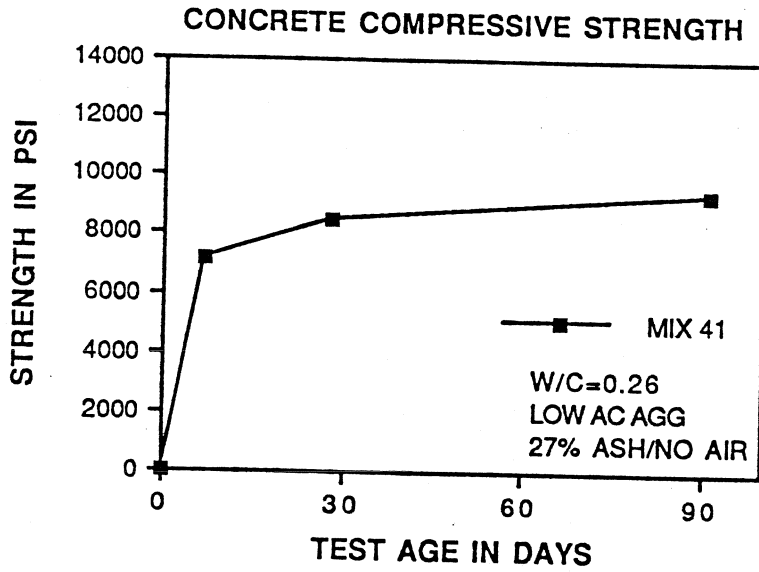


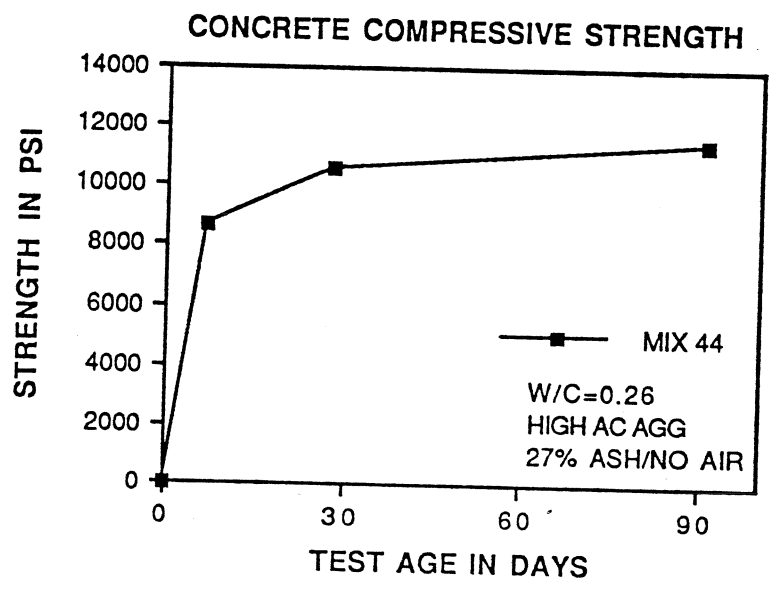
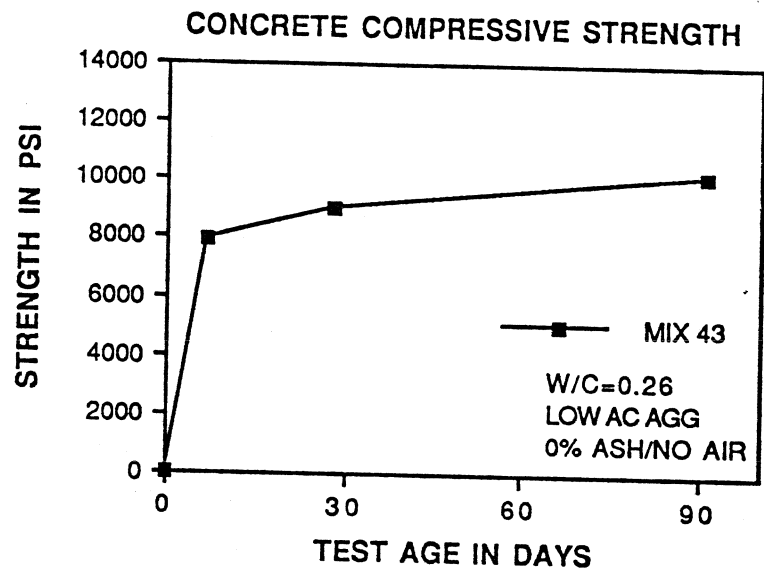


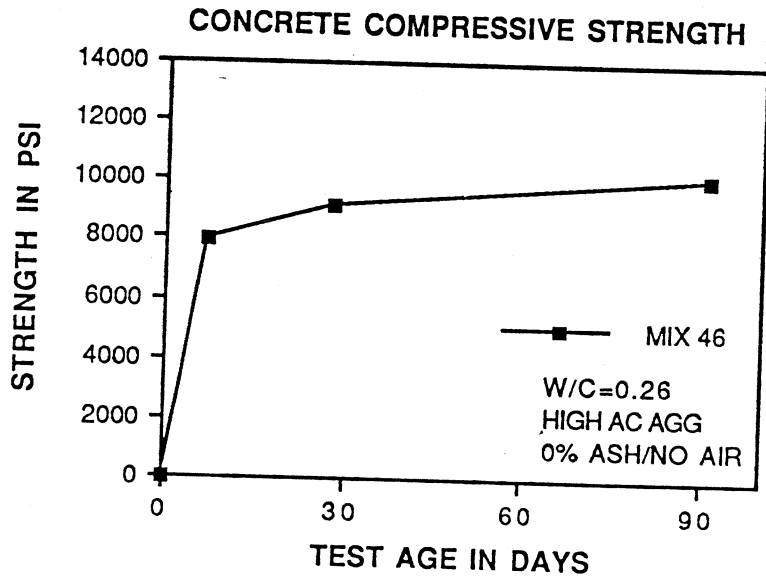
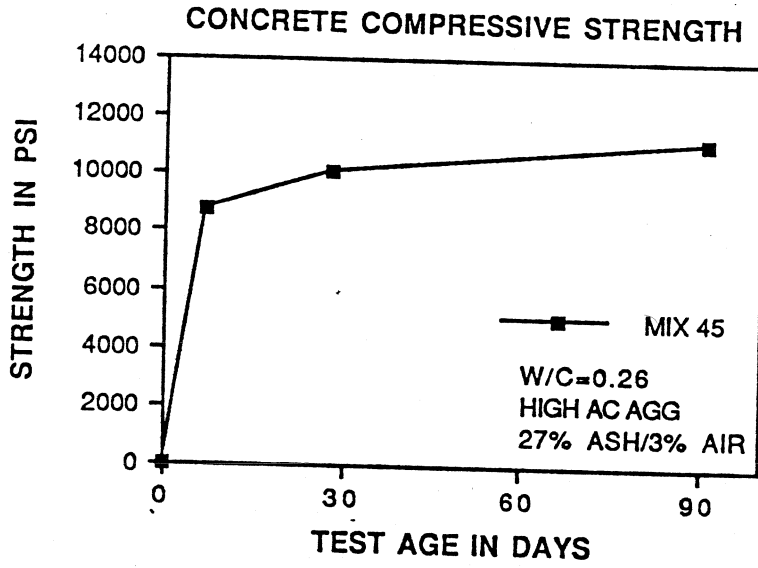


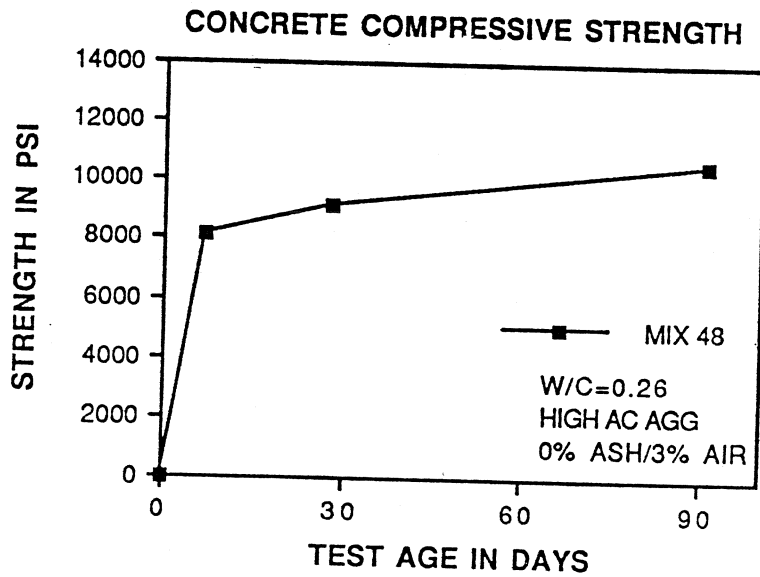
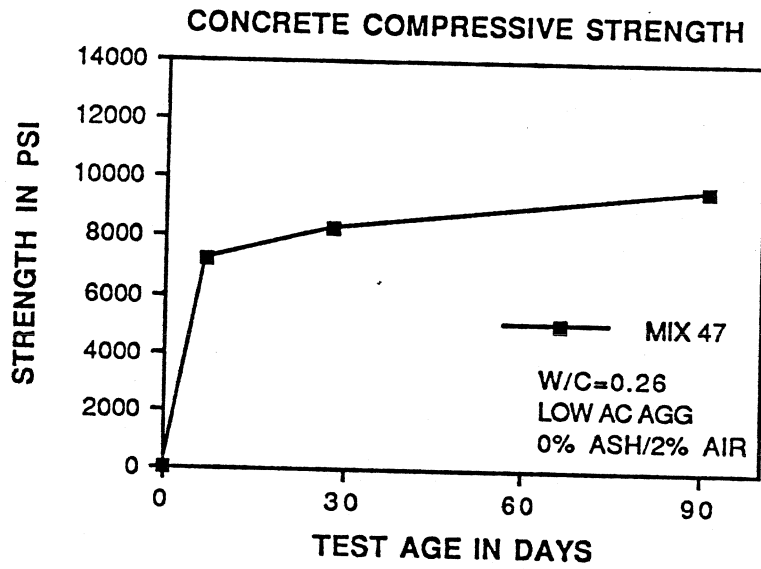


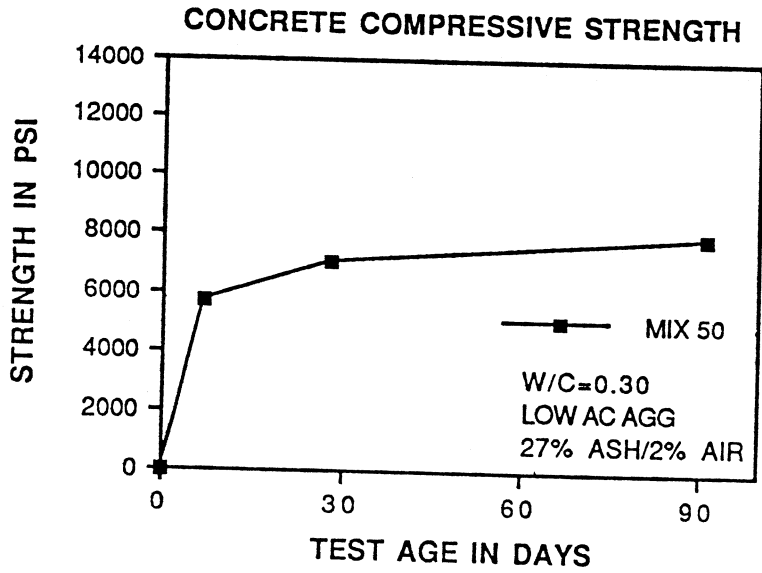
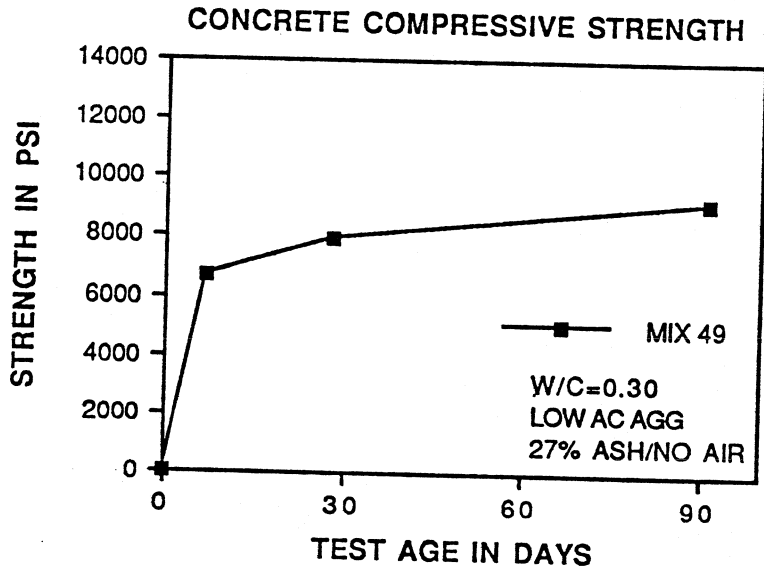


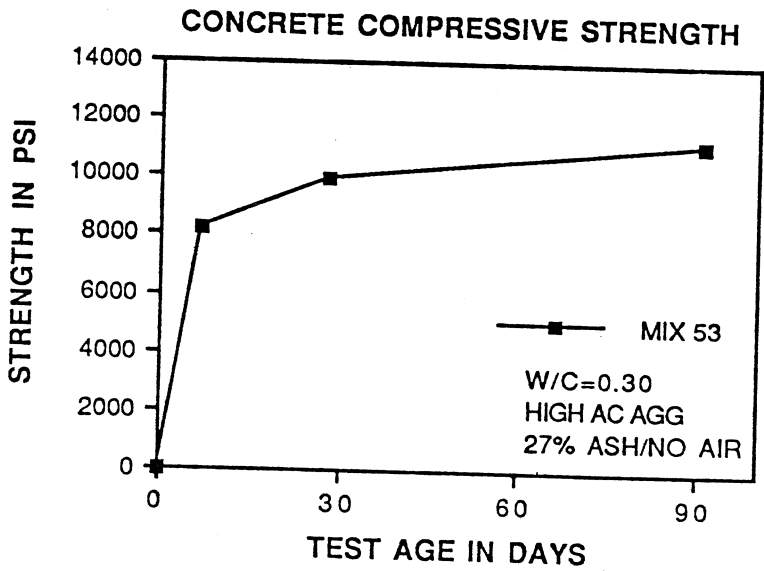
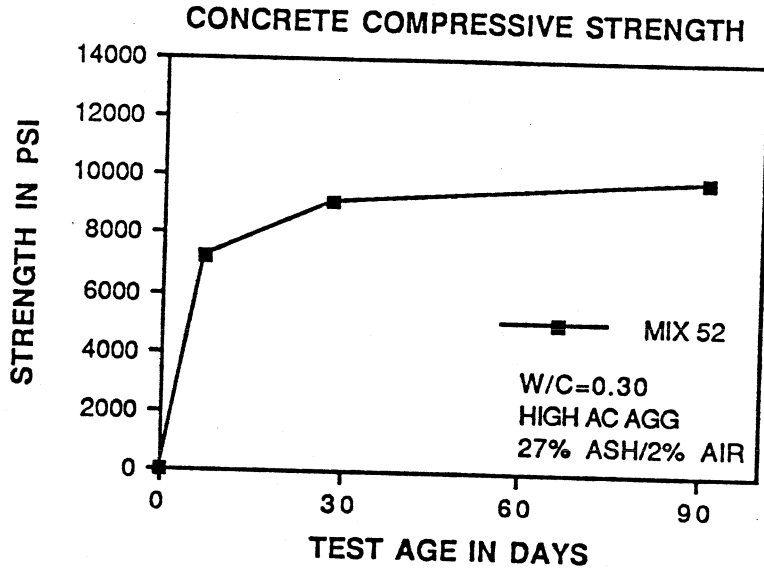


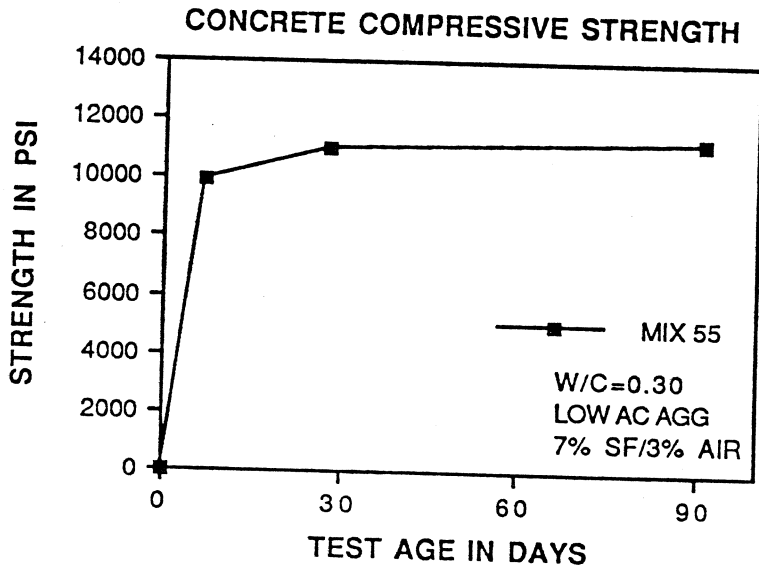
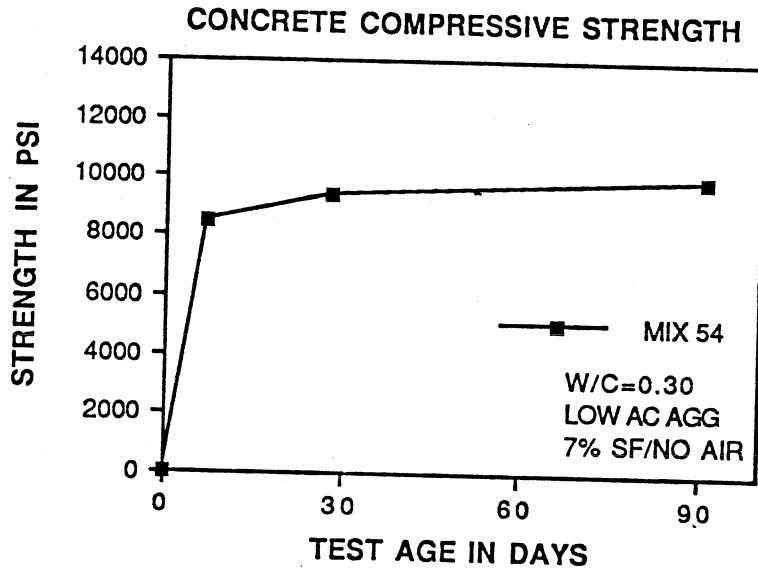


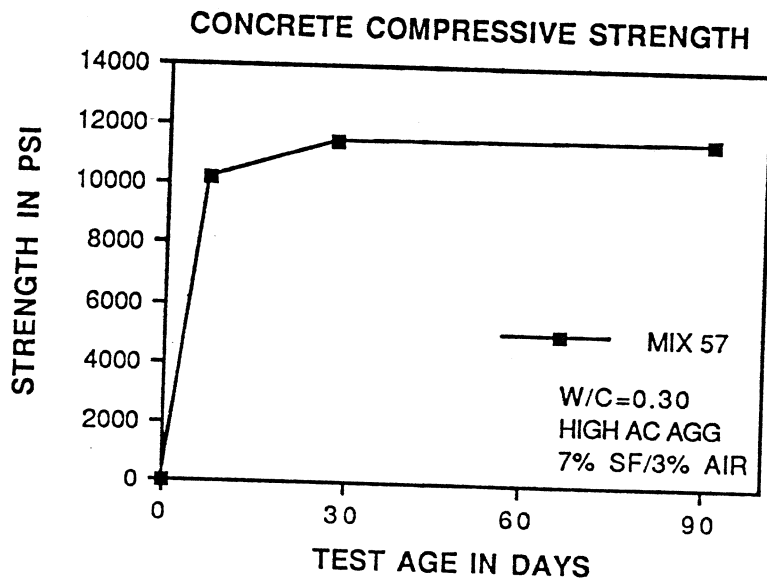
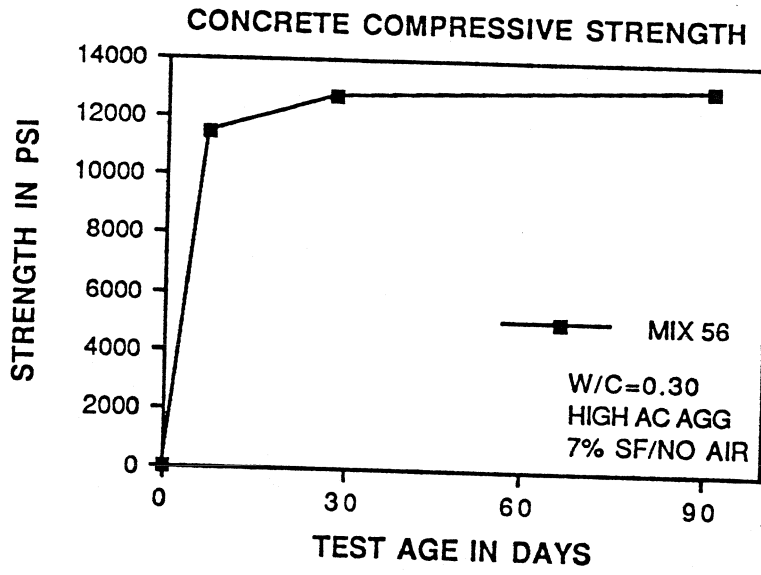


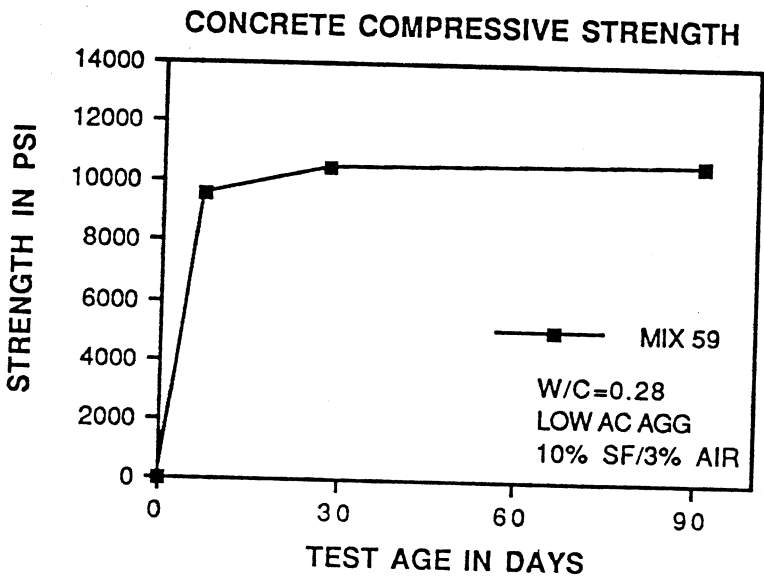
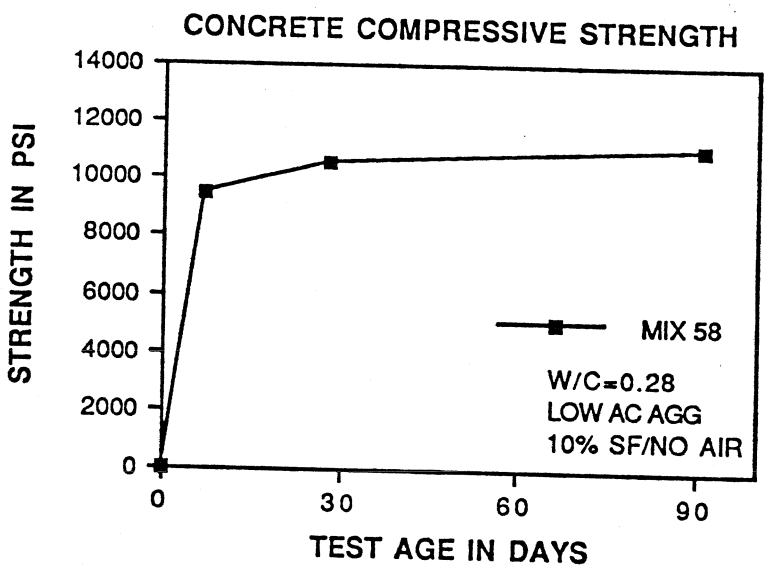


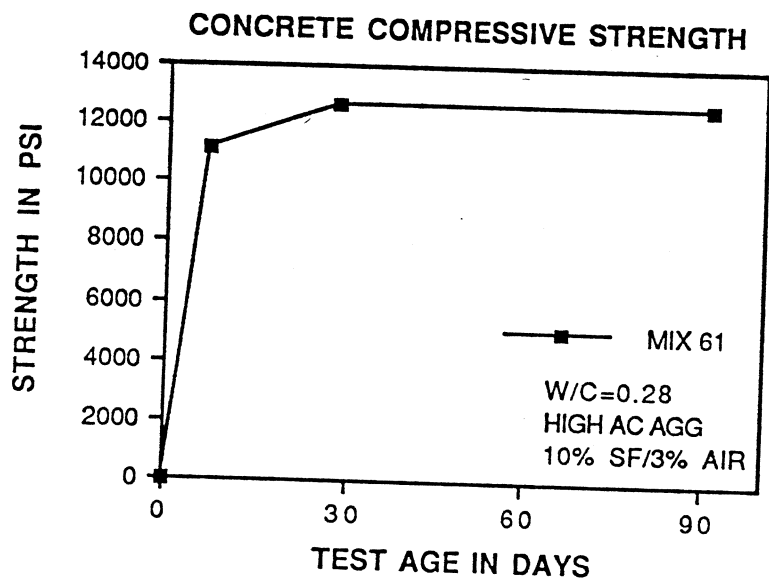
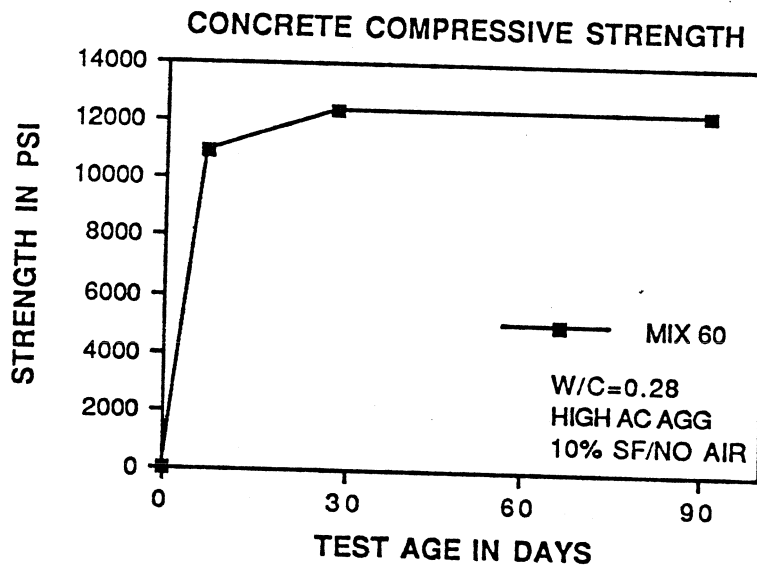


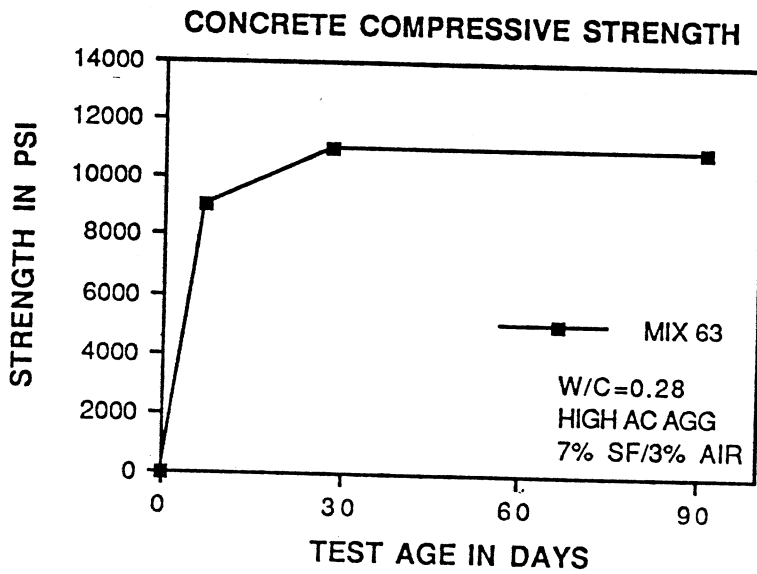
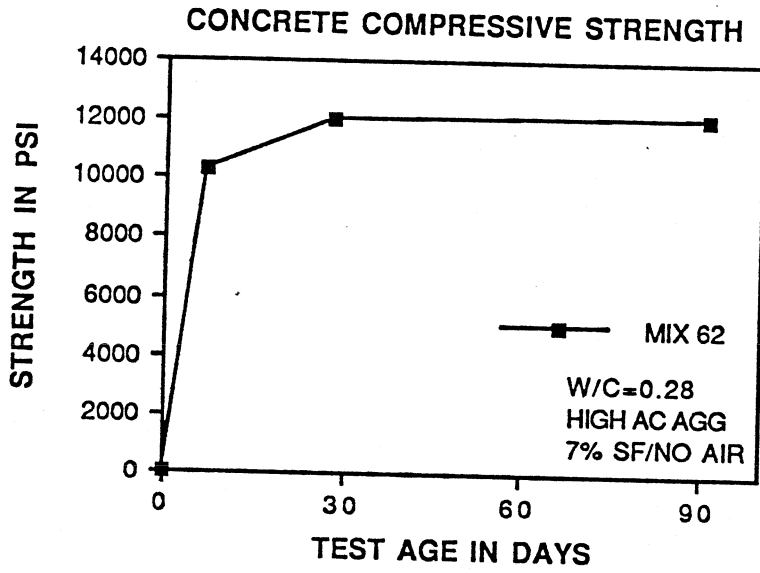


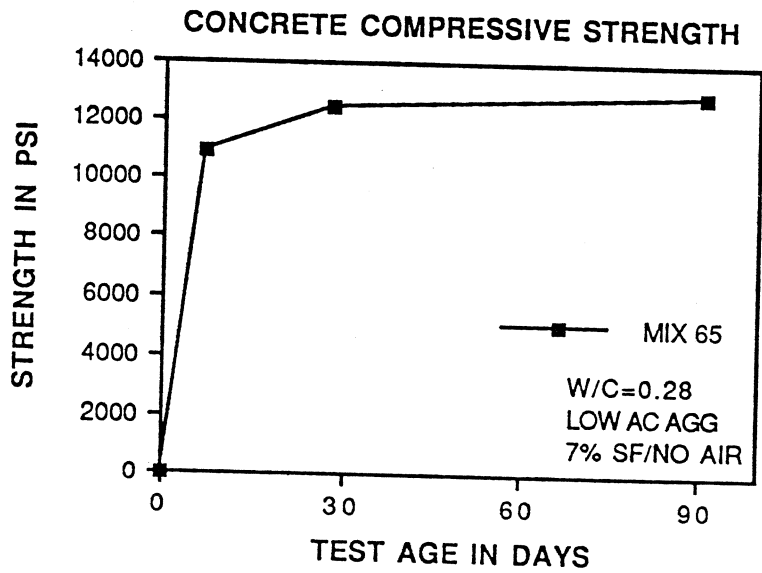
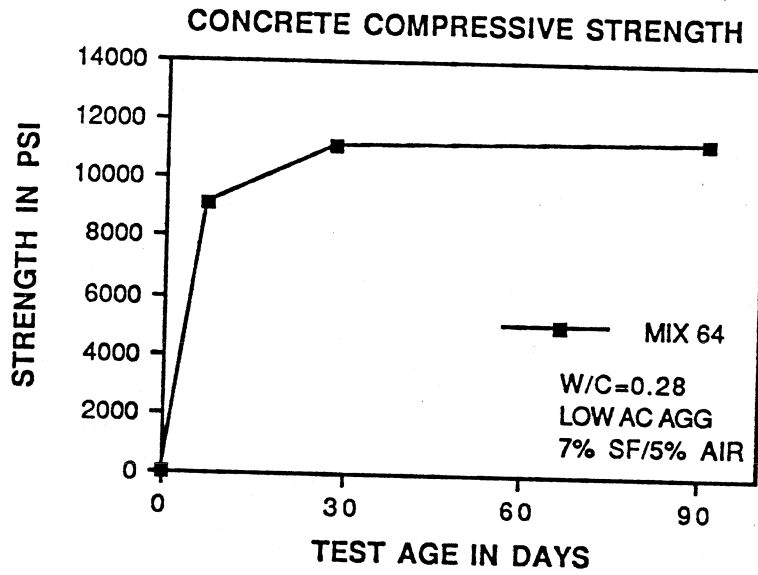


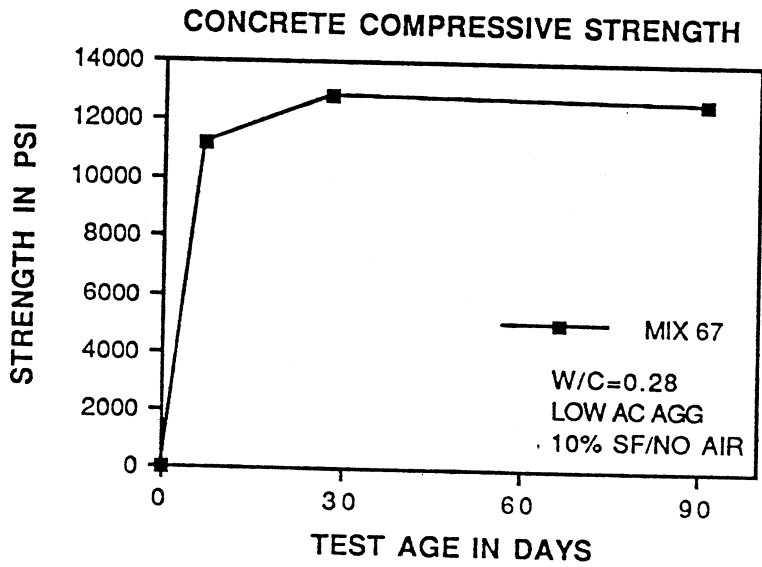
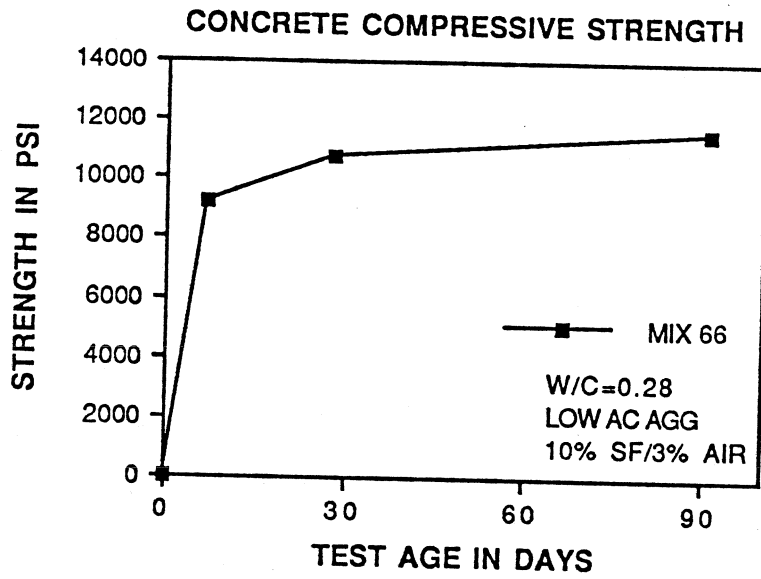


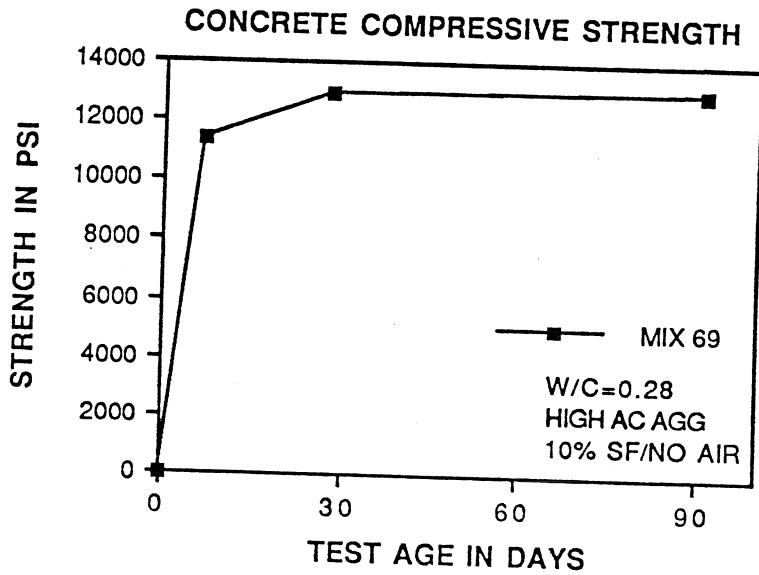
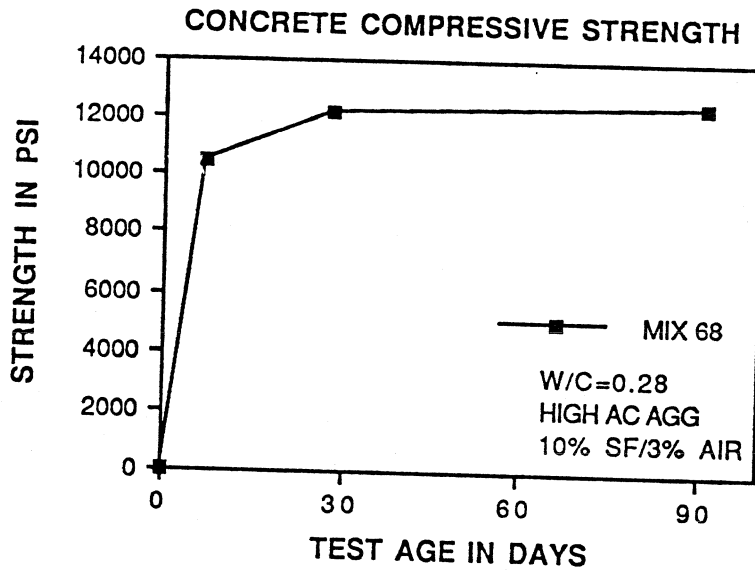




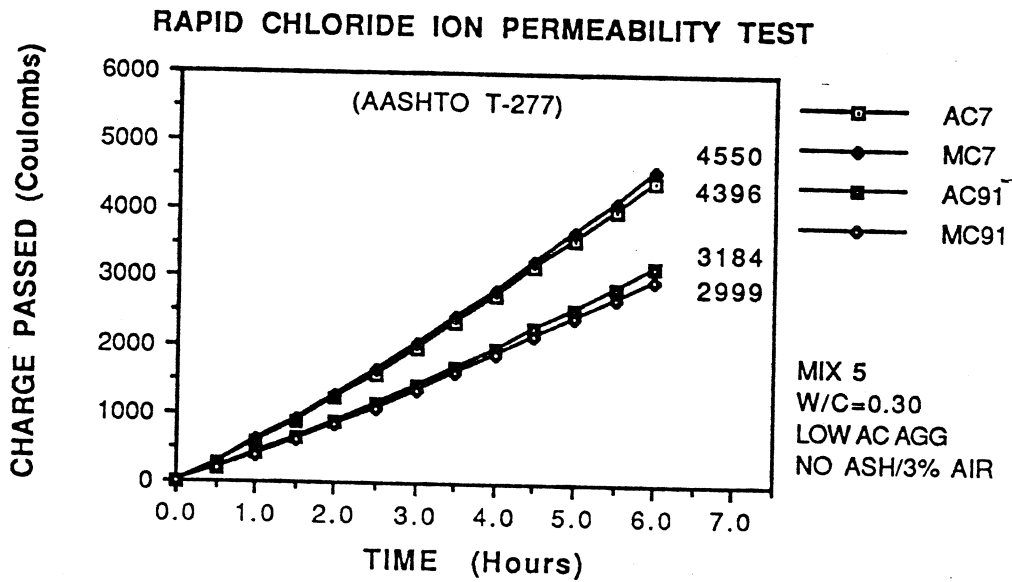
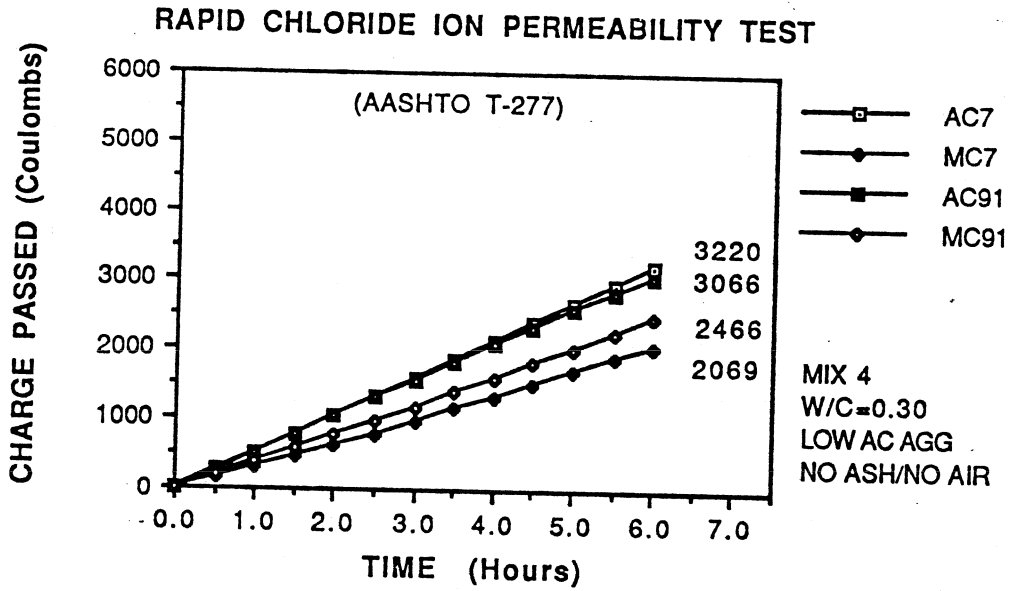


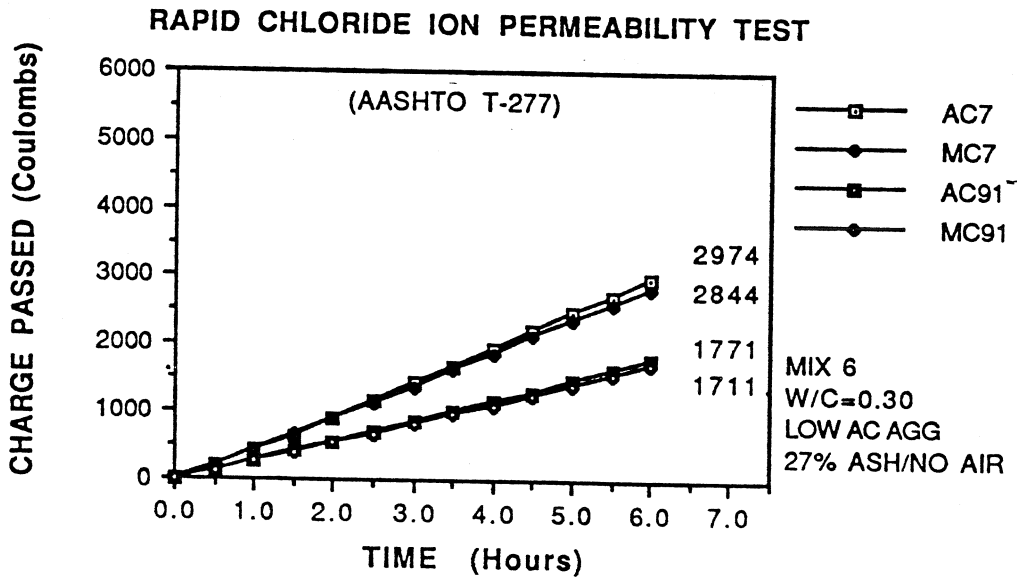
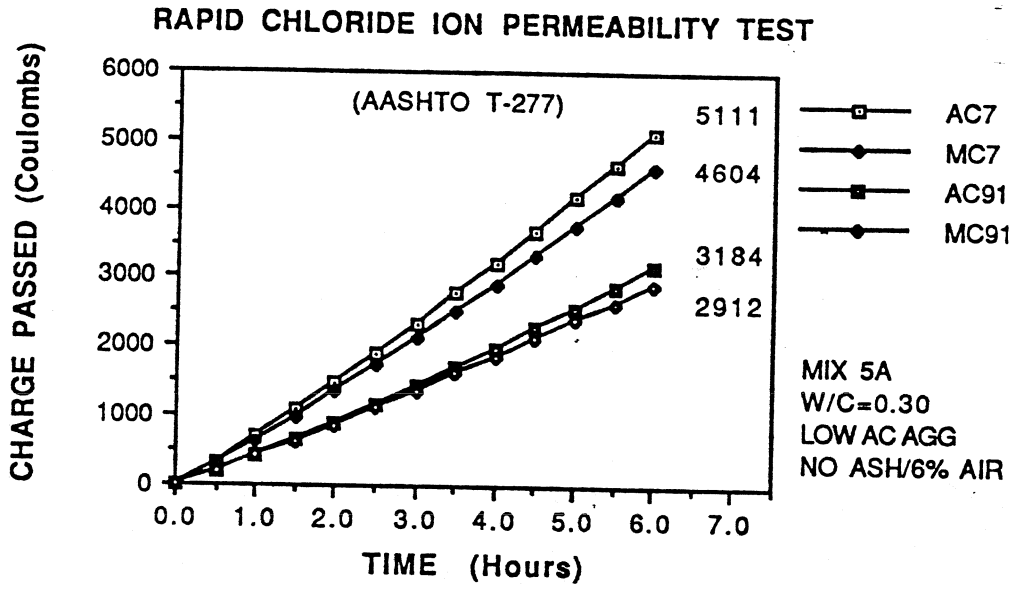


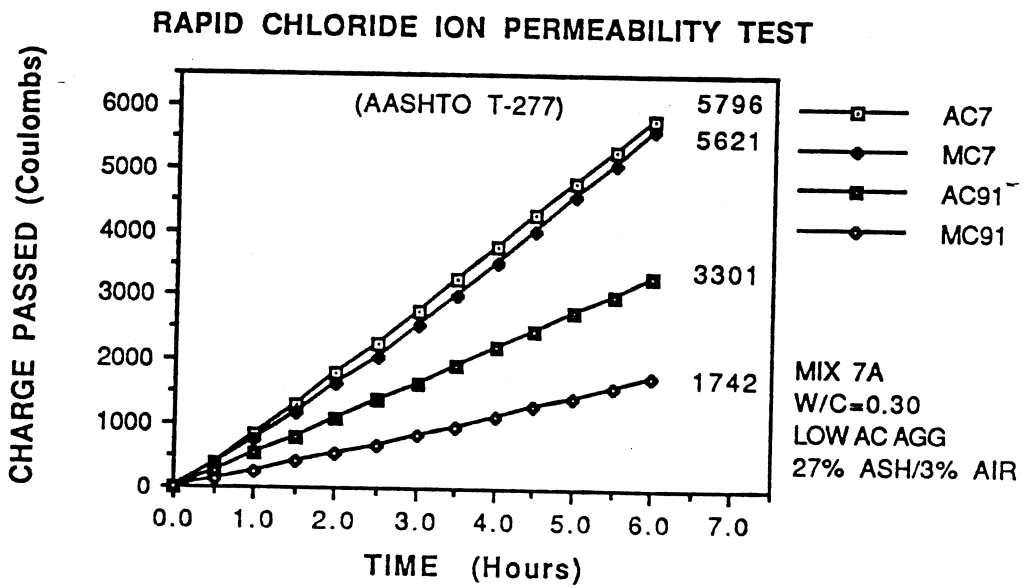
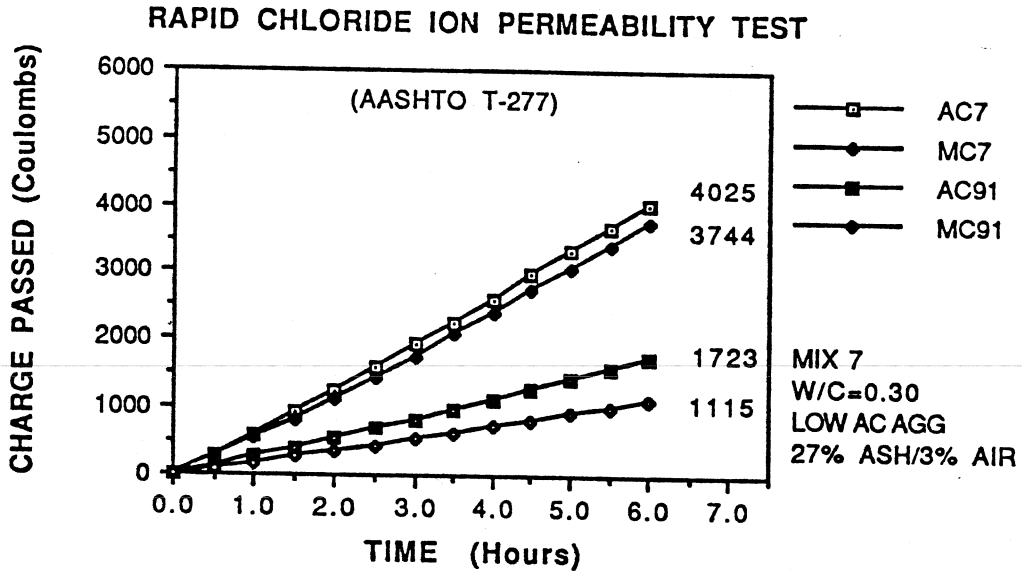


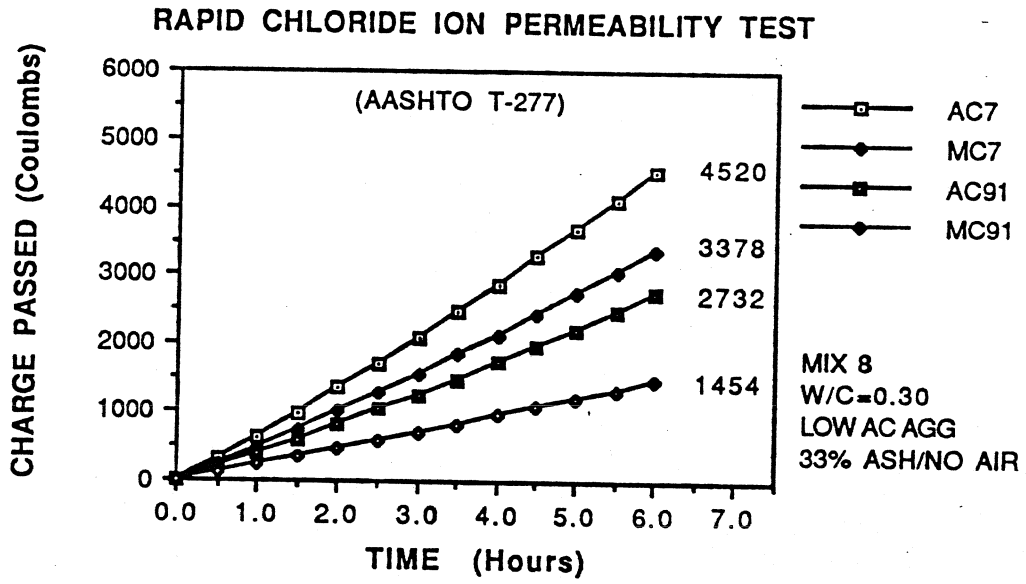


APPENDIX D
RAPID CHLORIDE ION PERMEABILITY DATA

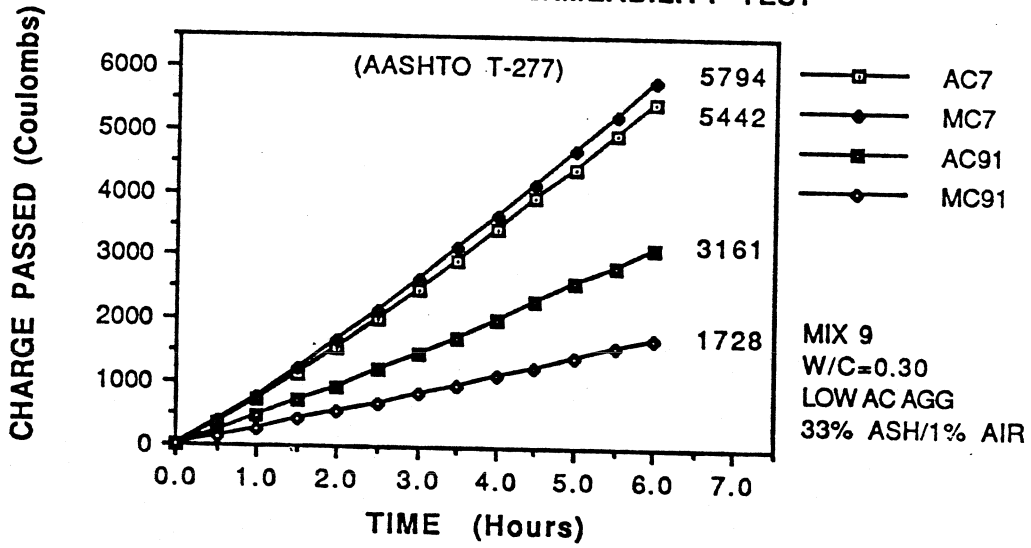




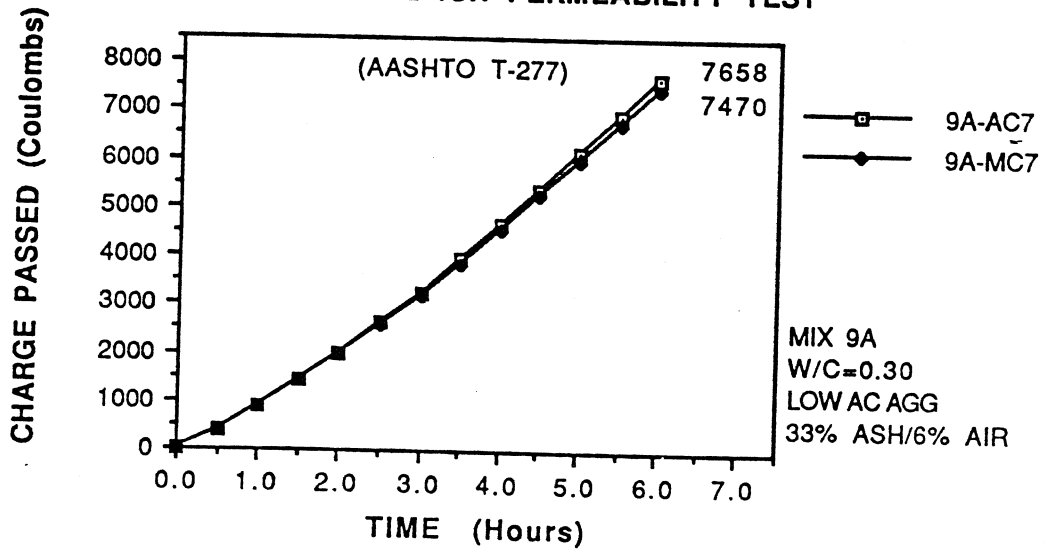


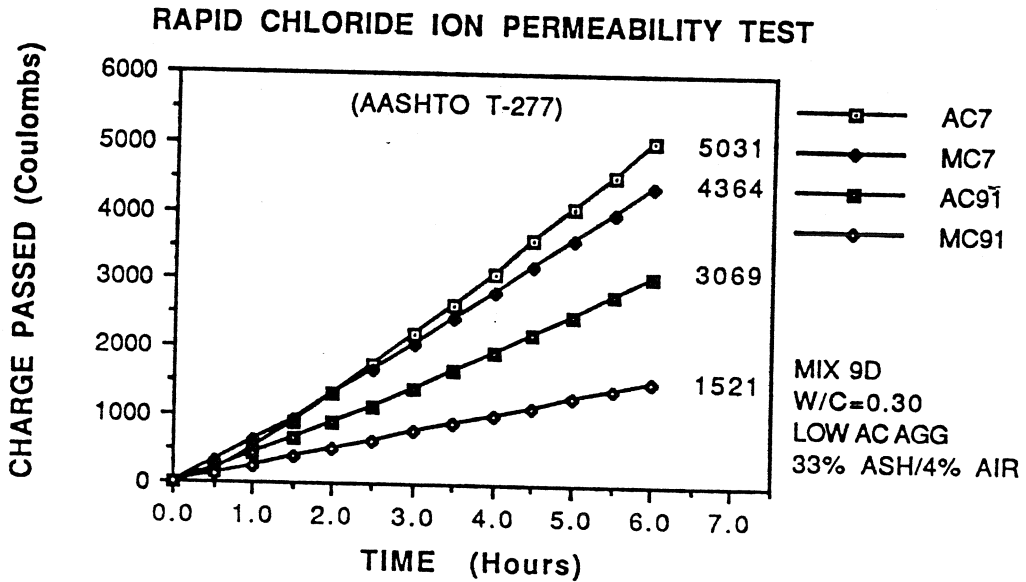
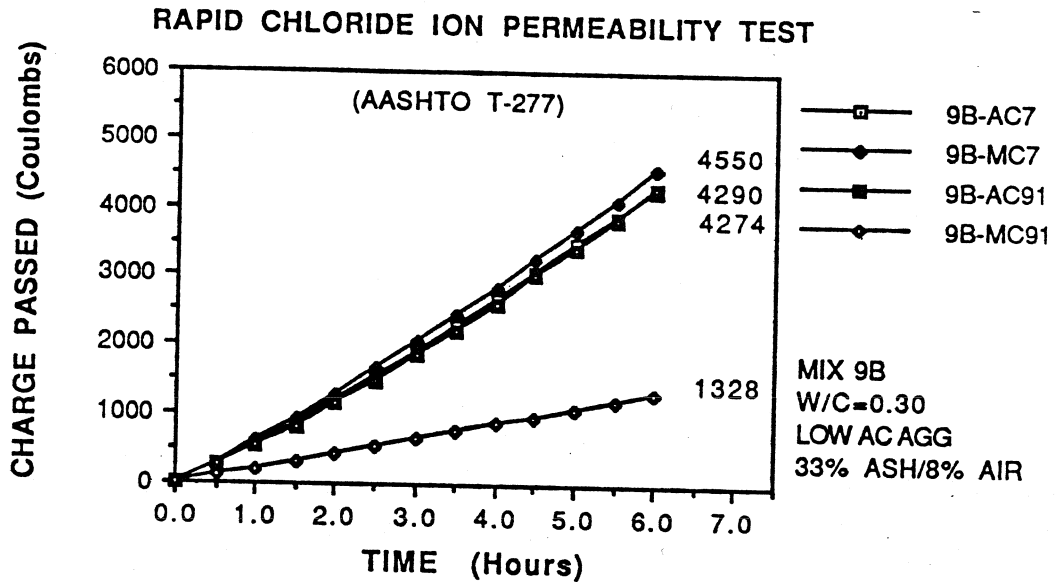


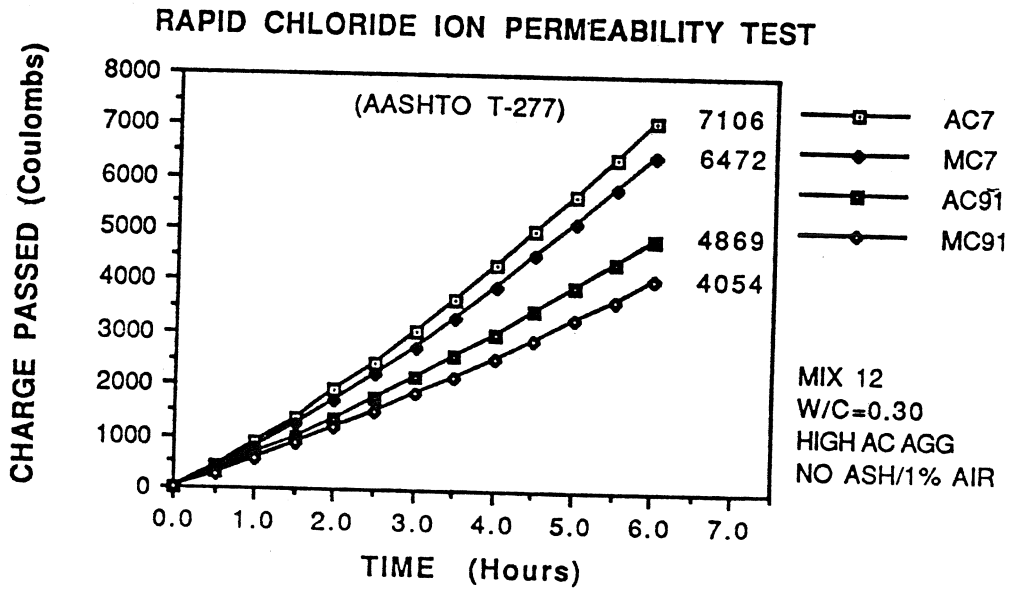
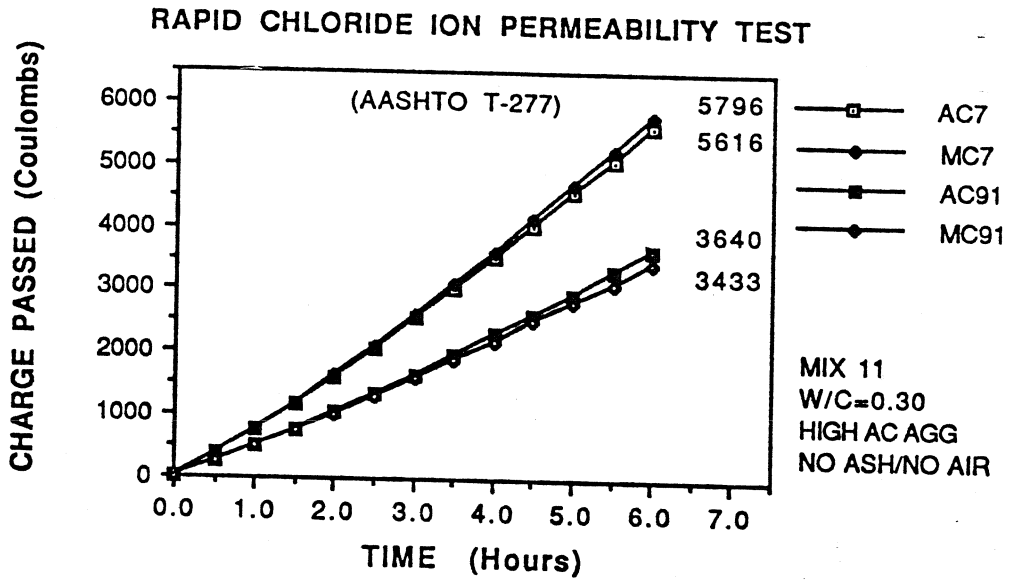
RAPID CHLORIDE ION PERMEABILITY TEST

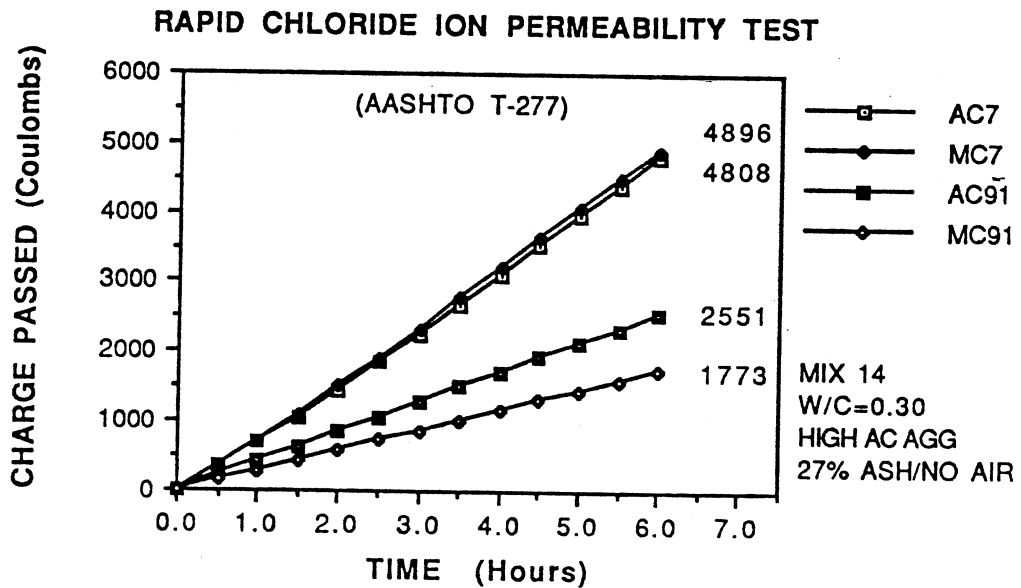
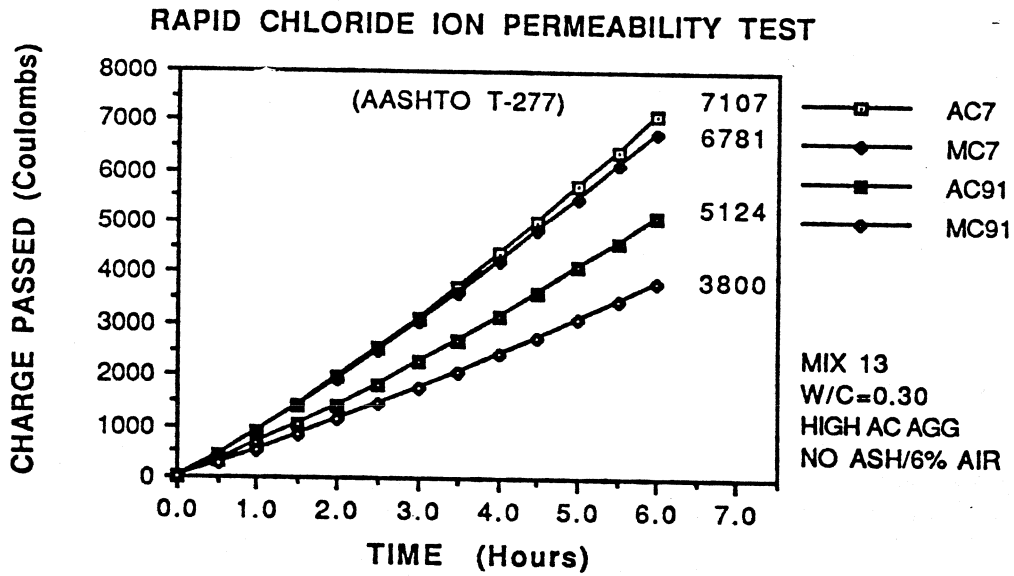


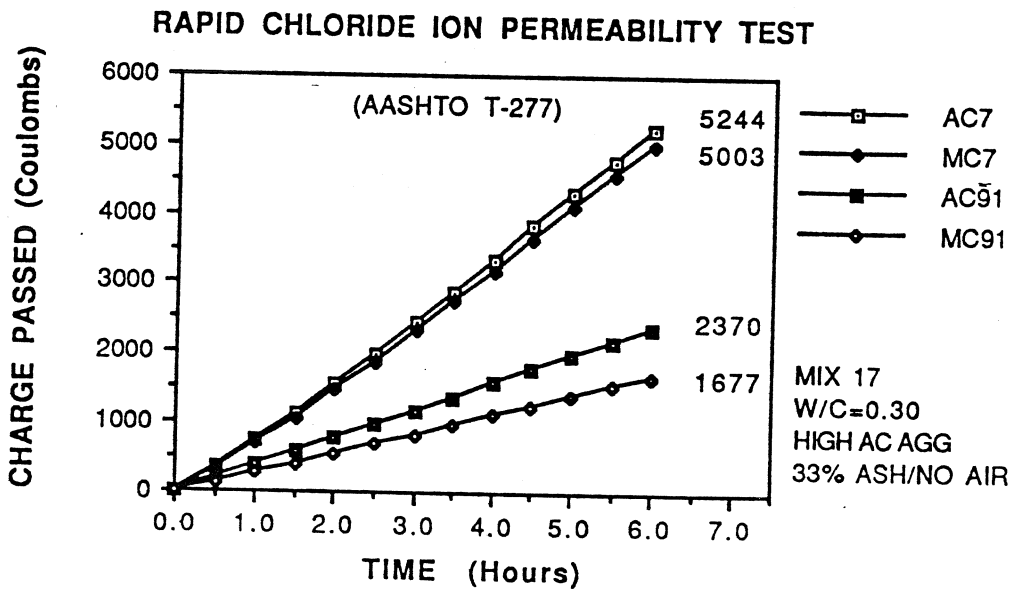
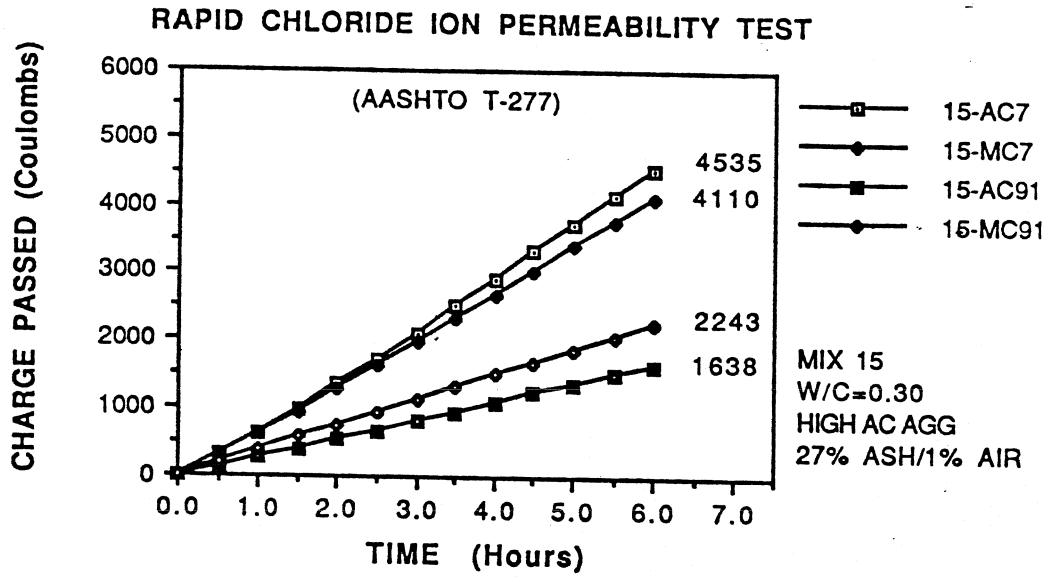
RAPID CHLORIDE ION PERMEABILITY TEST

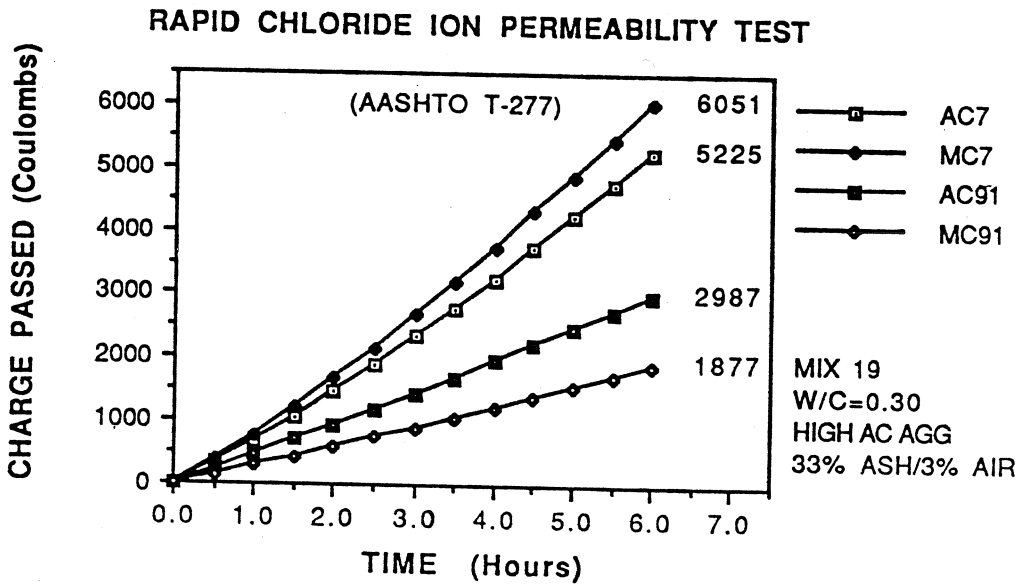
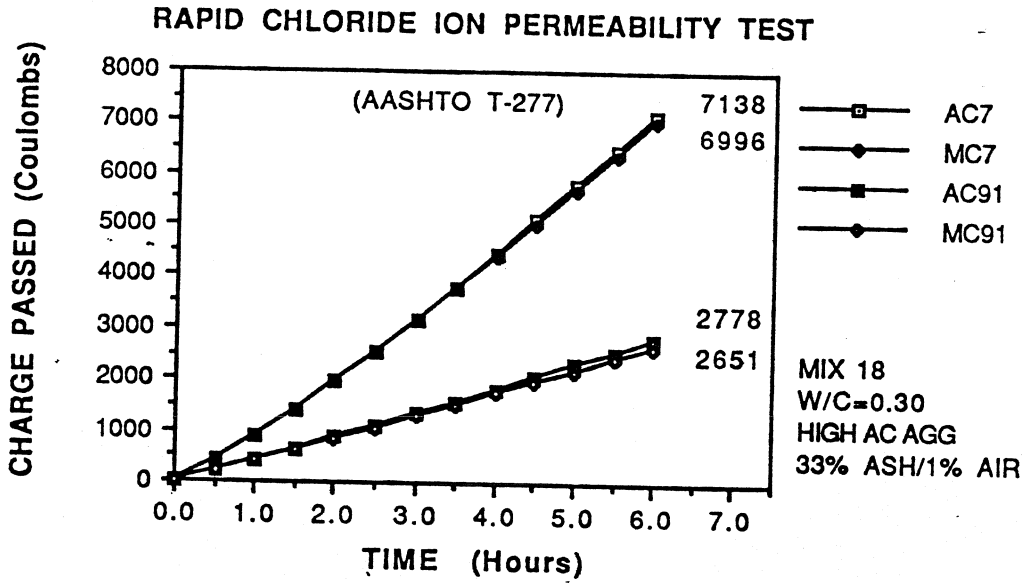


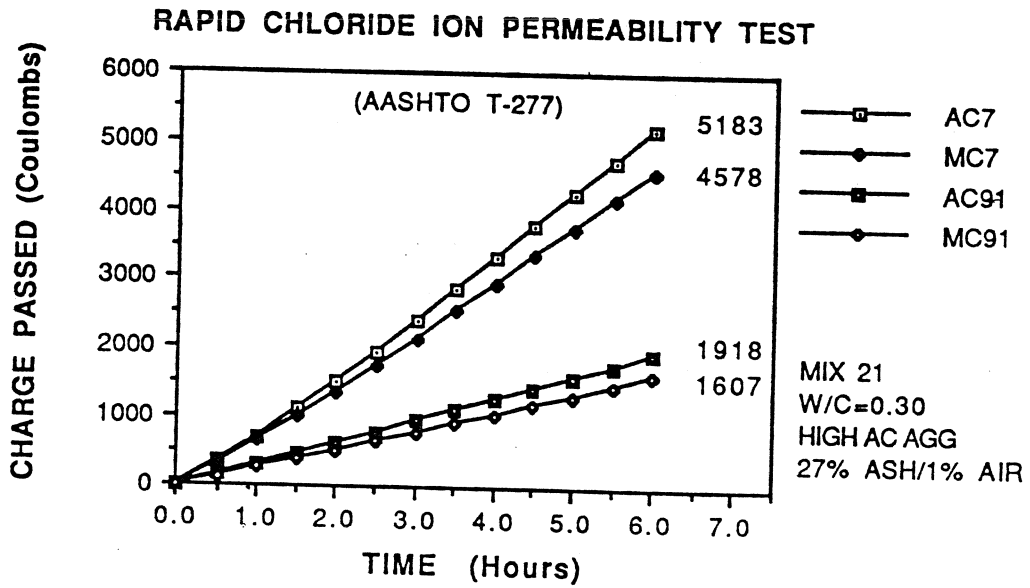
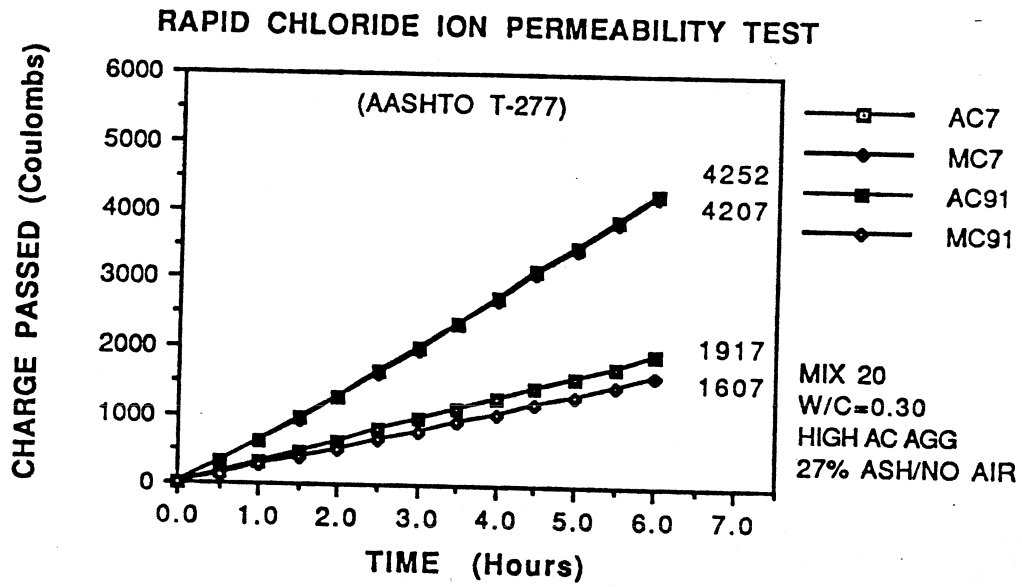


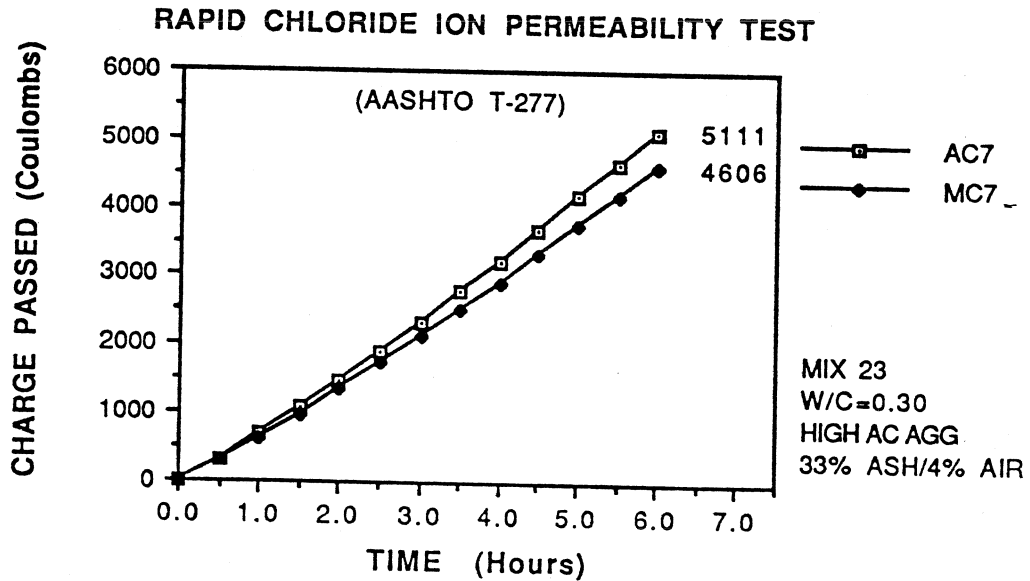
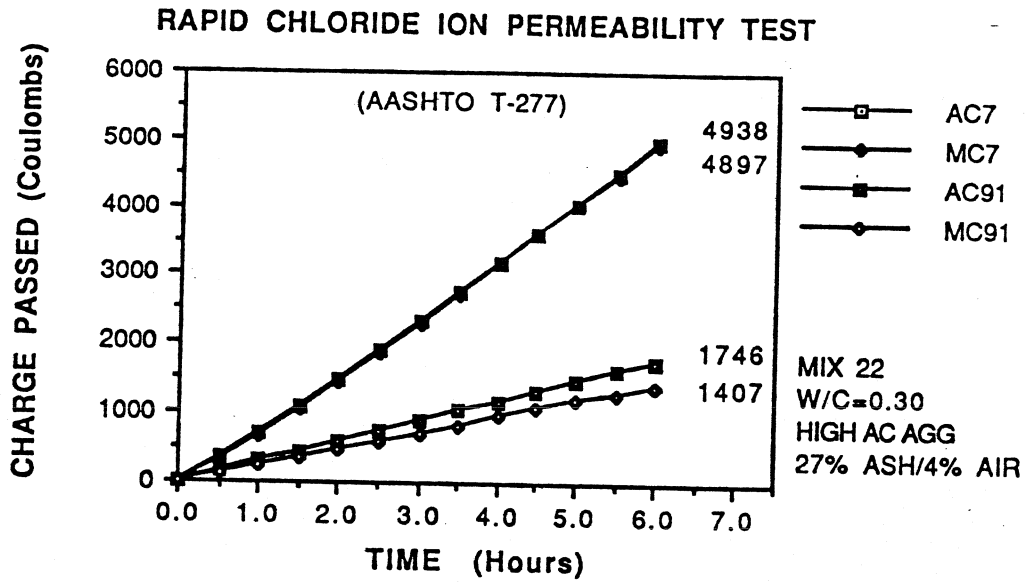


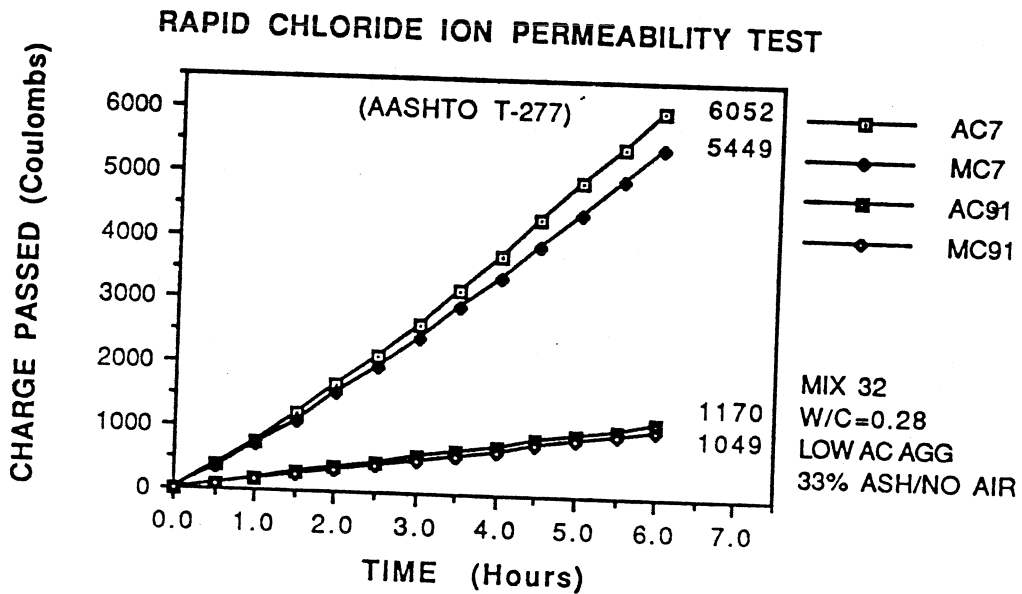
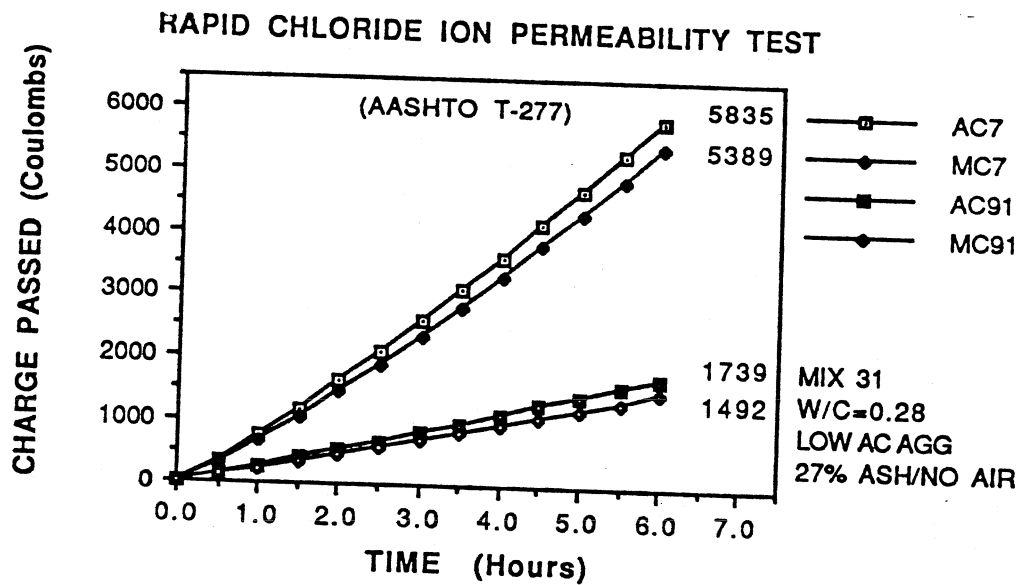


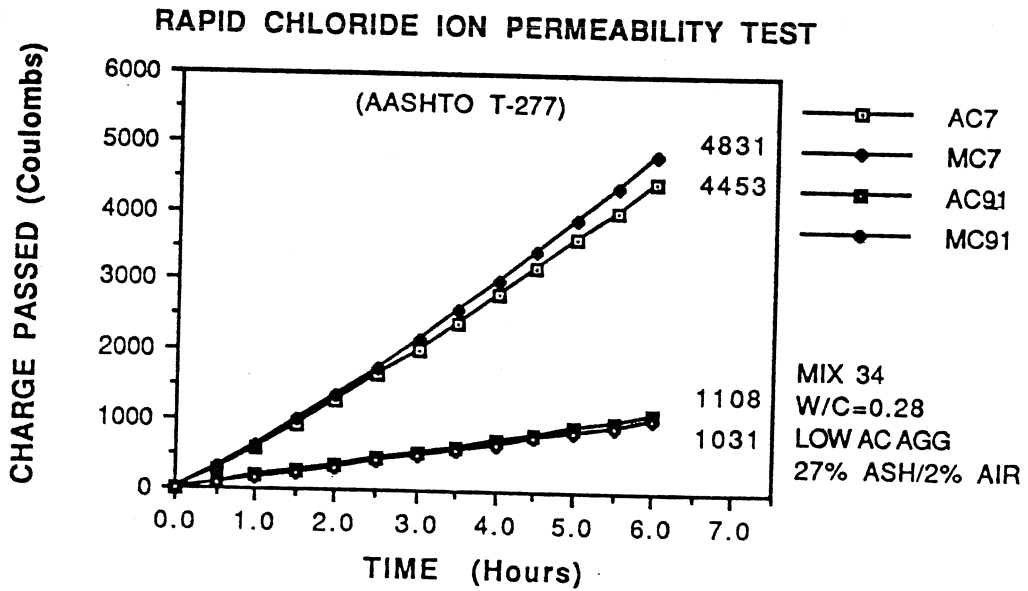
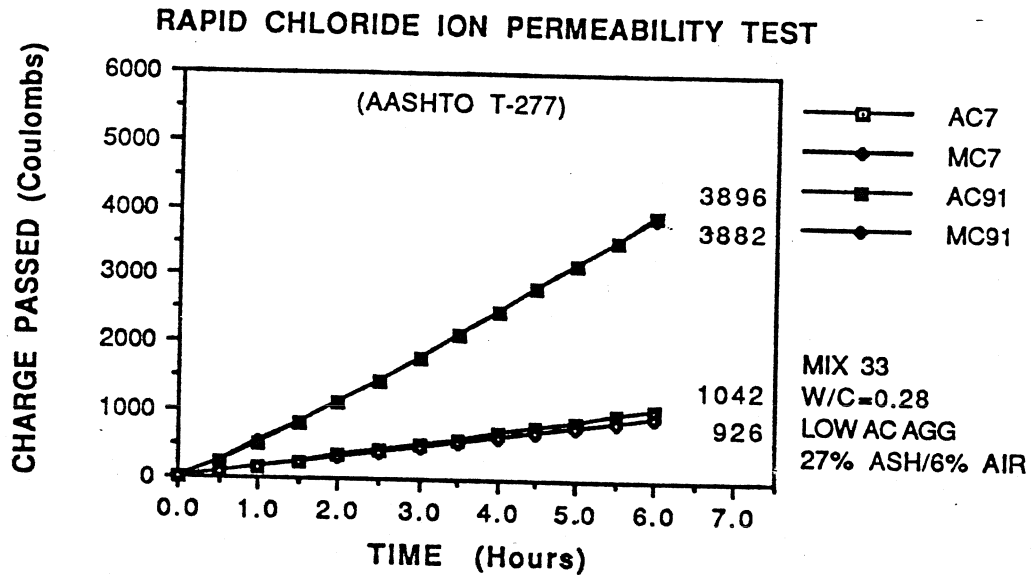


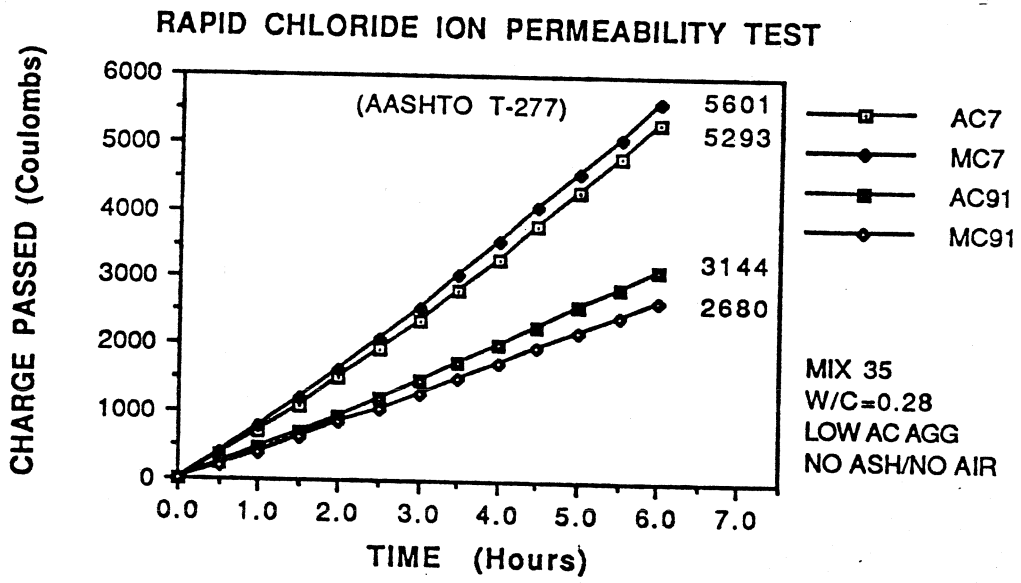


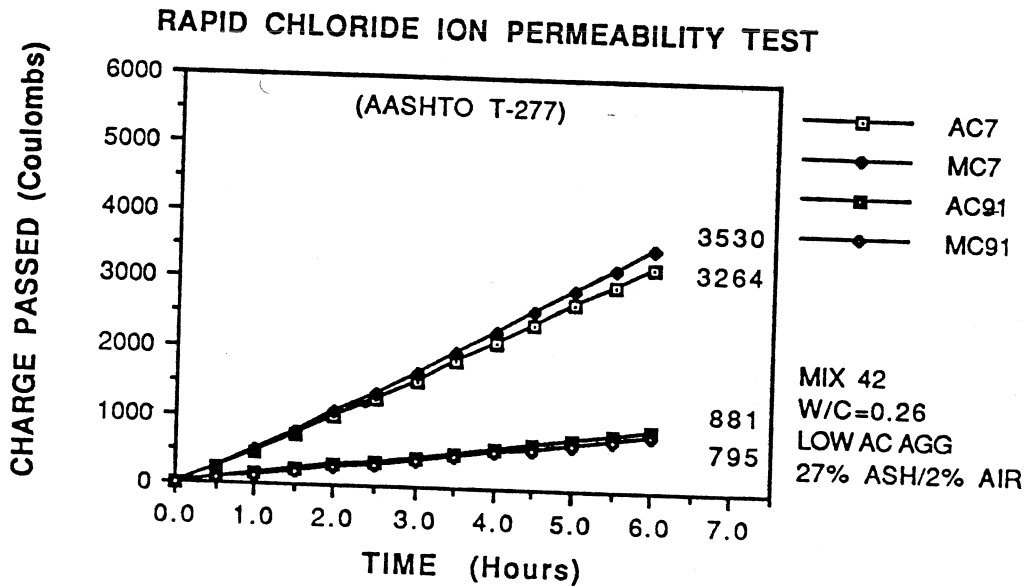
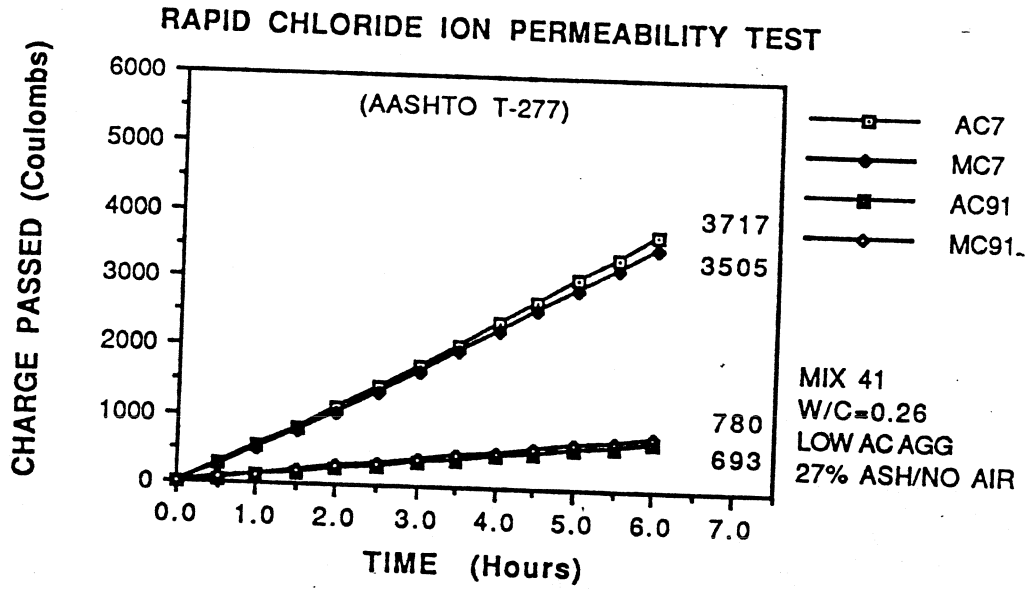


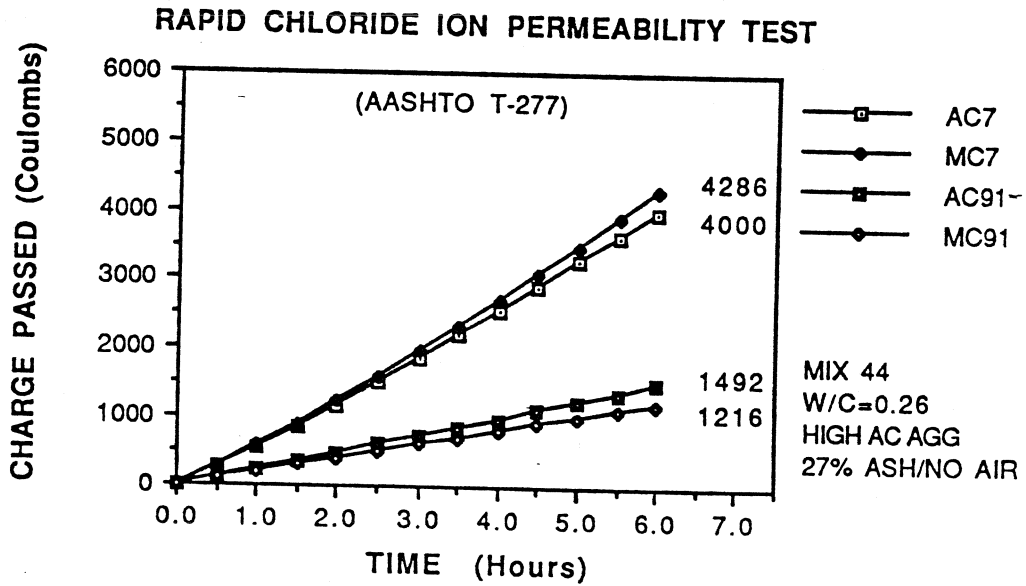
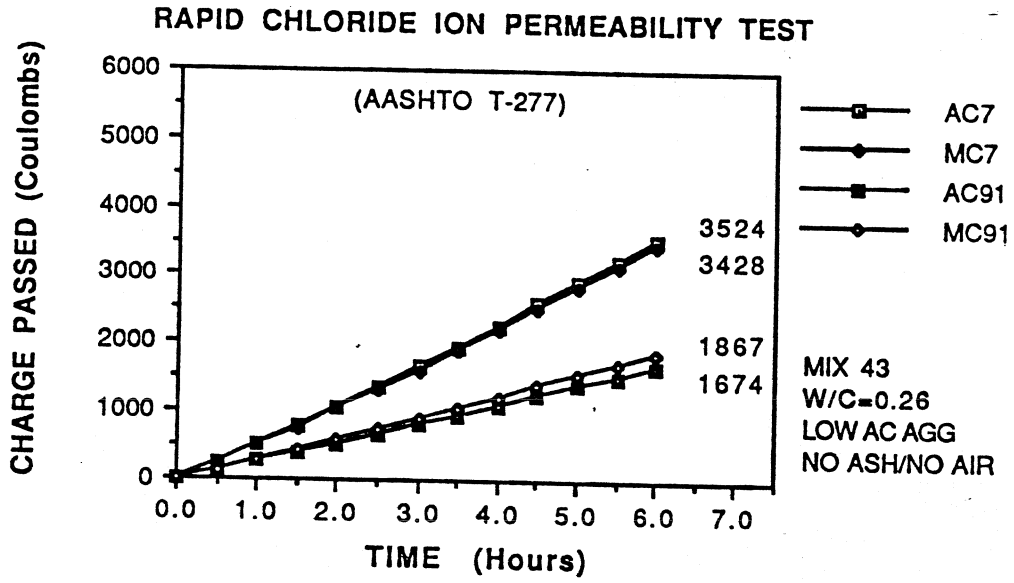


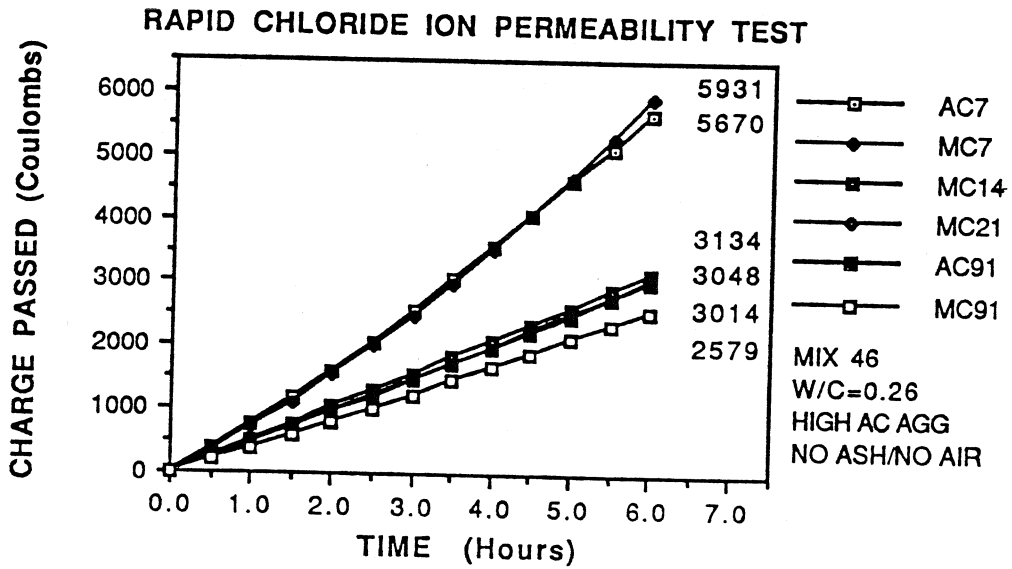
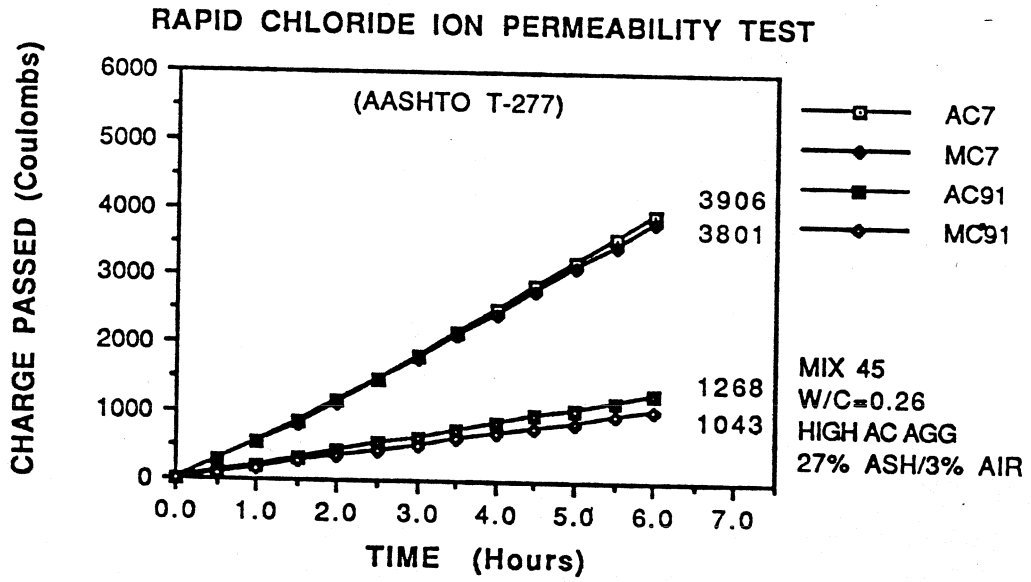


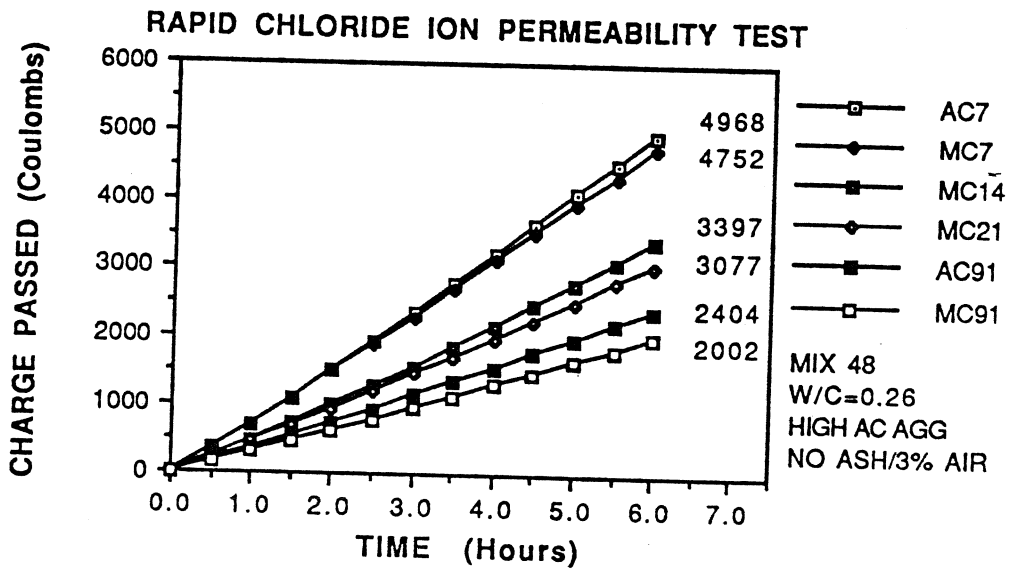
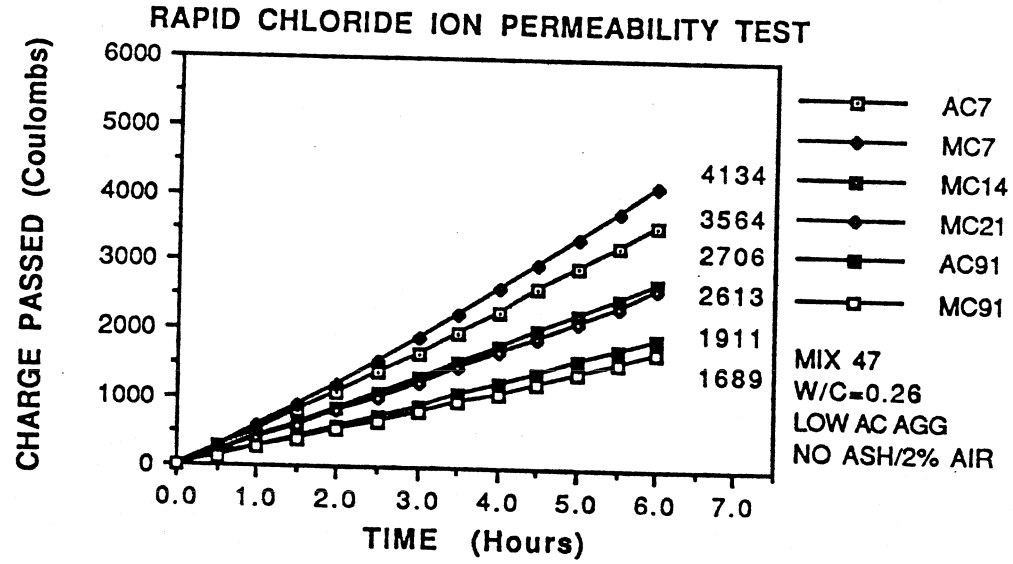


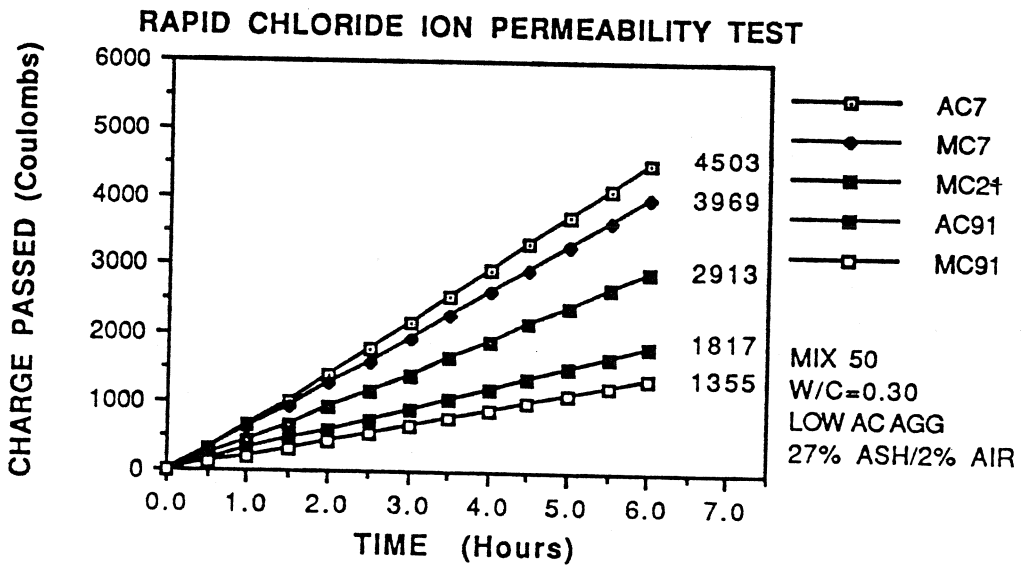
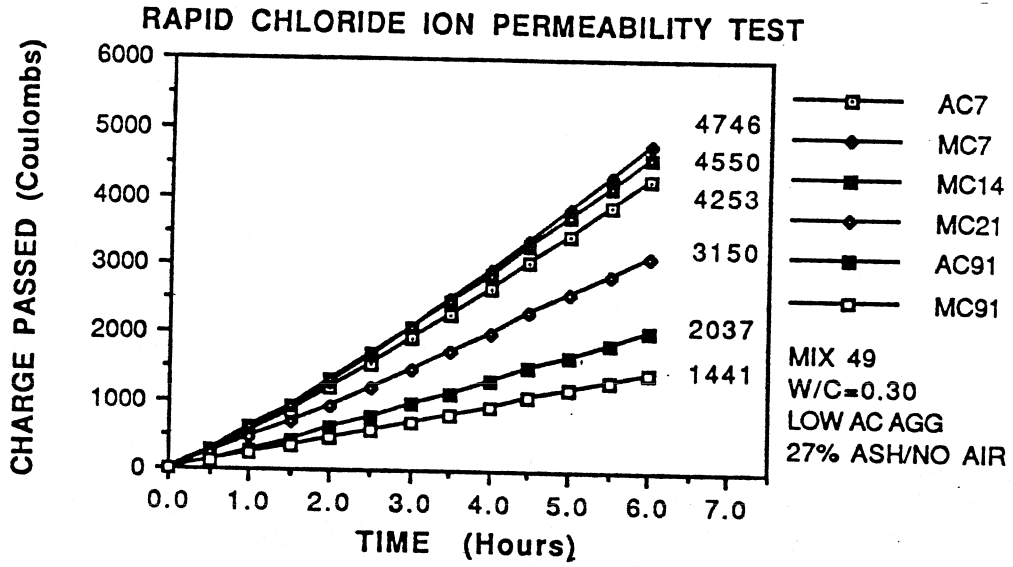


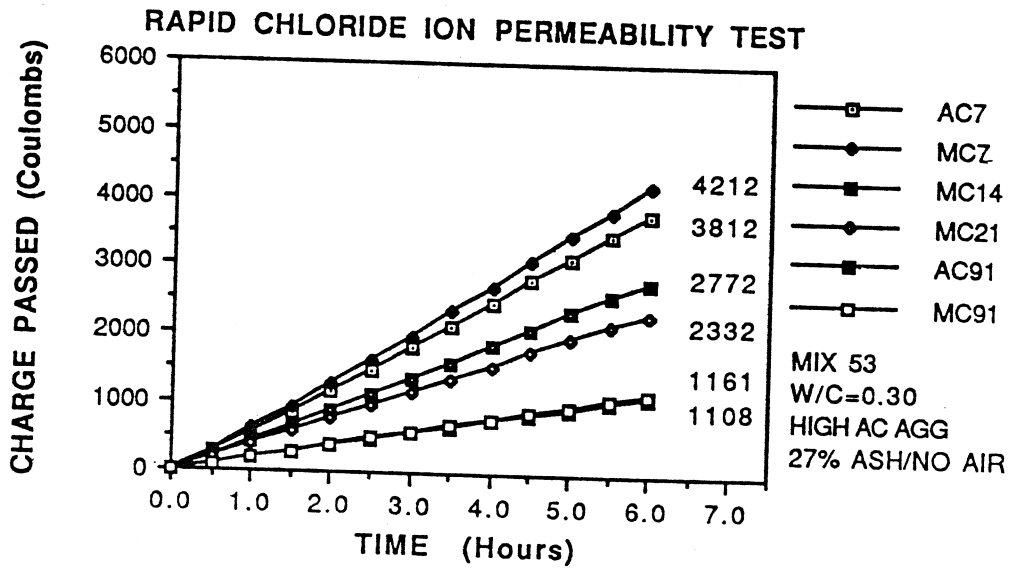
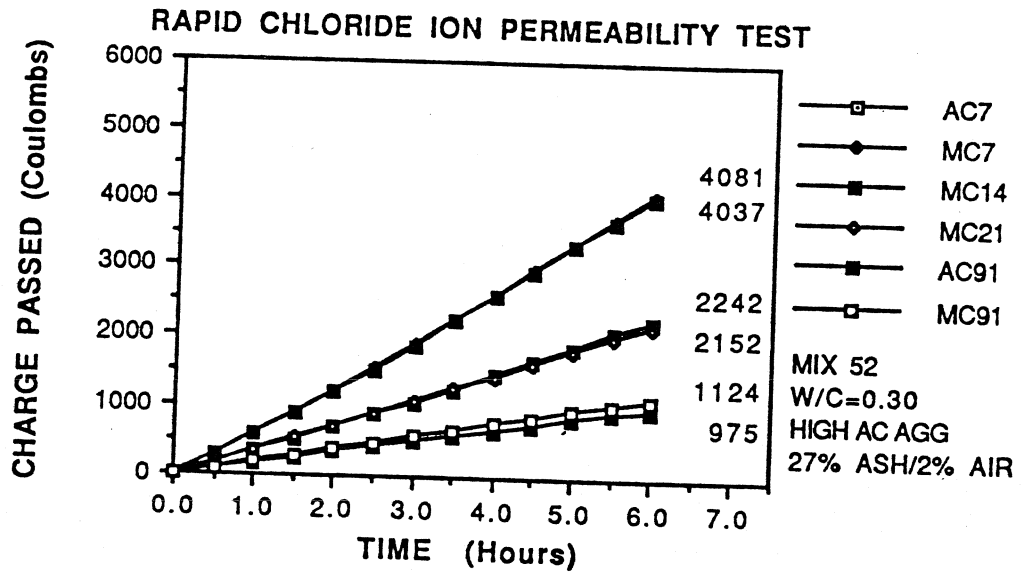




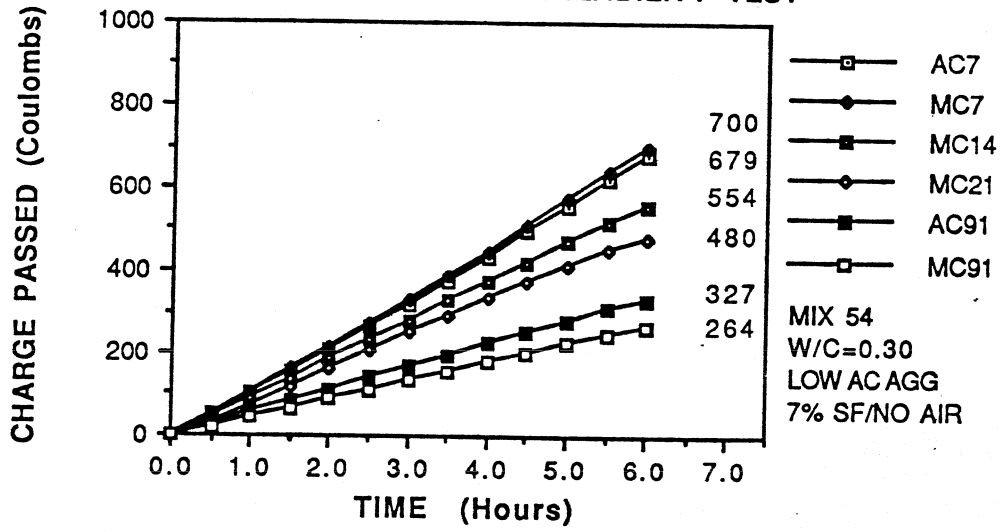




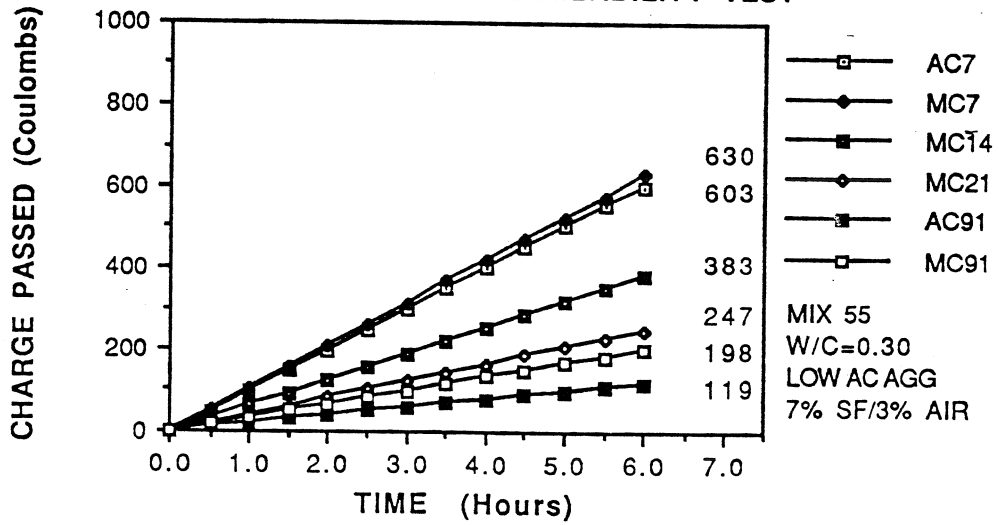


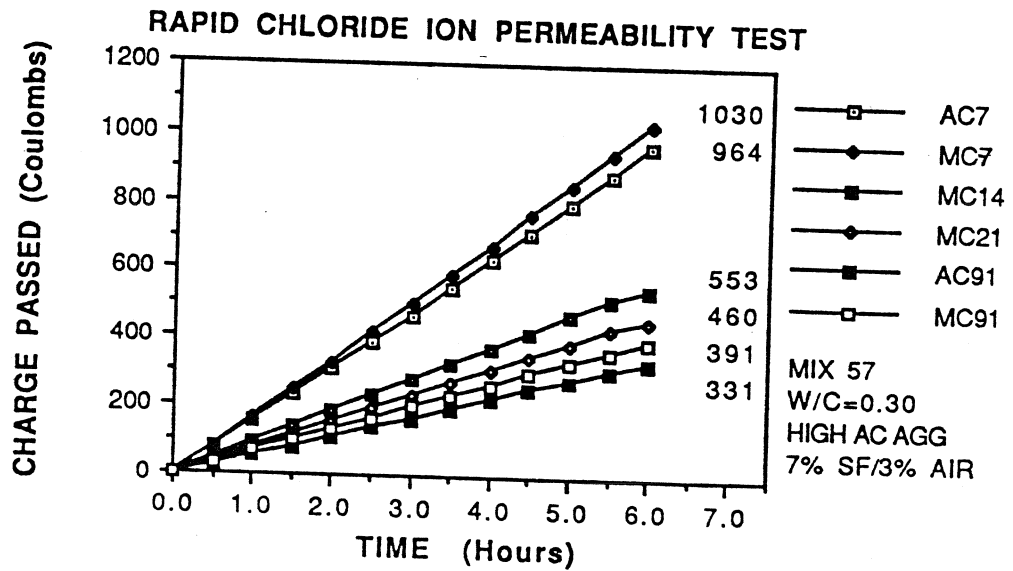
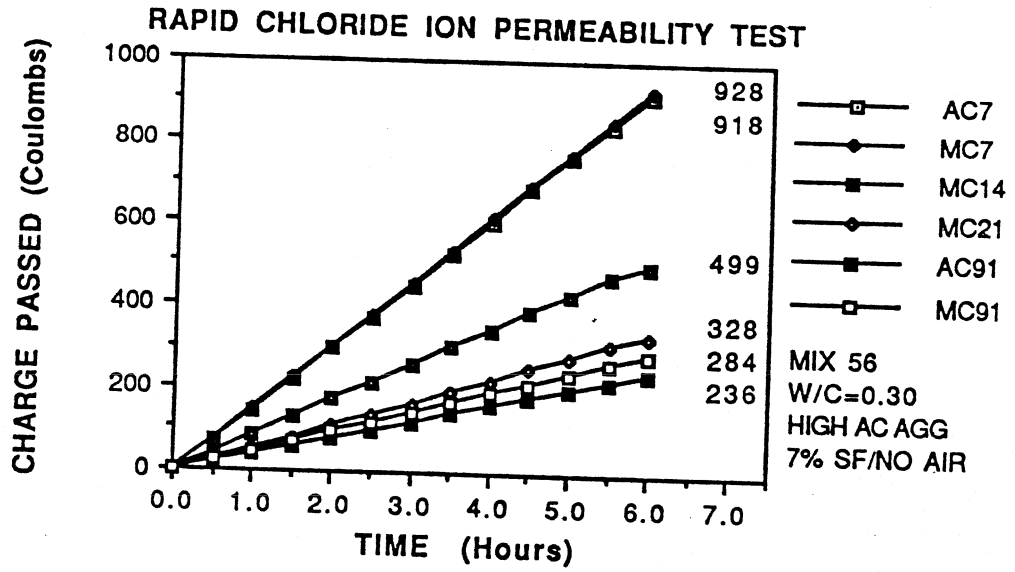


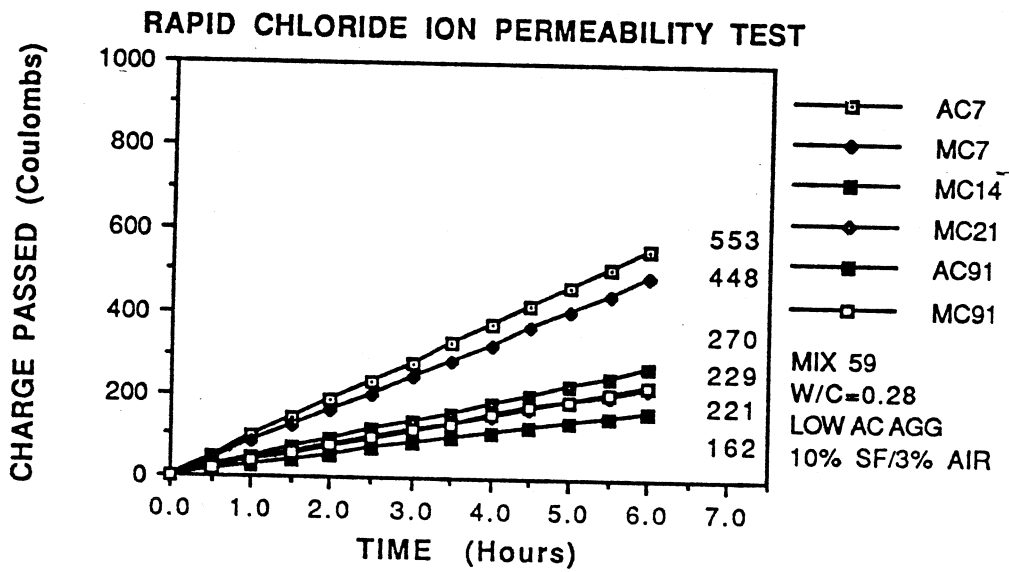
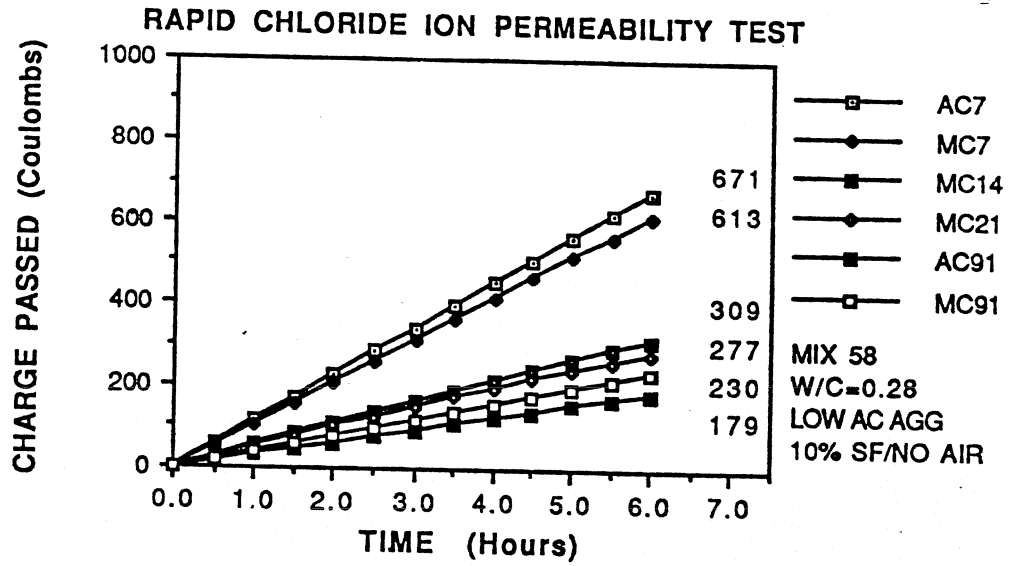
RAPID CHLORIDE ION PERMEABILITY TEST

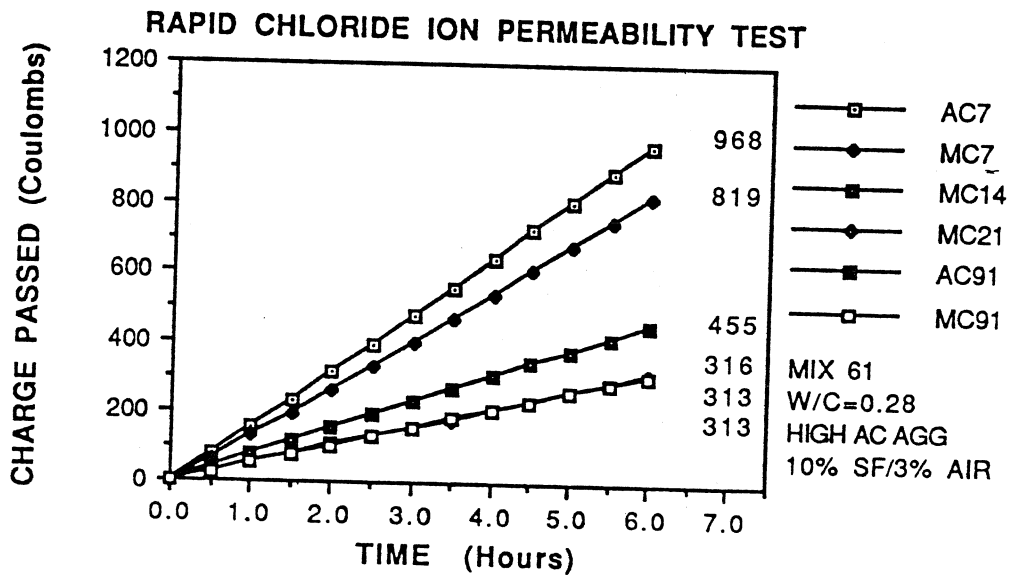
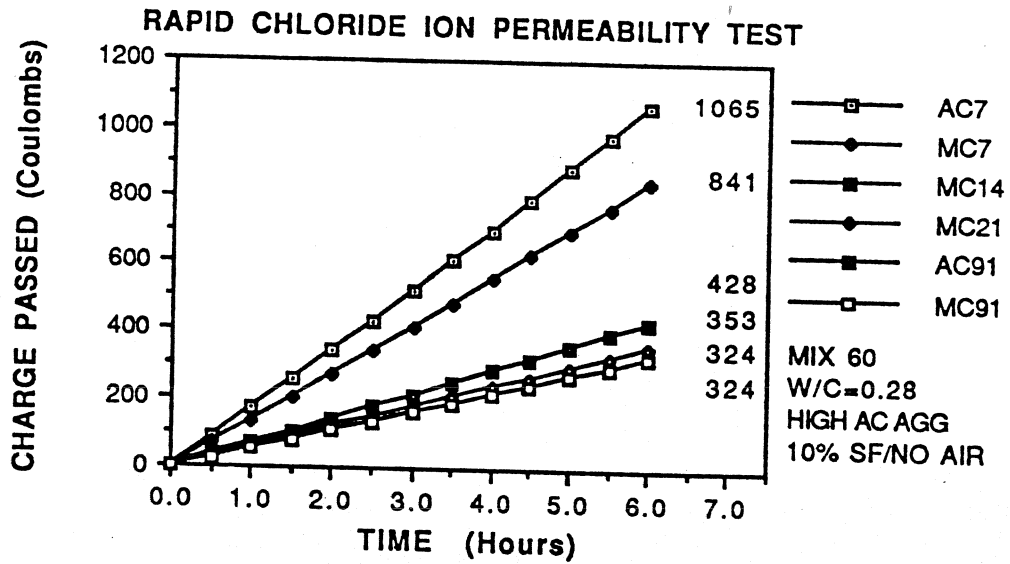


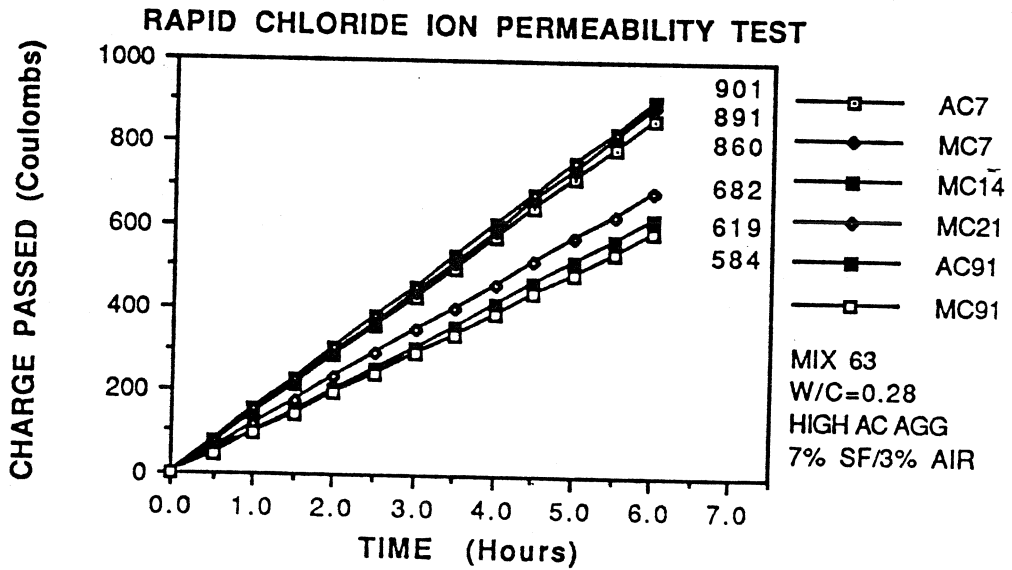
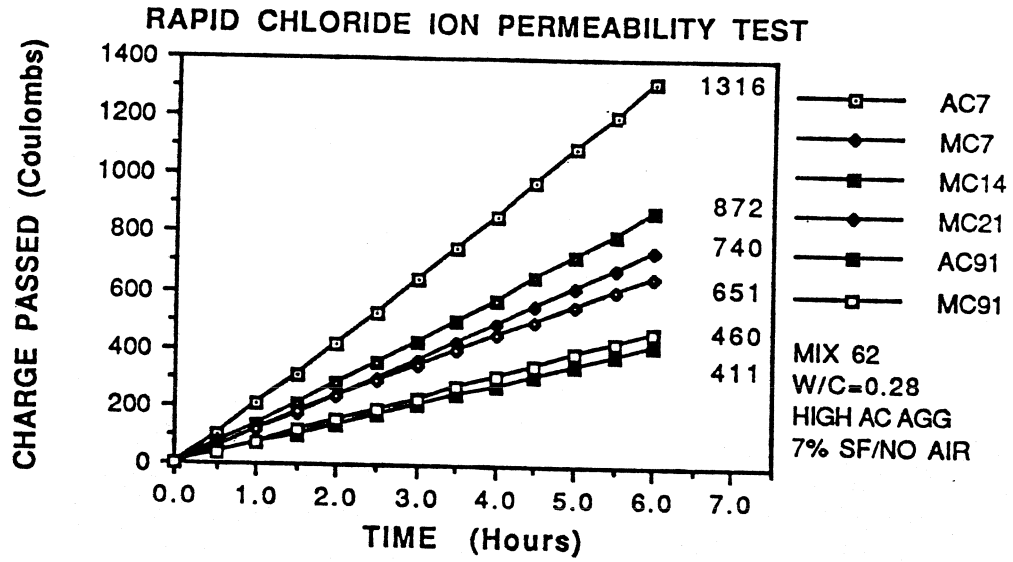
RAPID CHLORIDE ION PERMEABILITY TEST

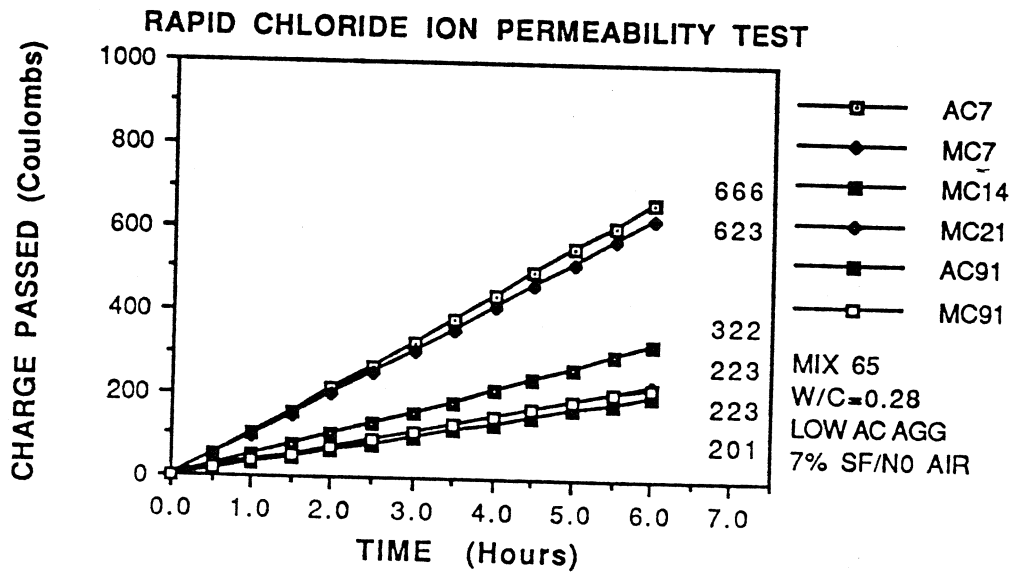
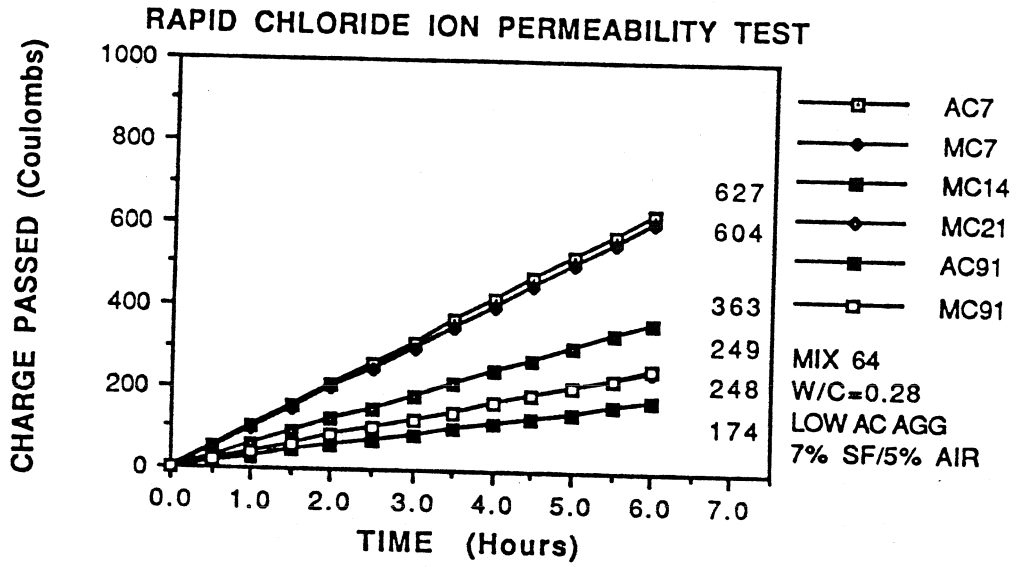


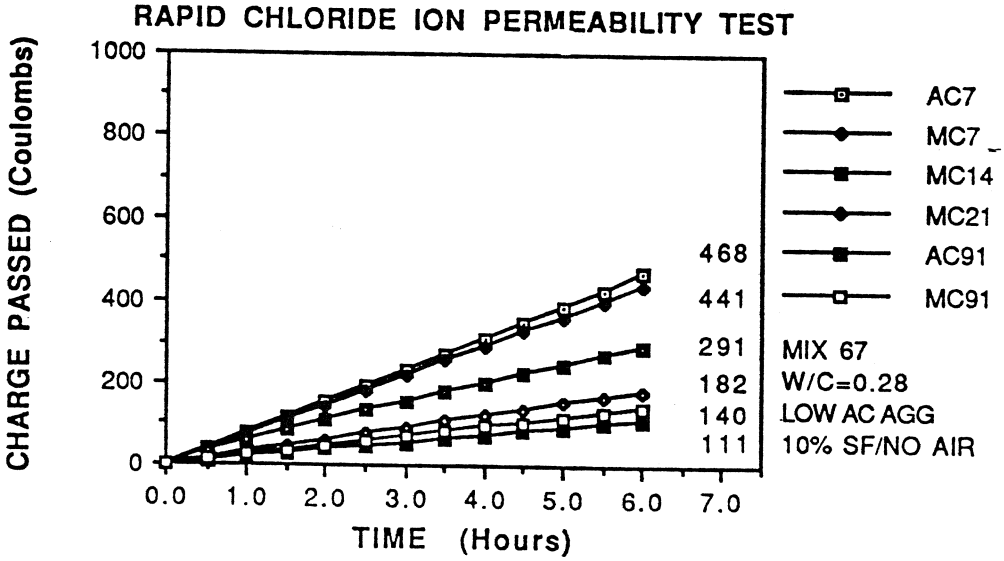
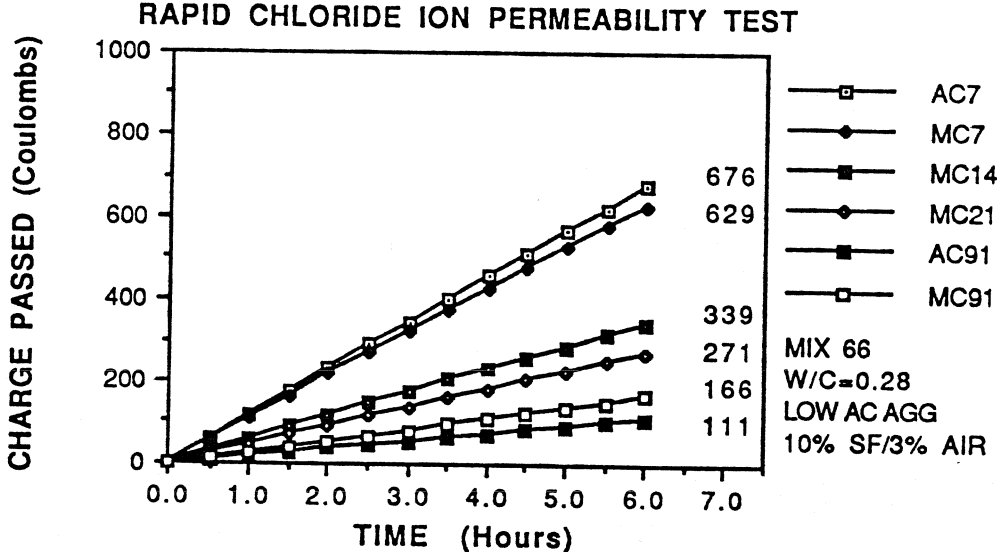


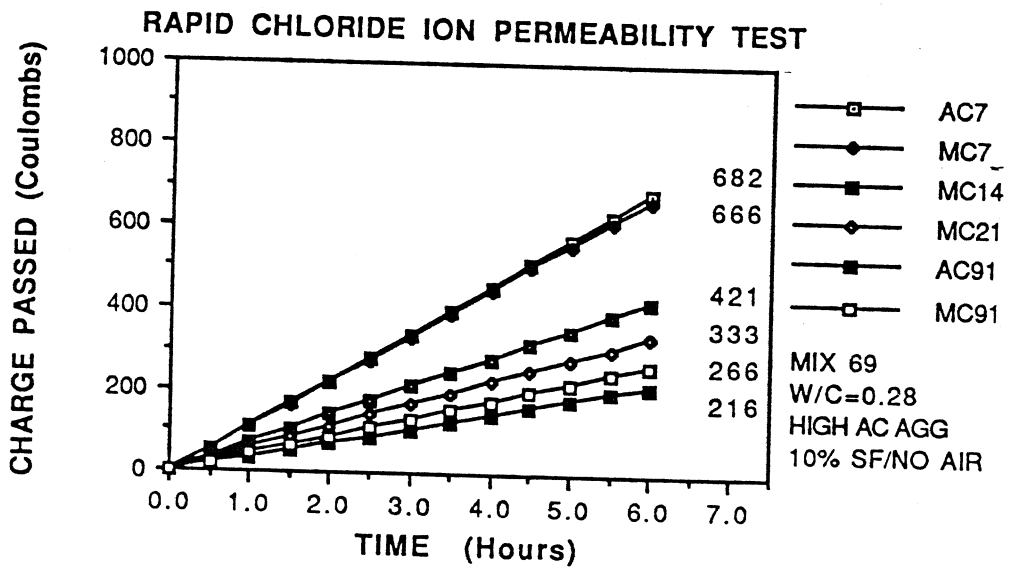
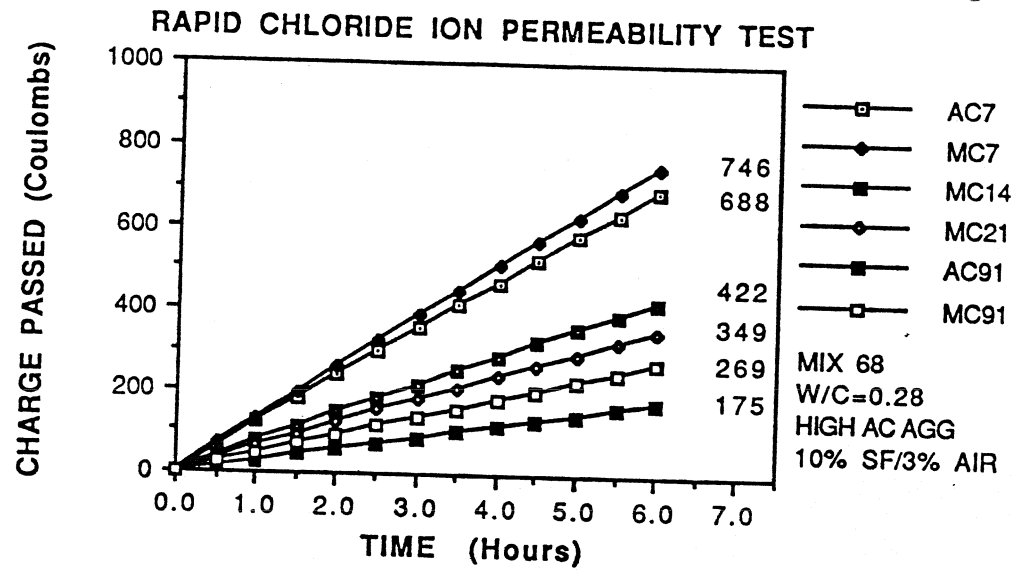




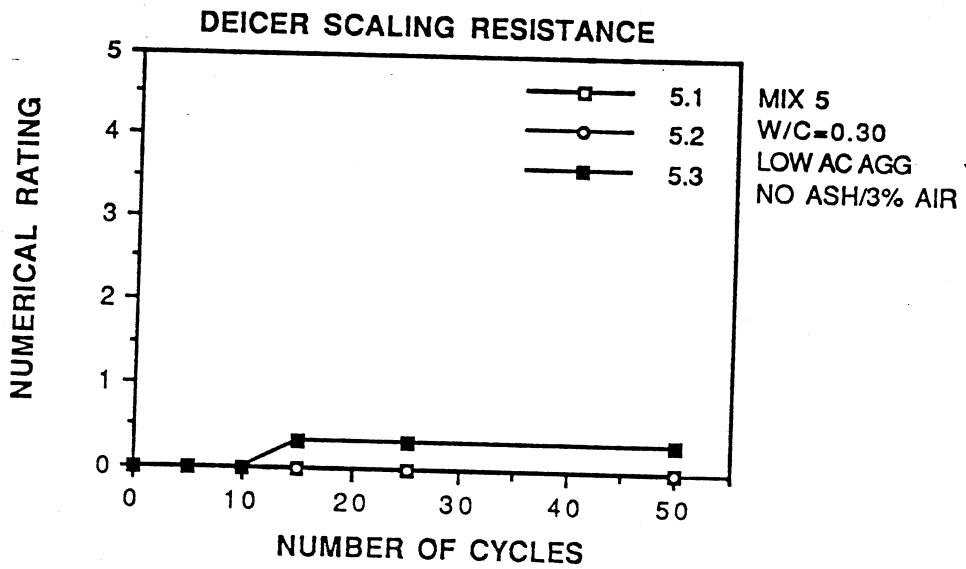
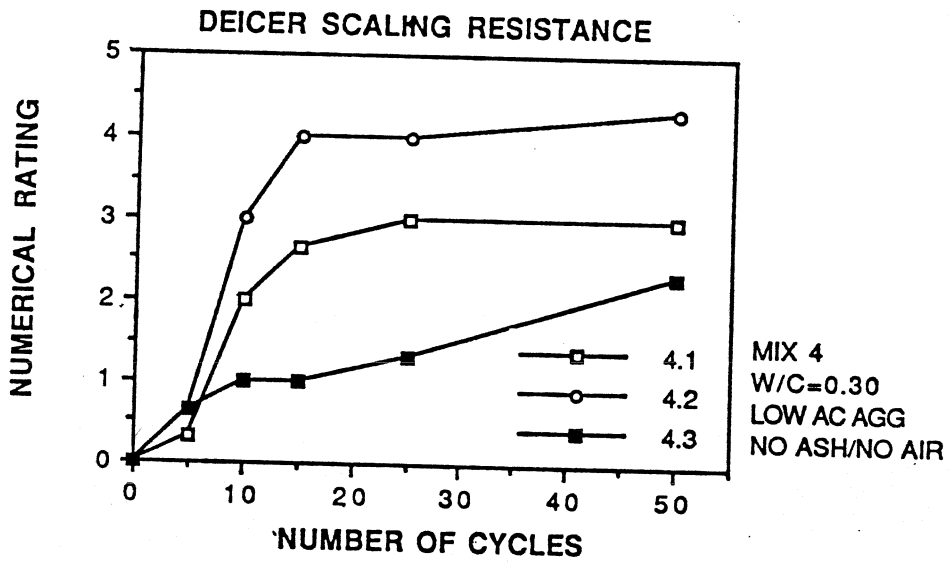


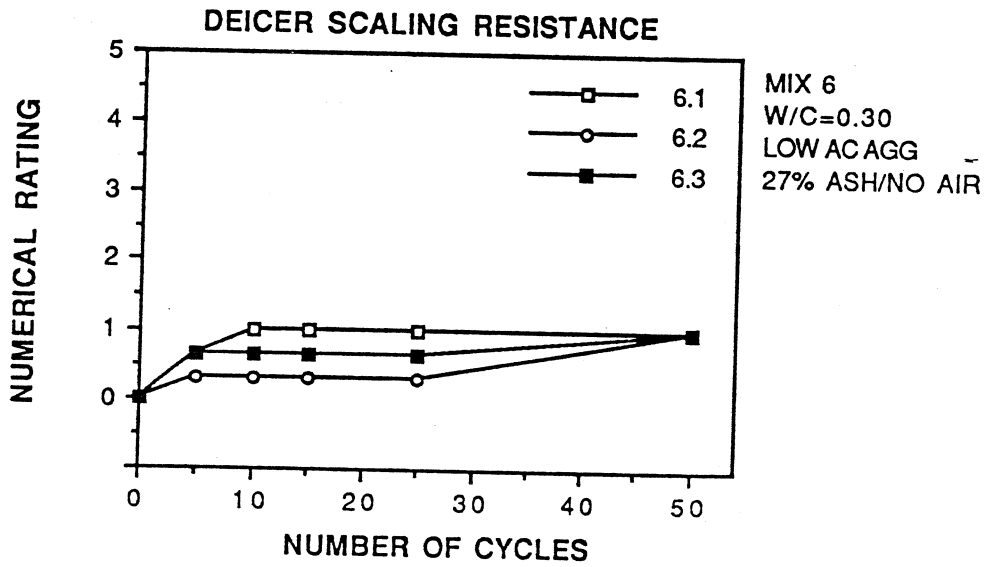
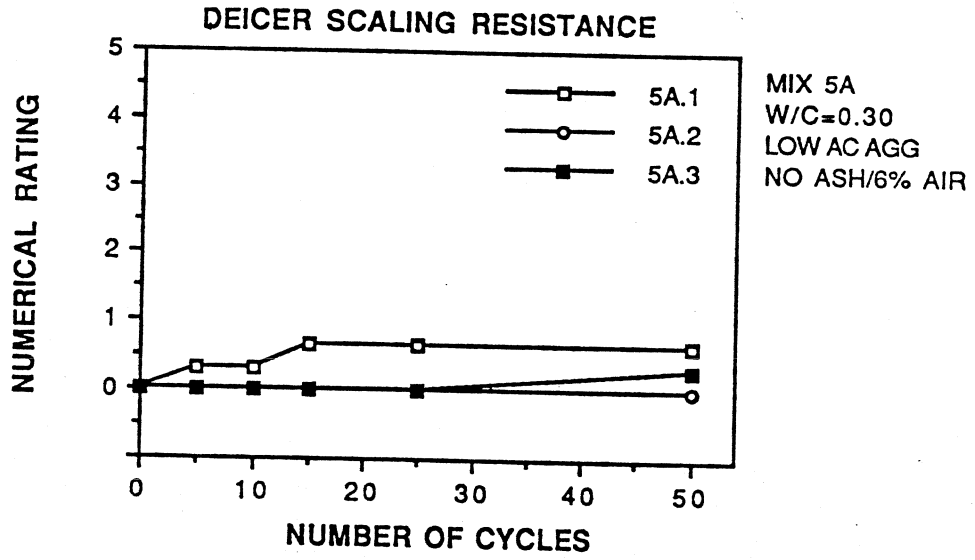


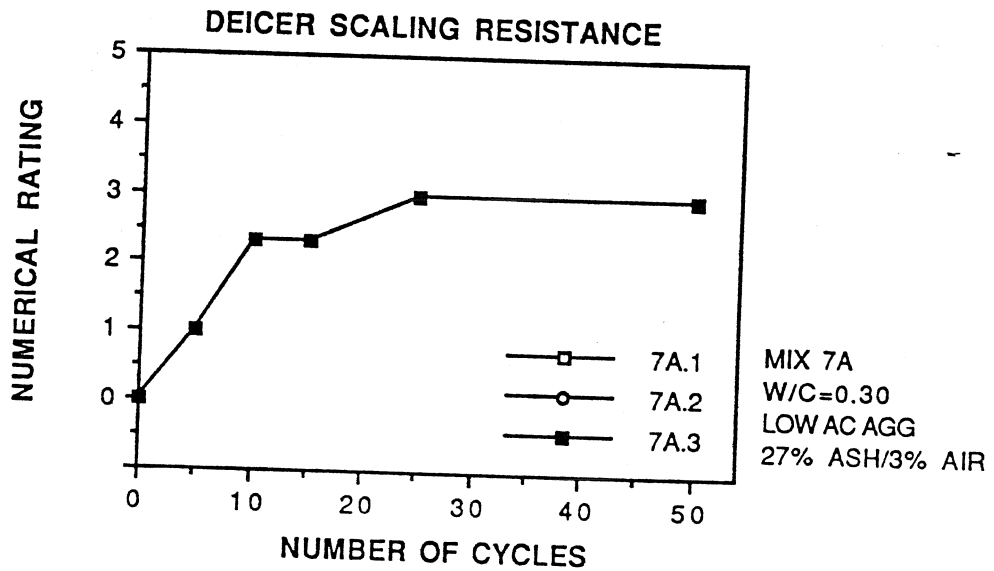
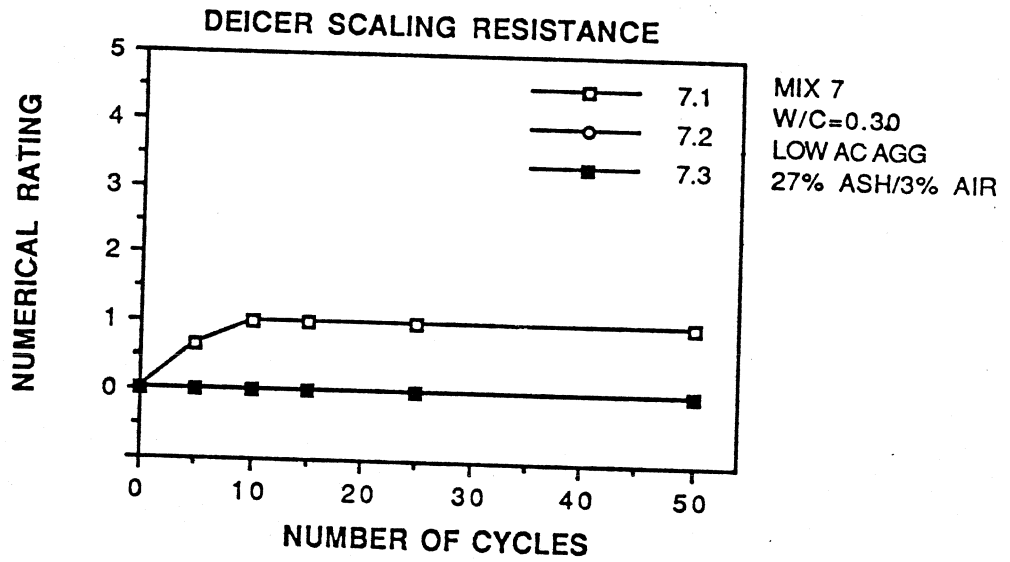


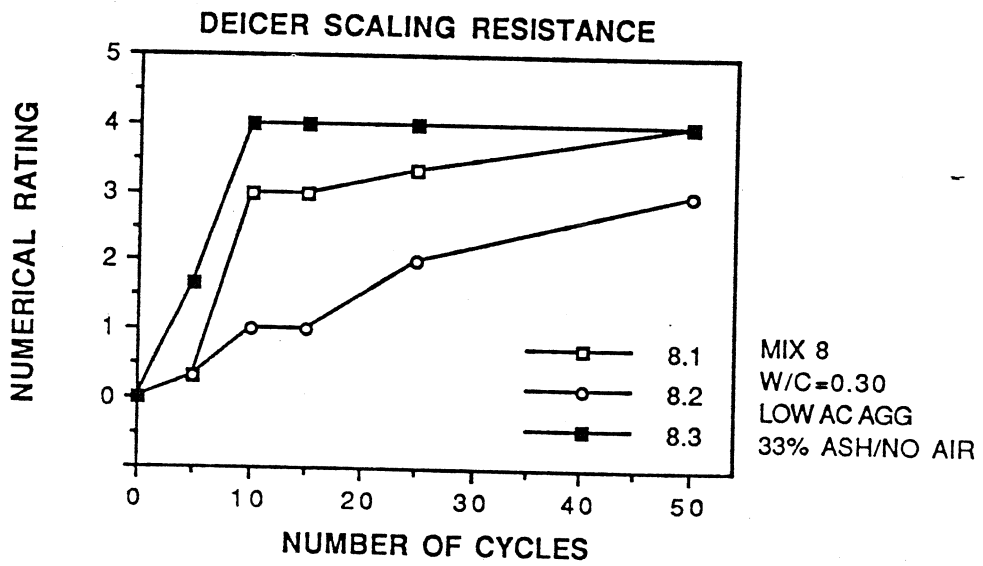
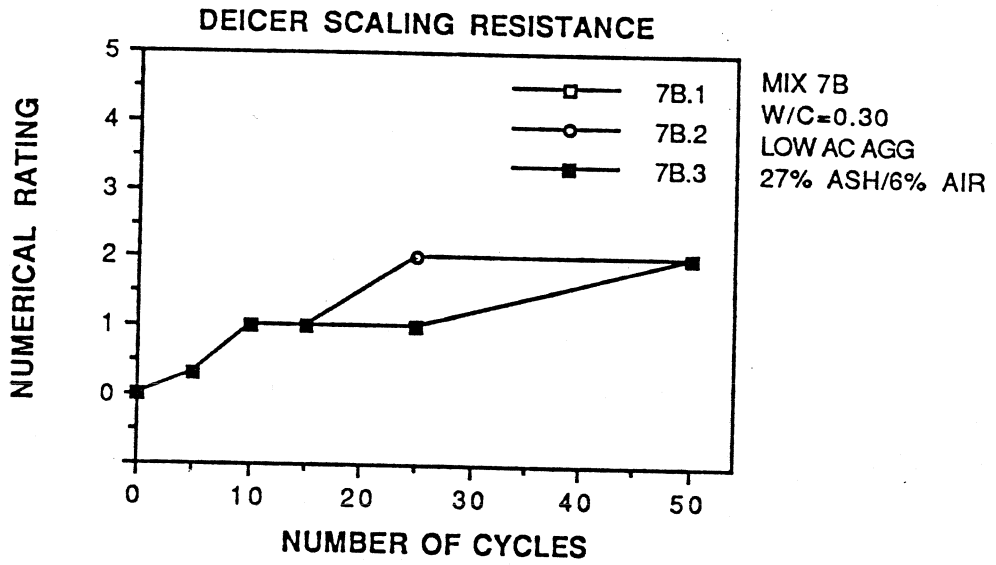


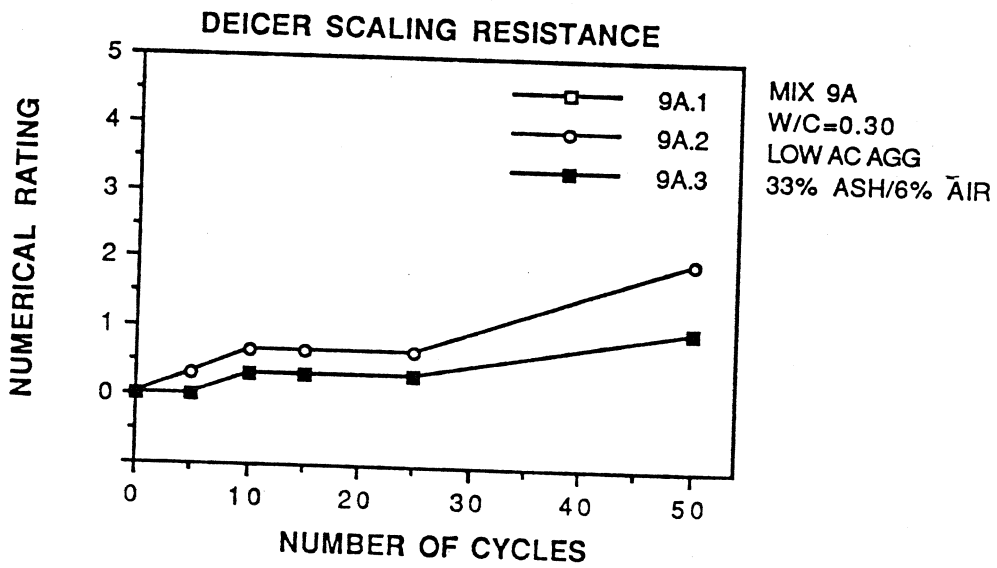
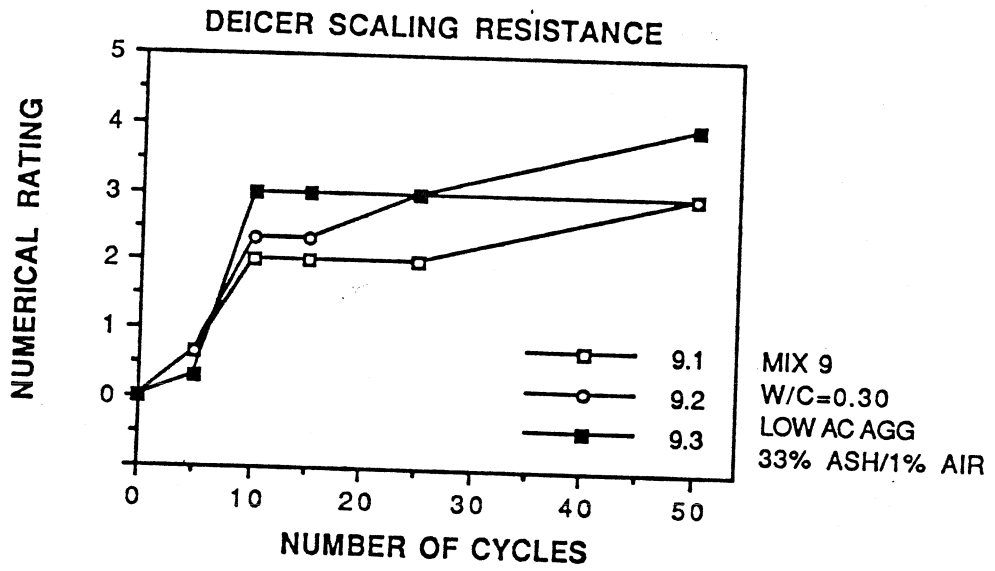
APPENDIX E
DEICER SCALING RESISTANCE DATA

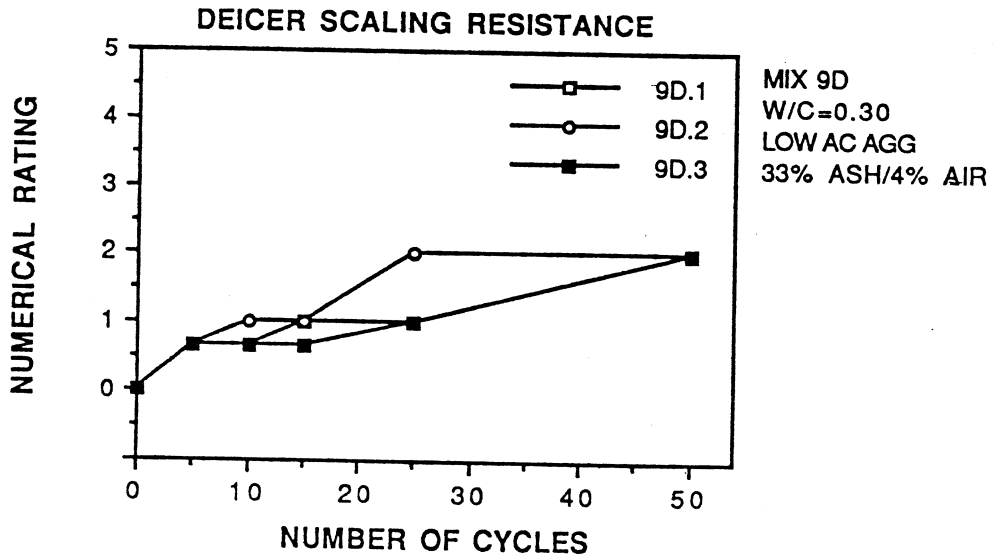
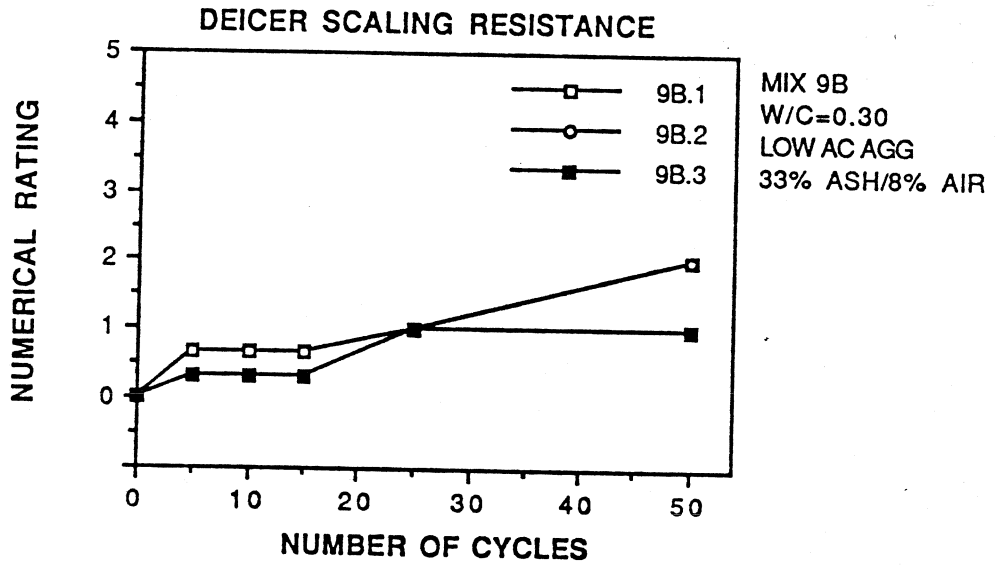


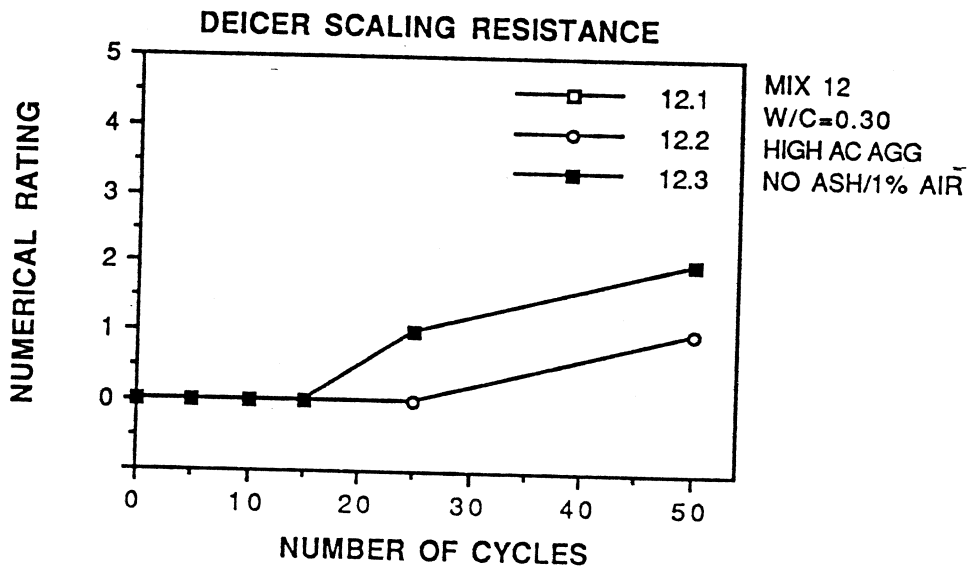
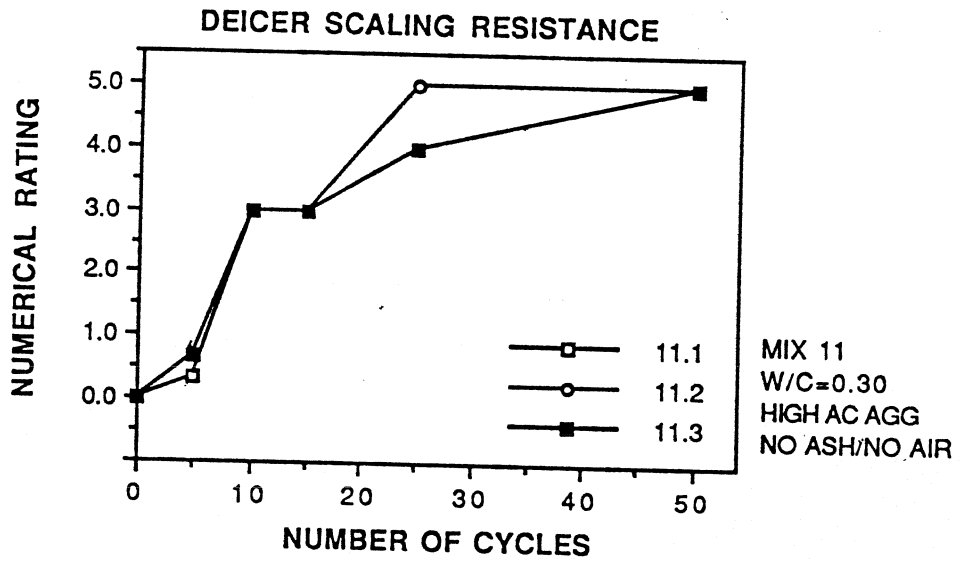


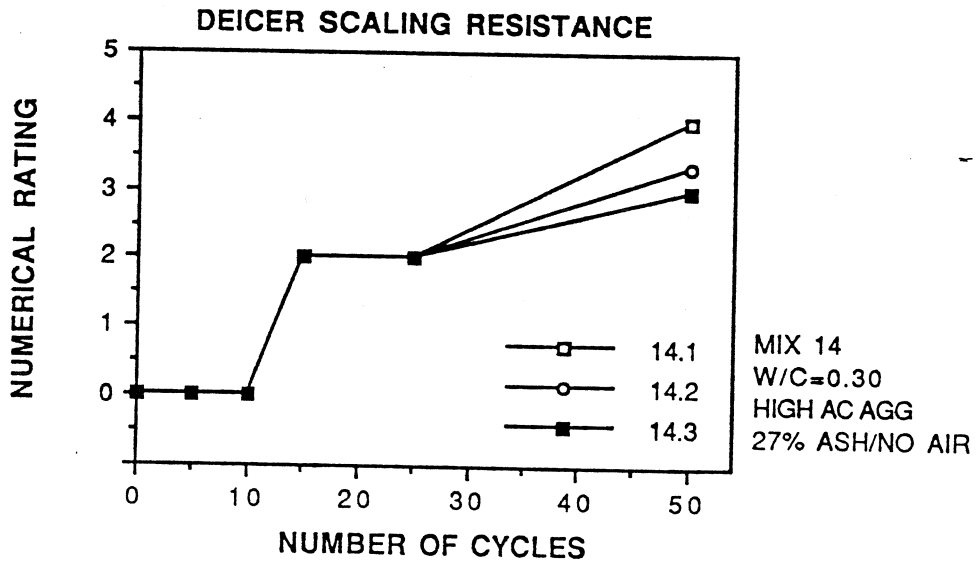
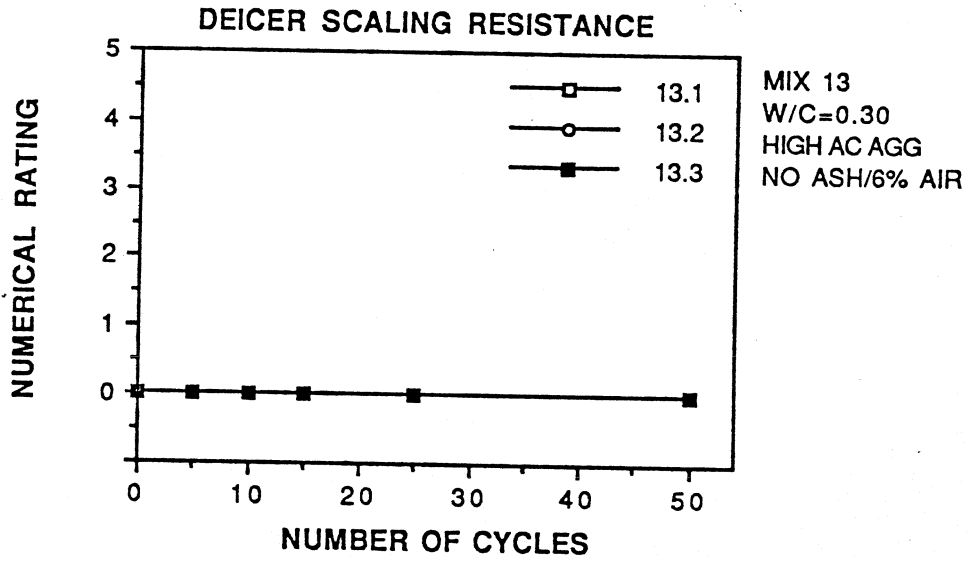


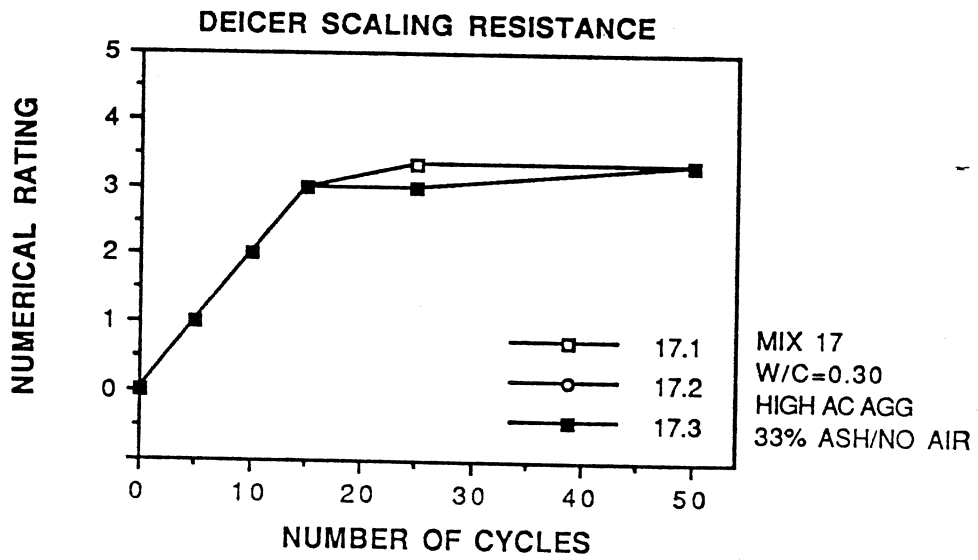
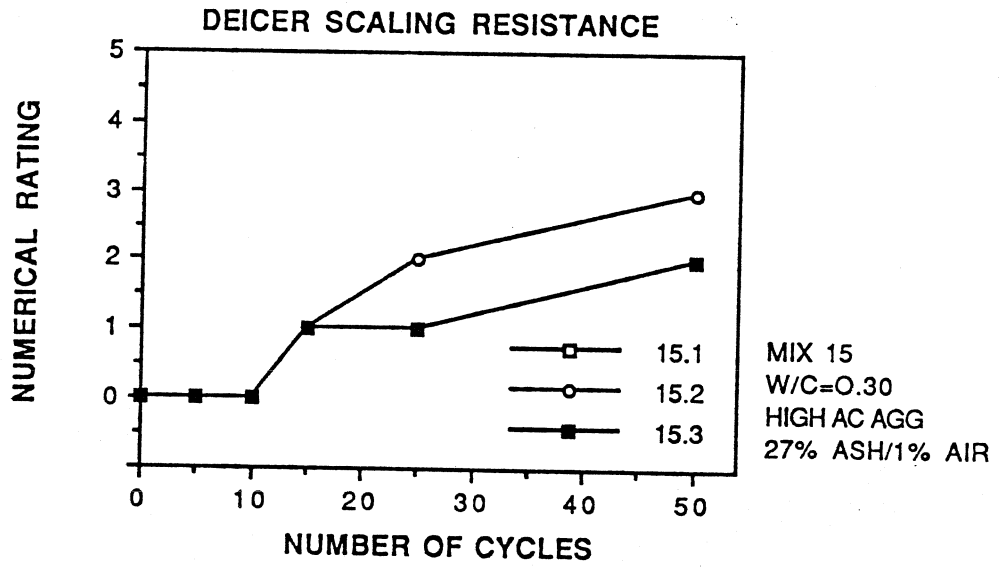


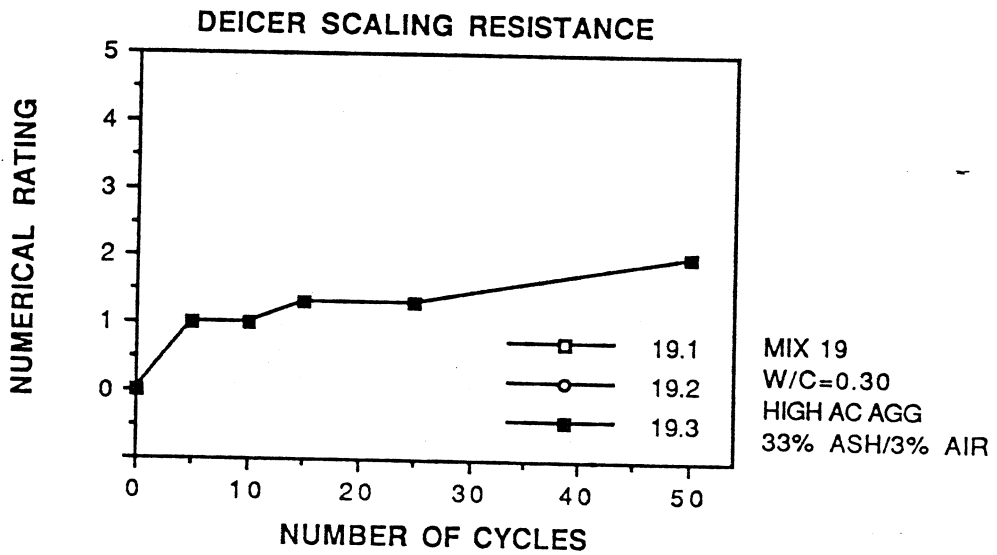
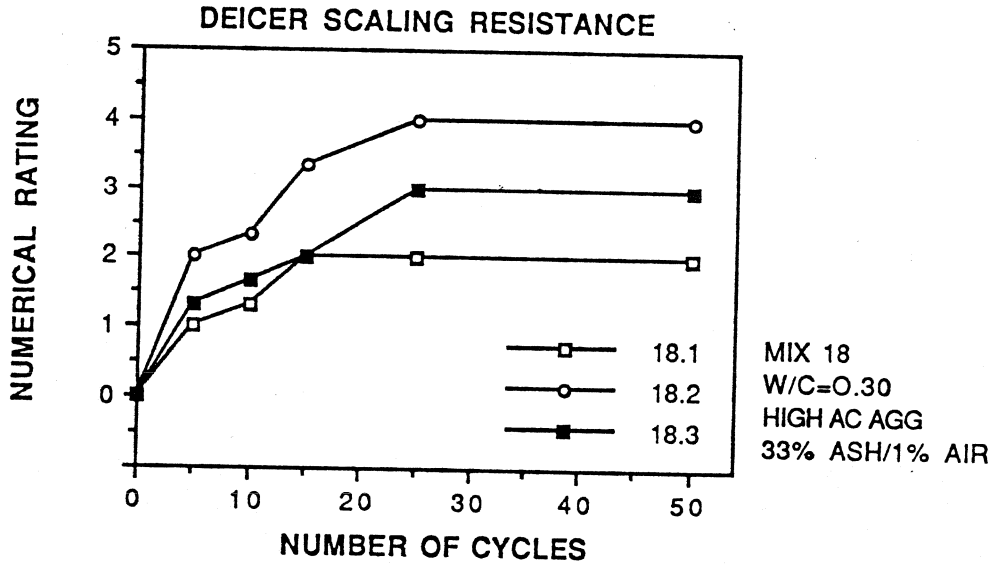


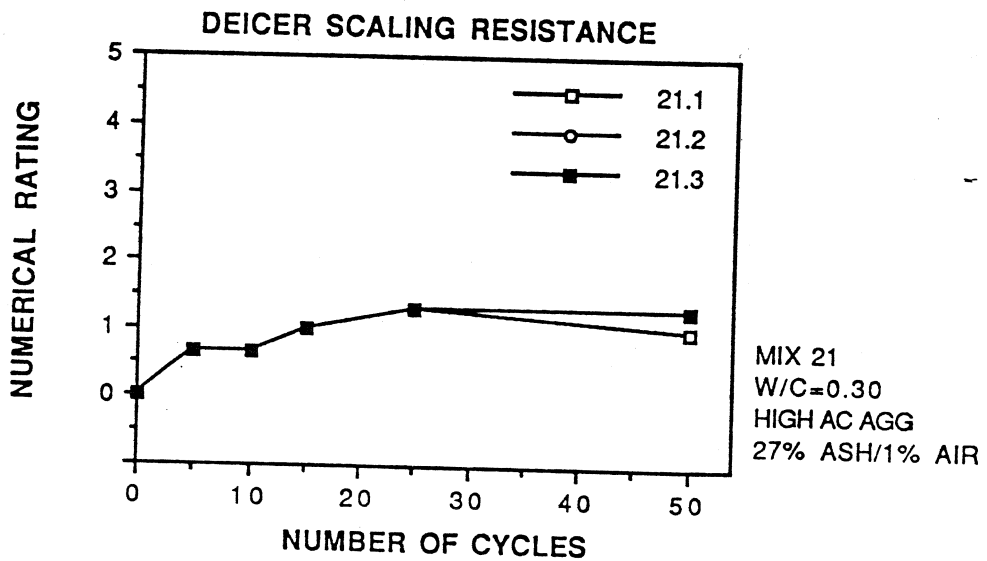
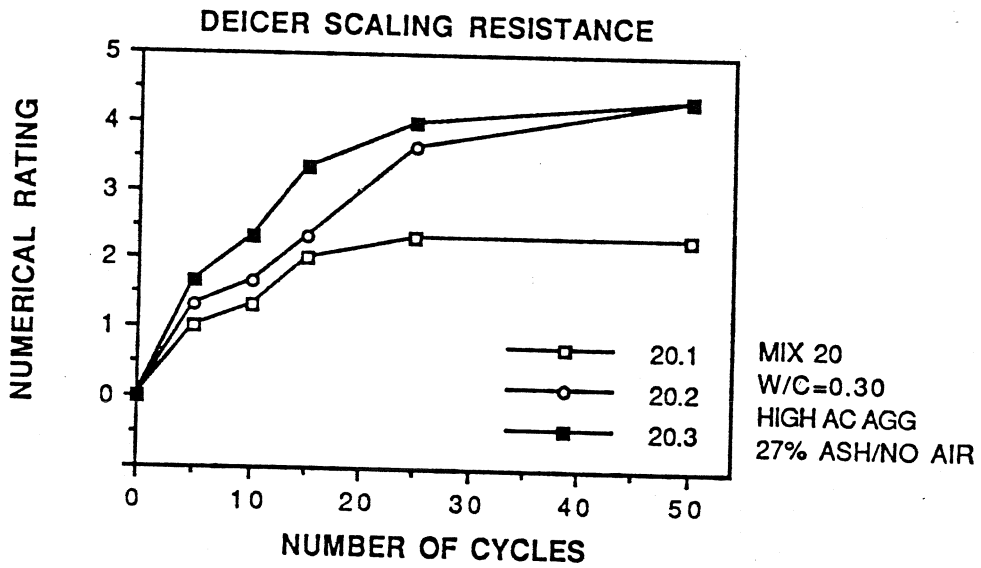


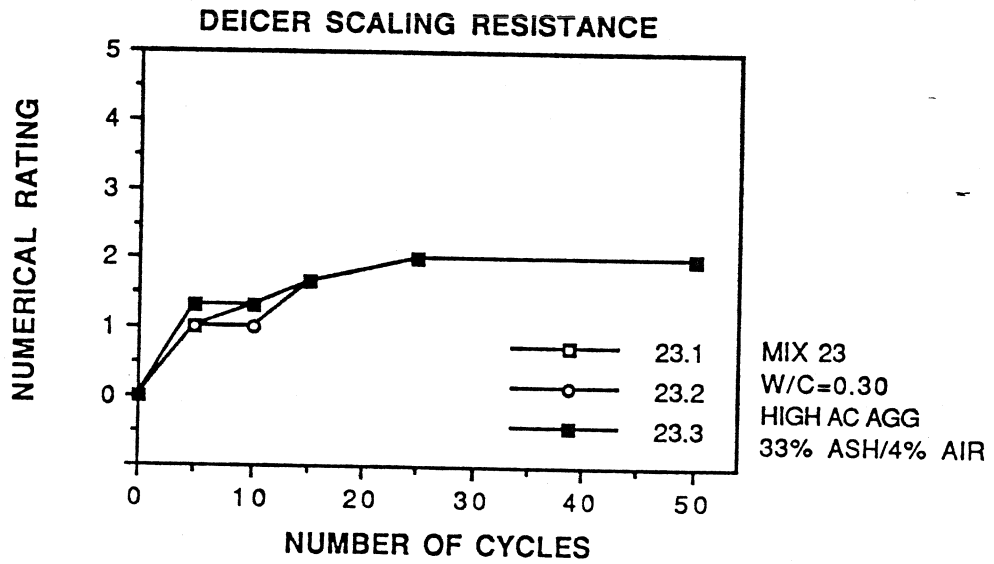
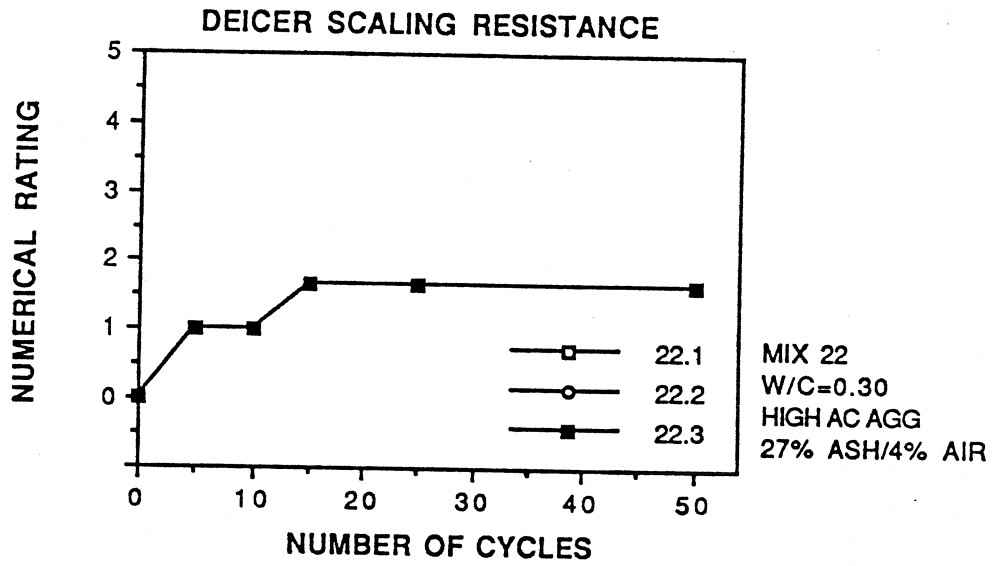


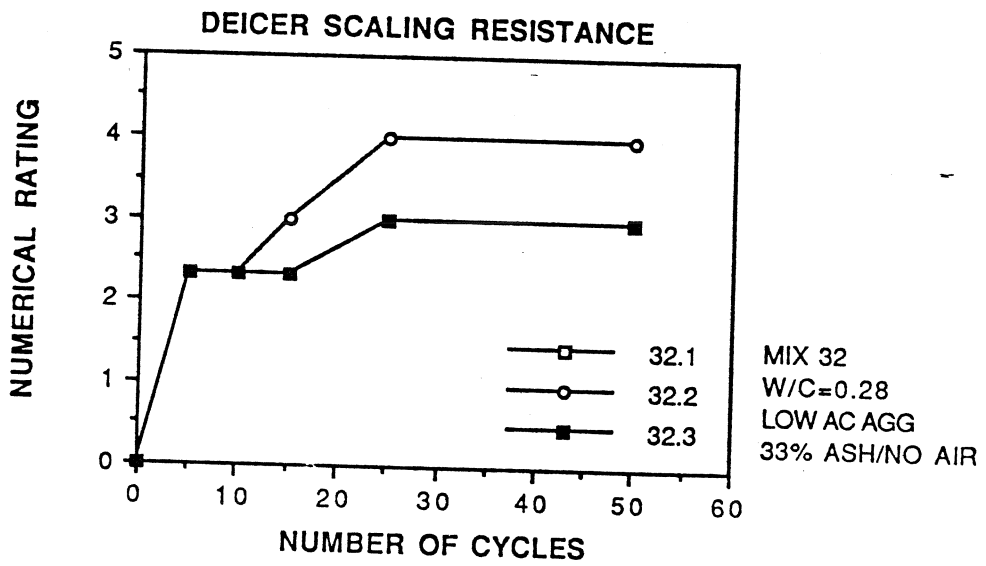
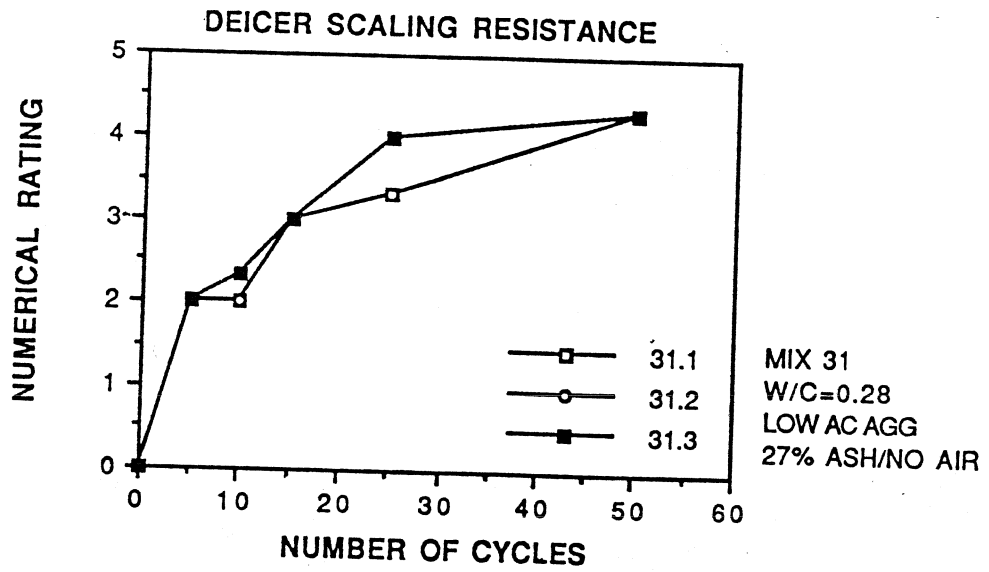


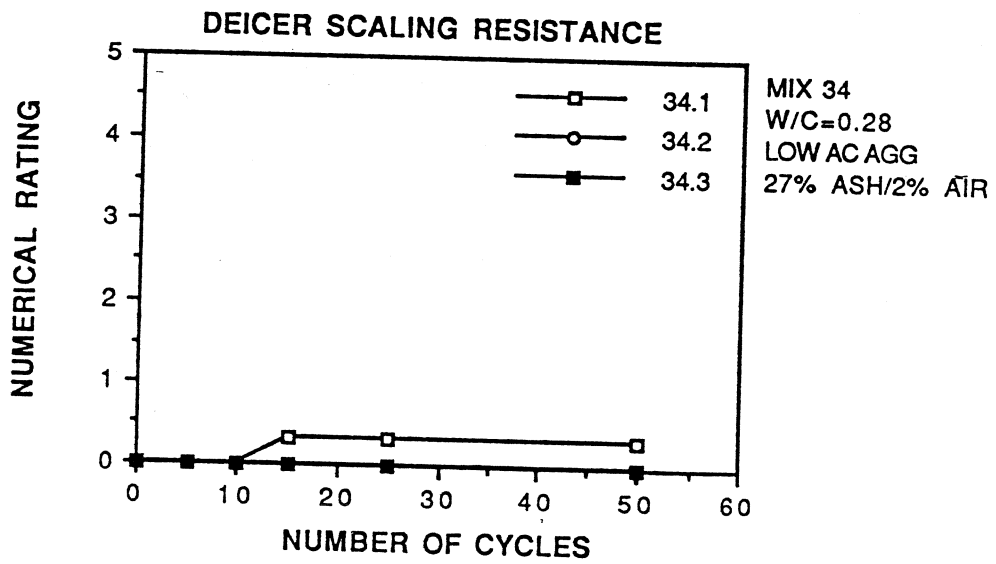
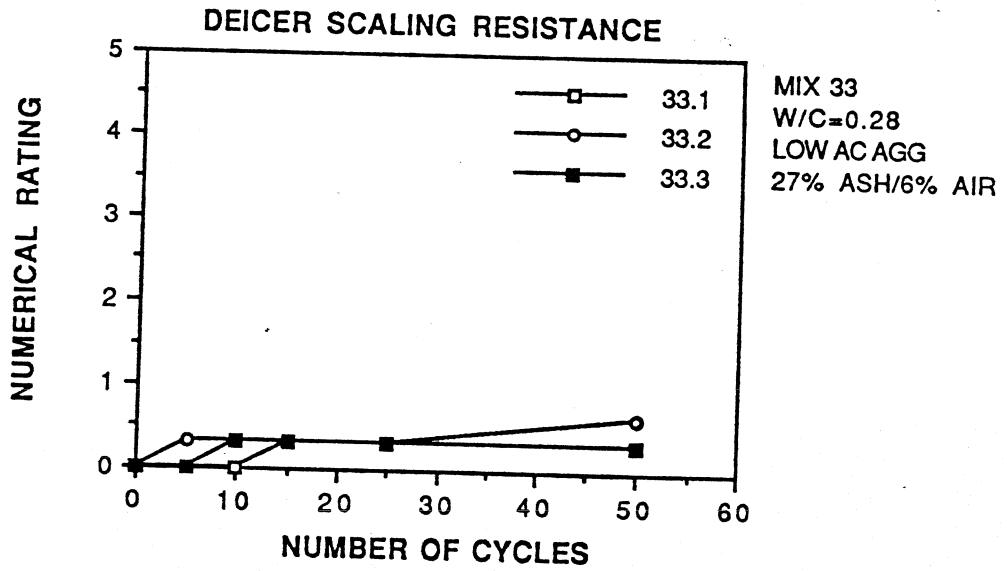


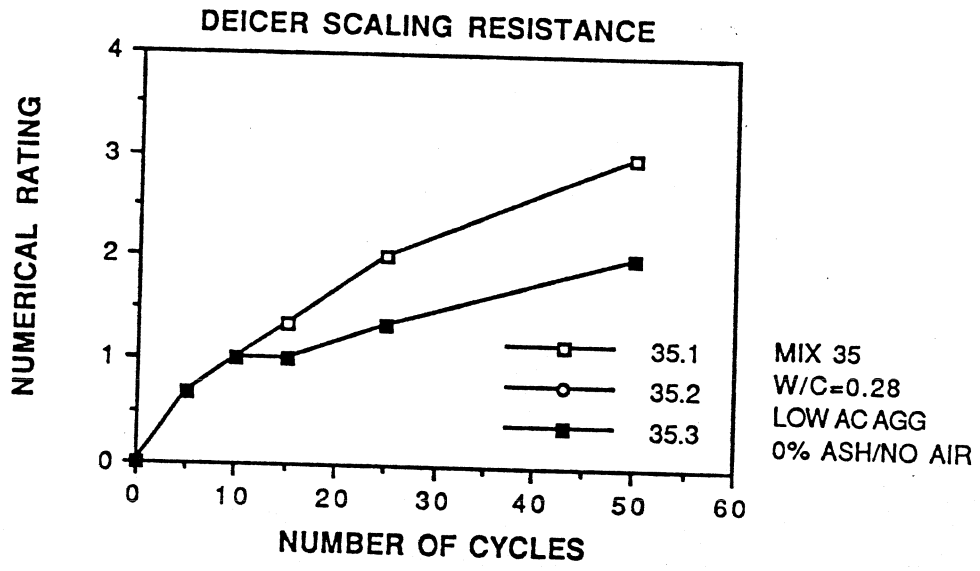


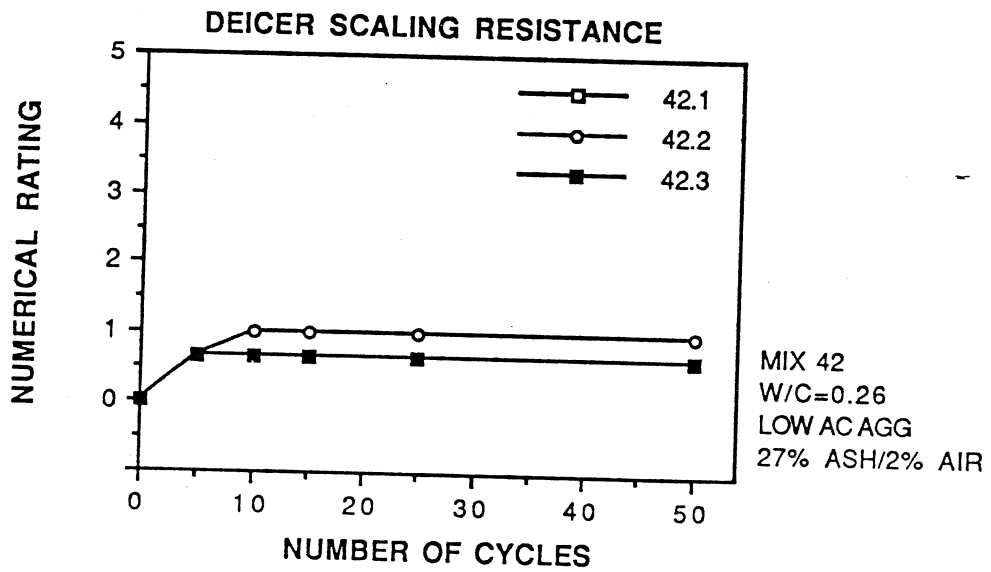
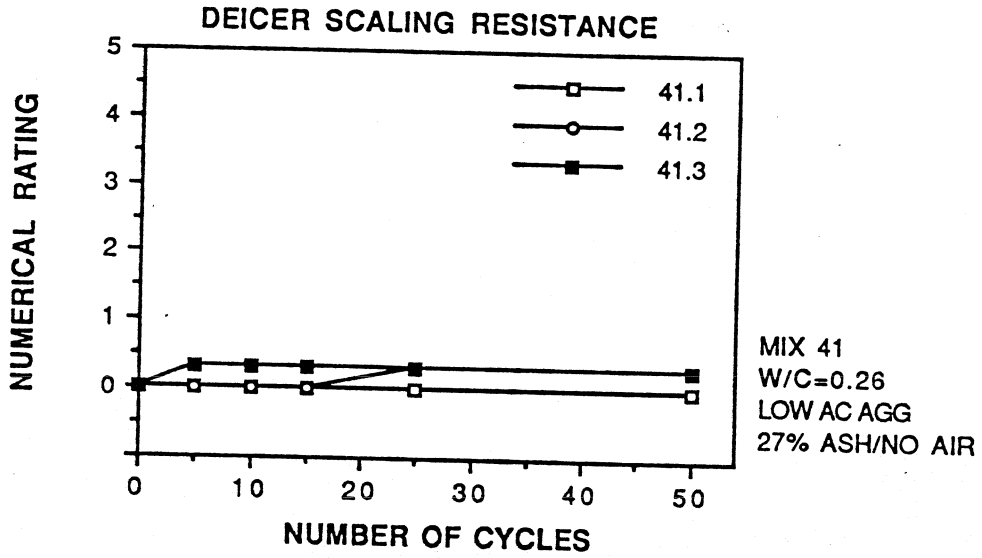


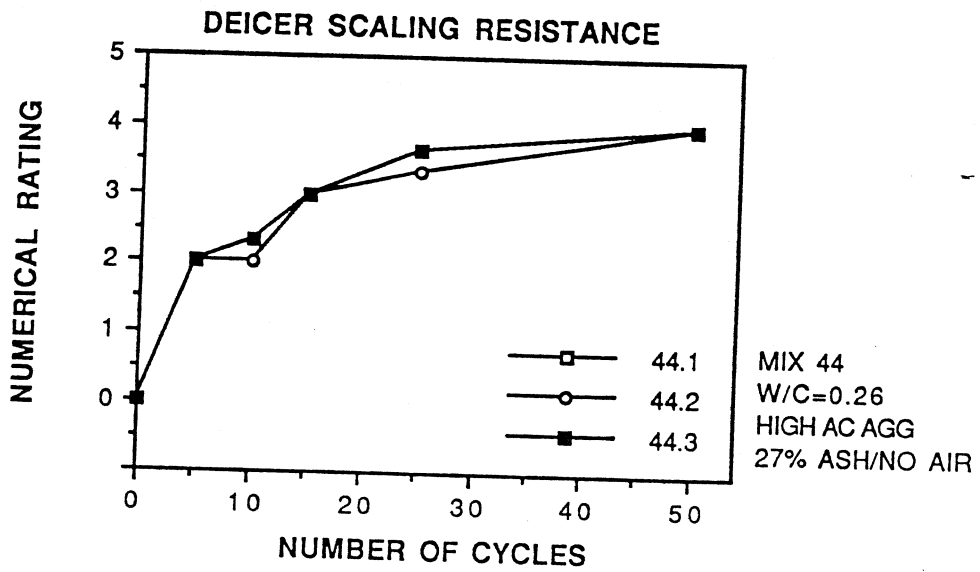
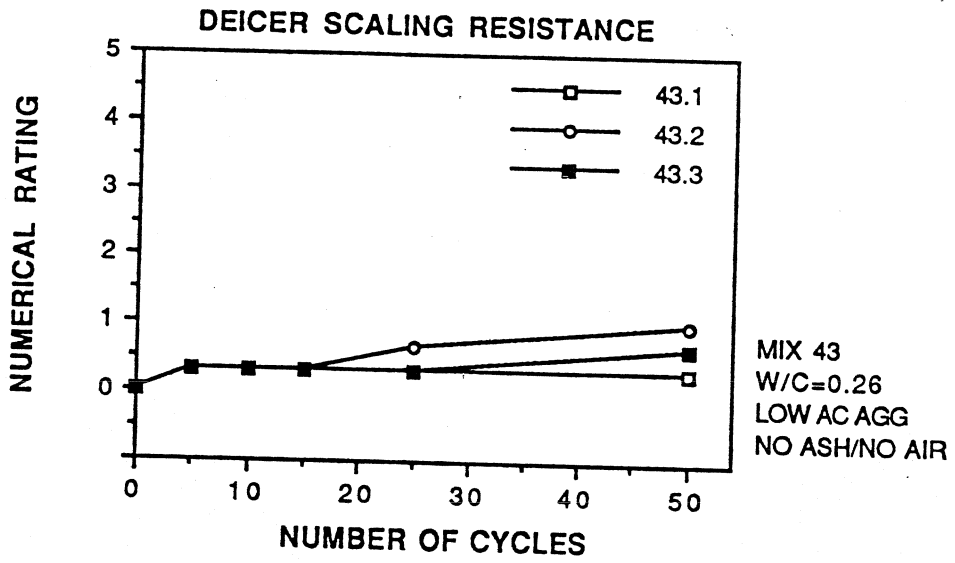


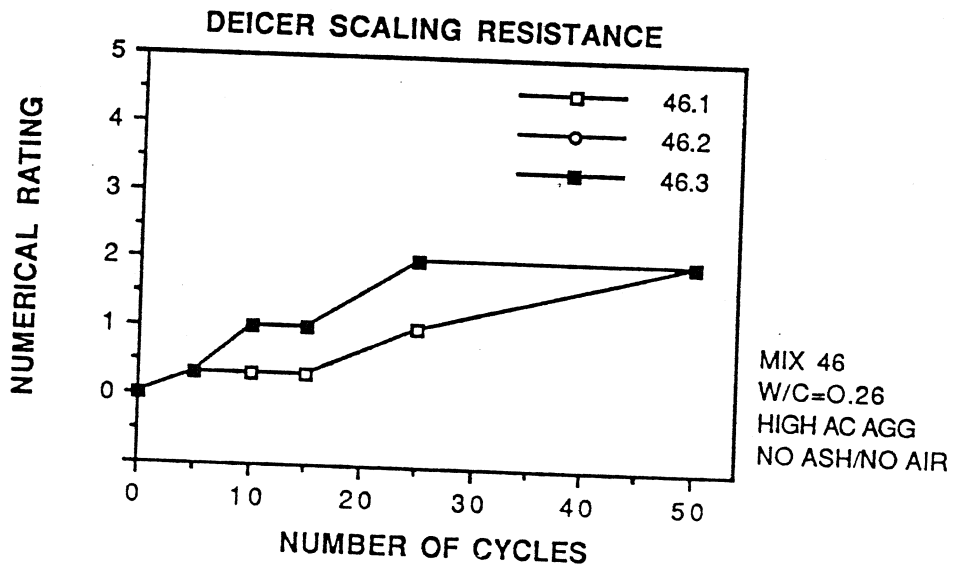
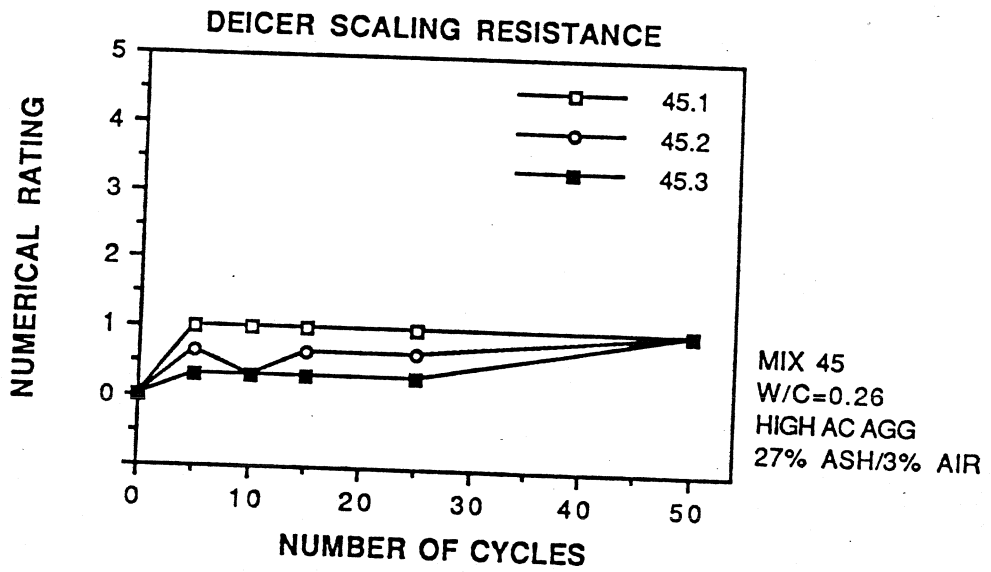


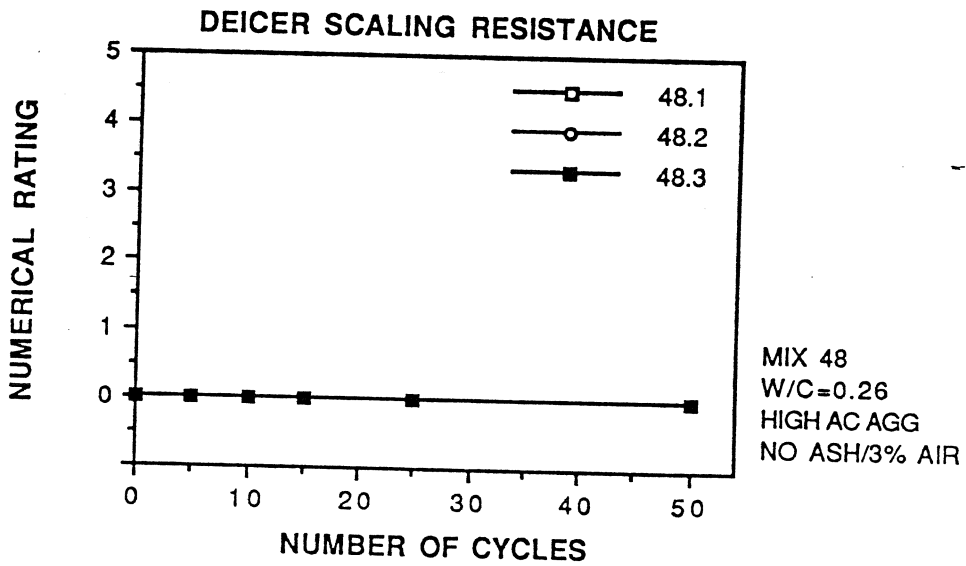
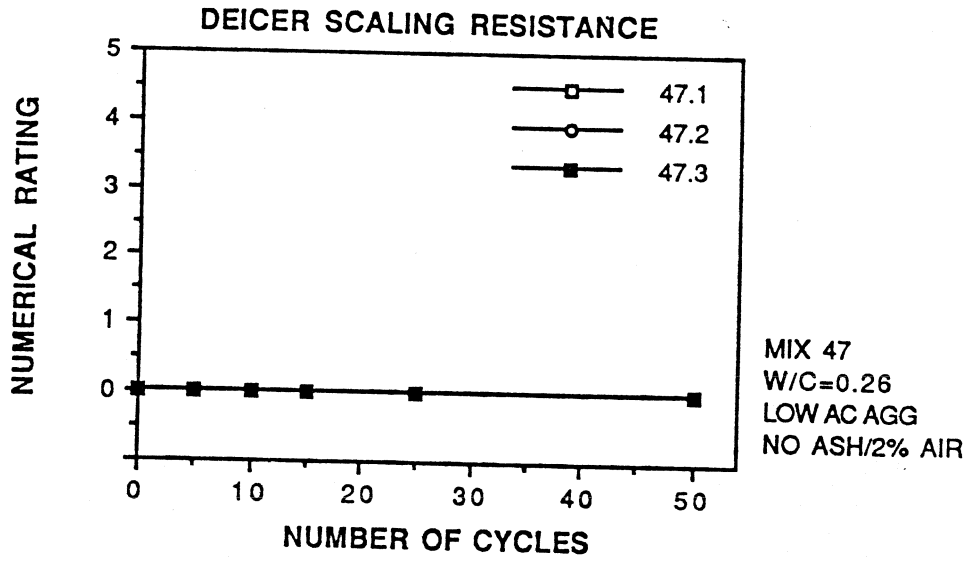


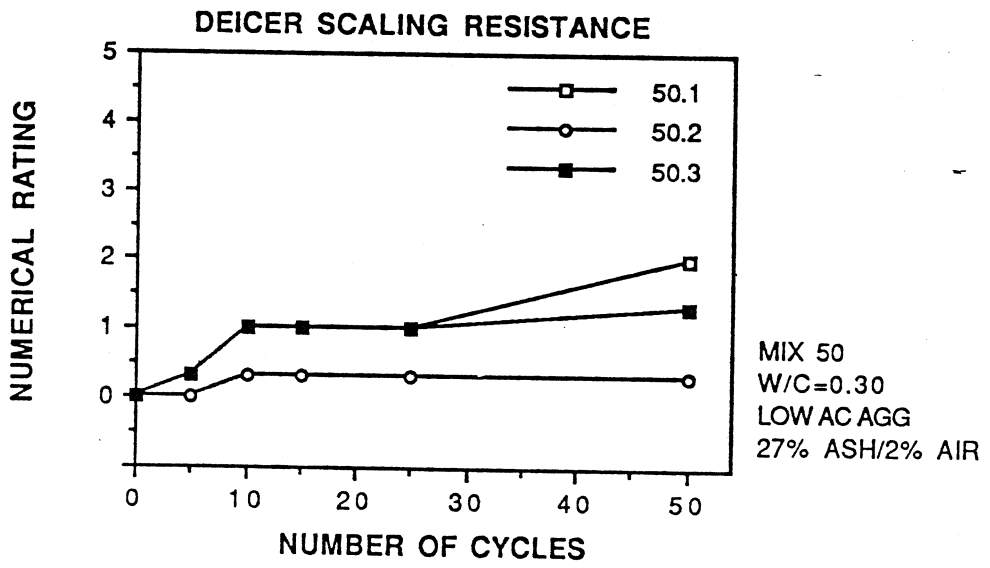
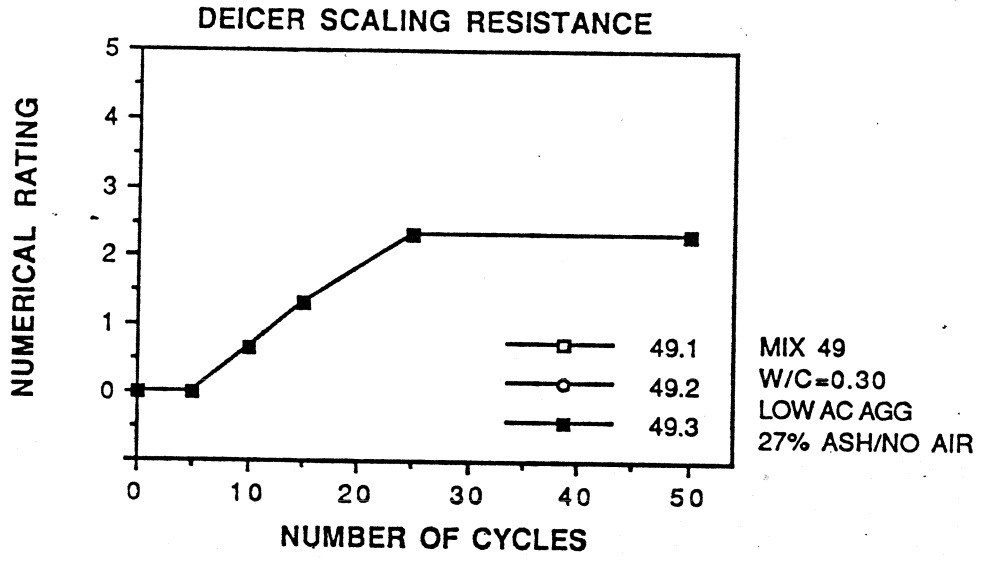


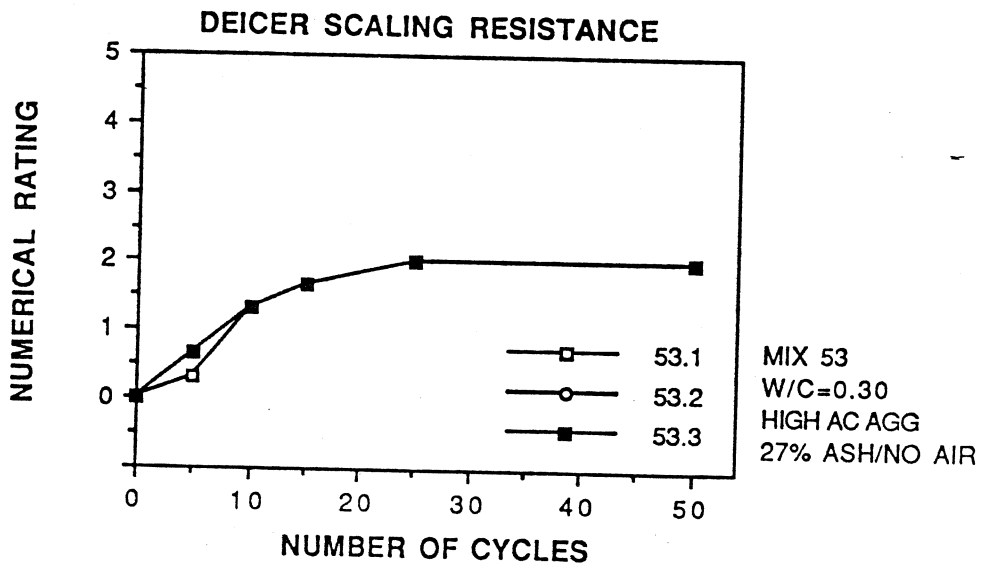
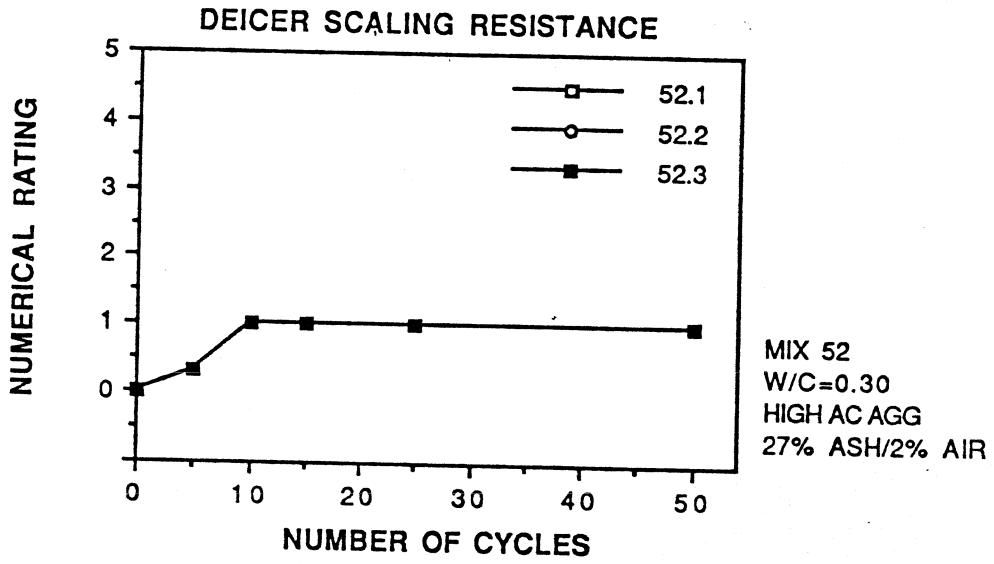


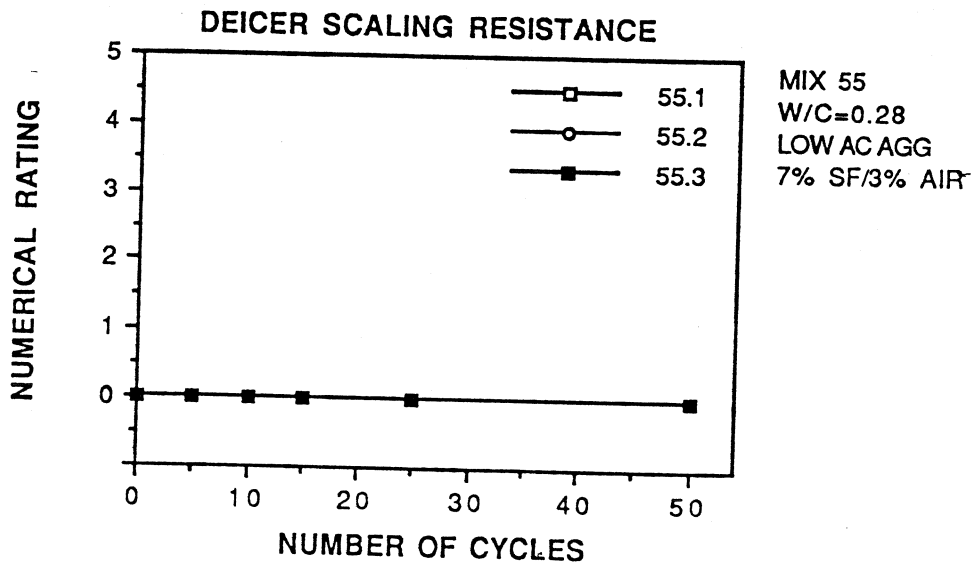
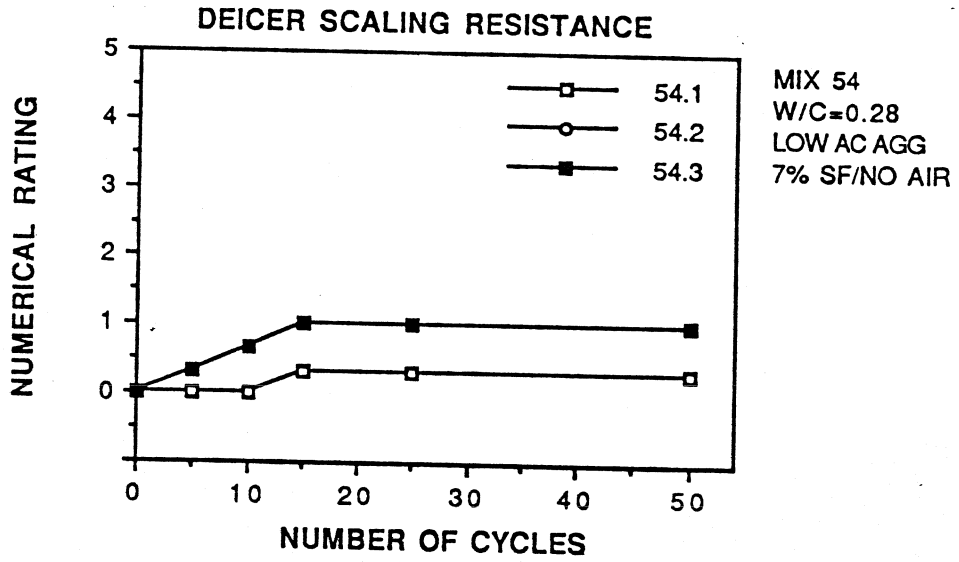


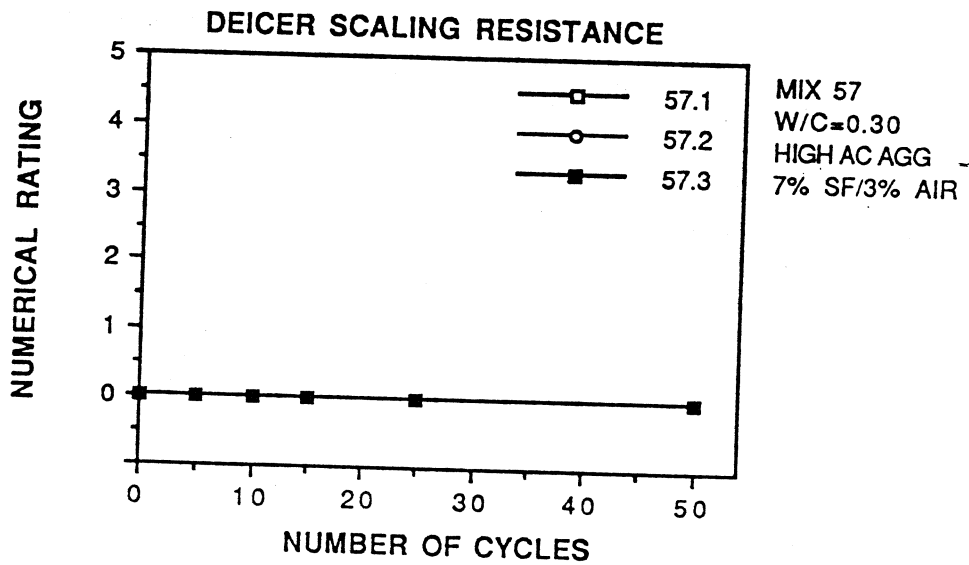
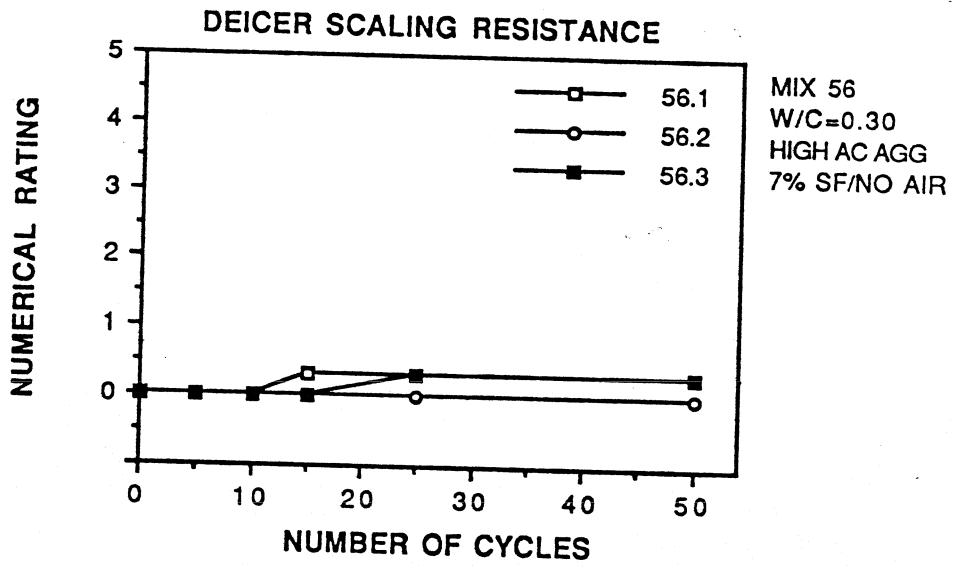


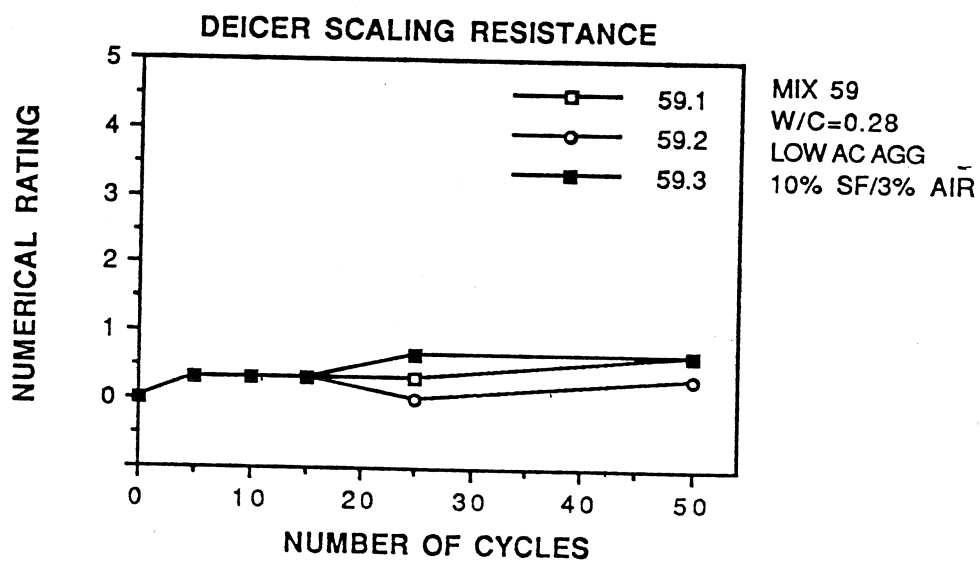
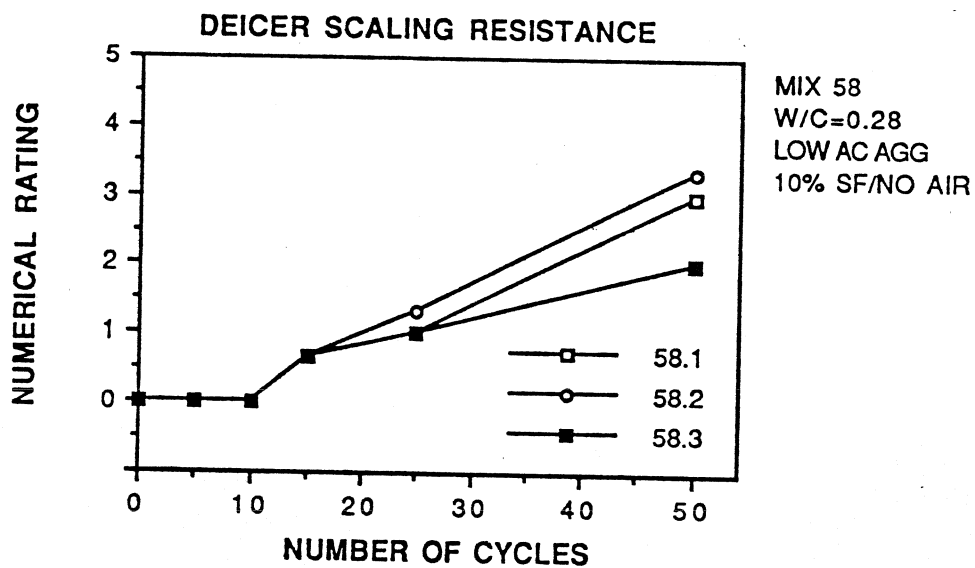


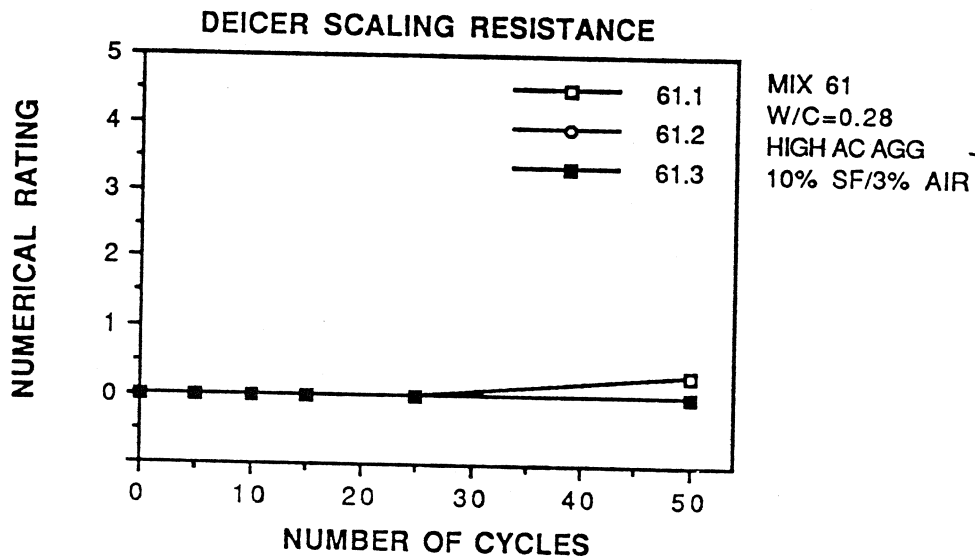
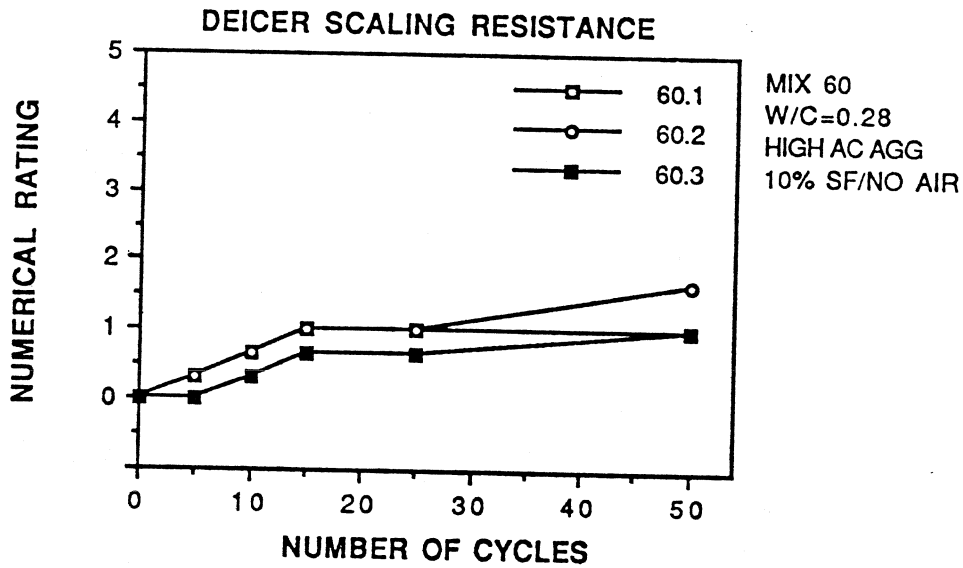


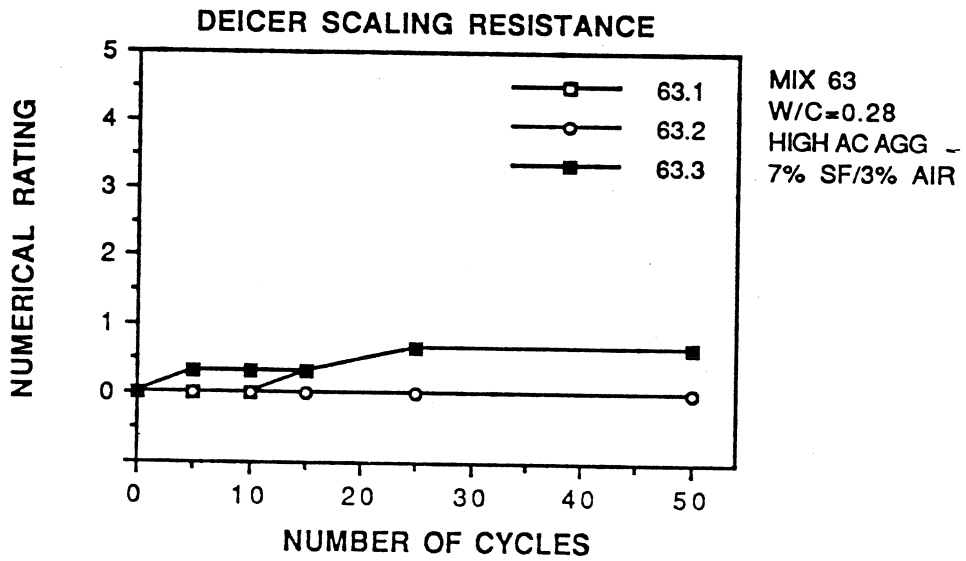
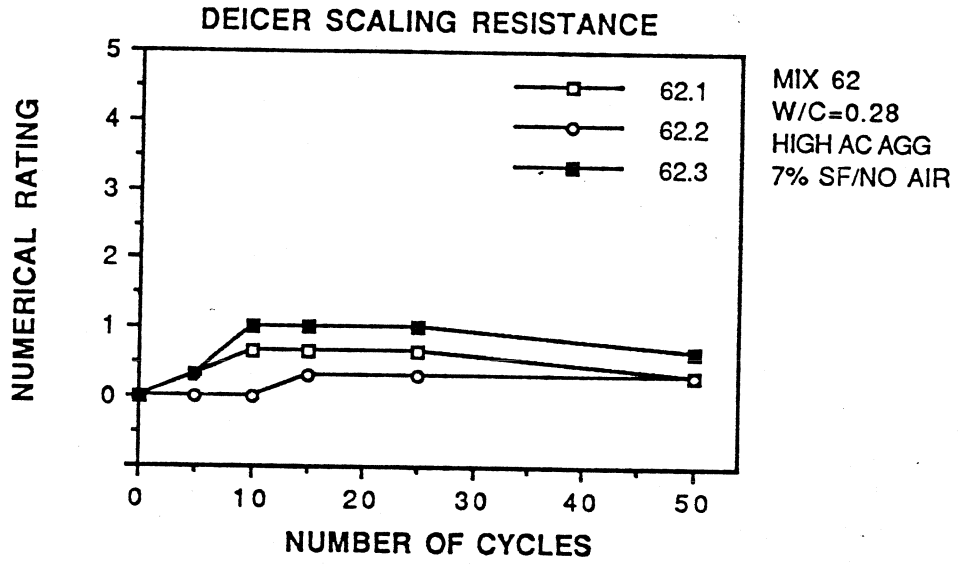


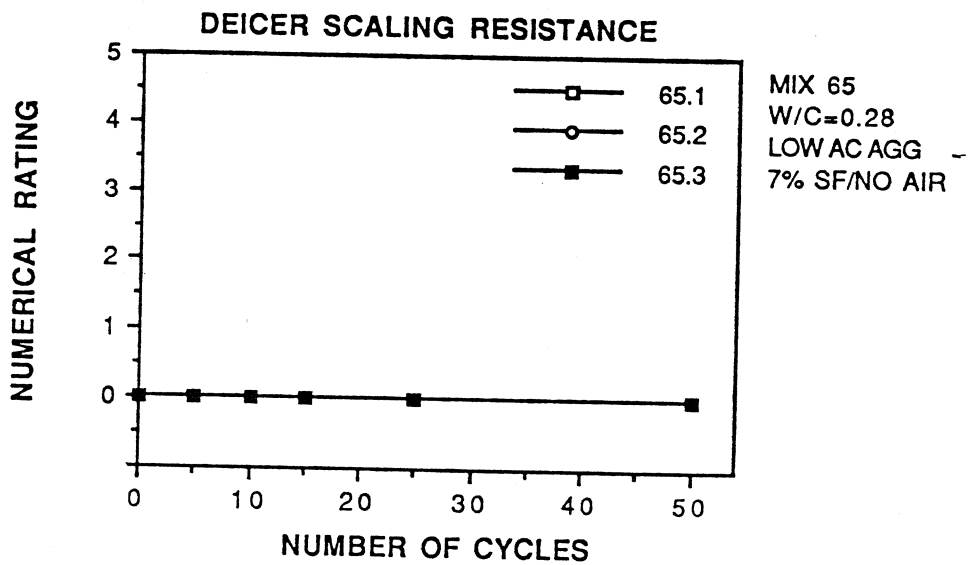
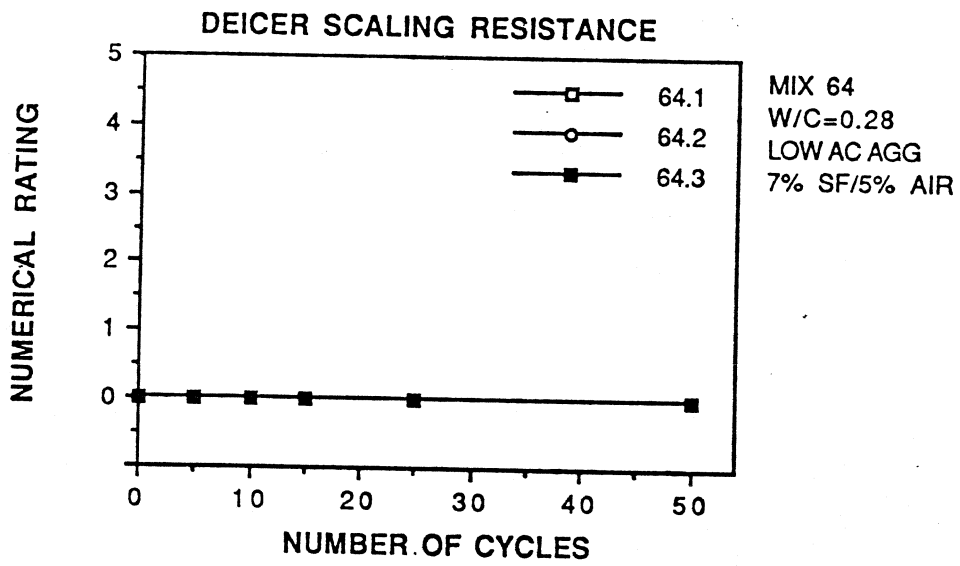


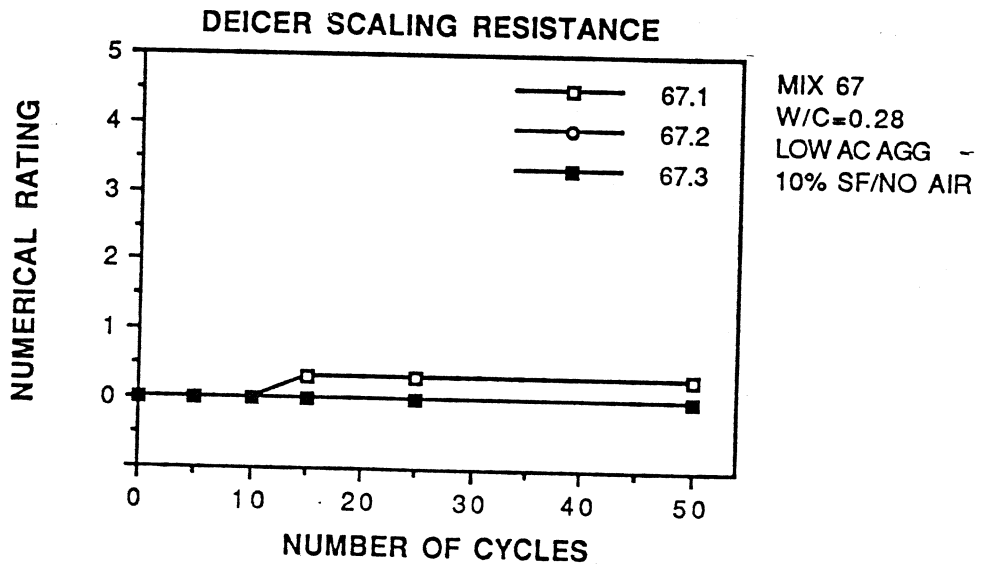
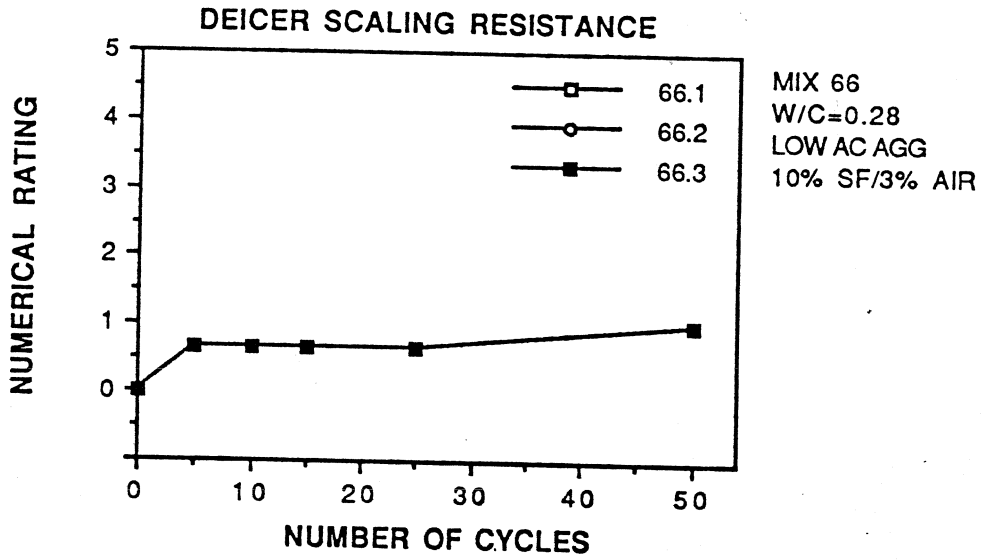


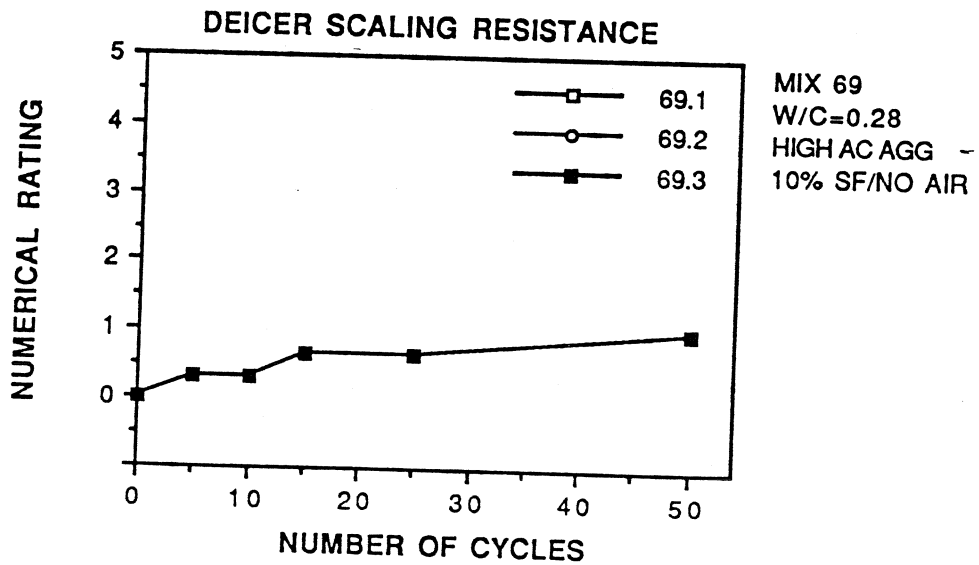
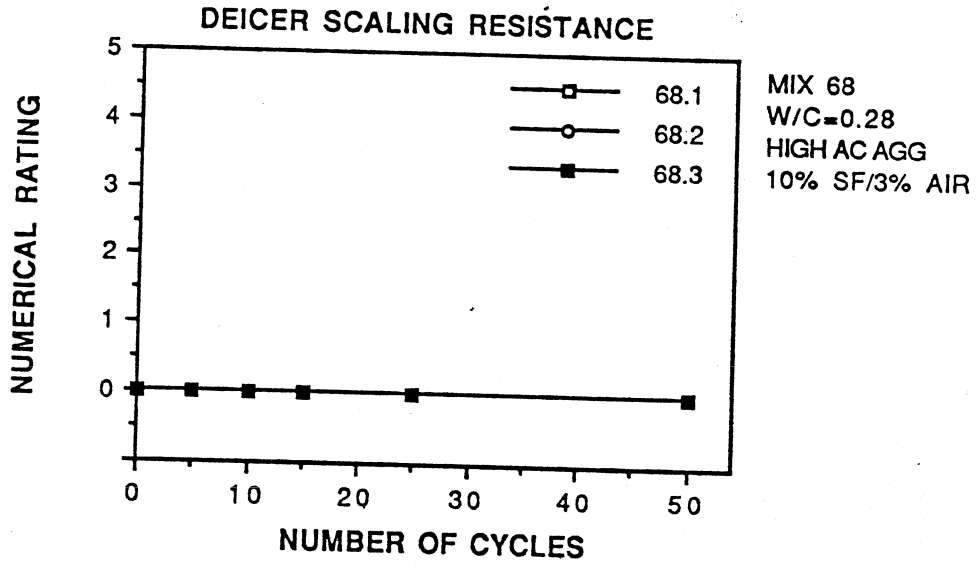




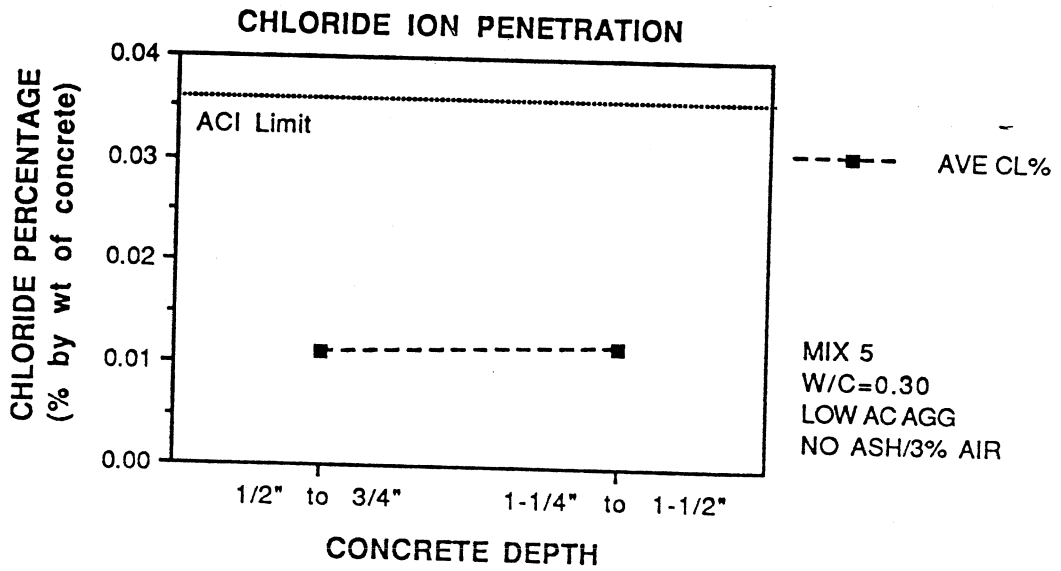
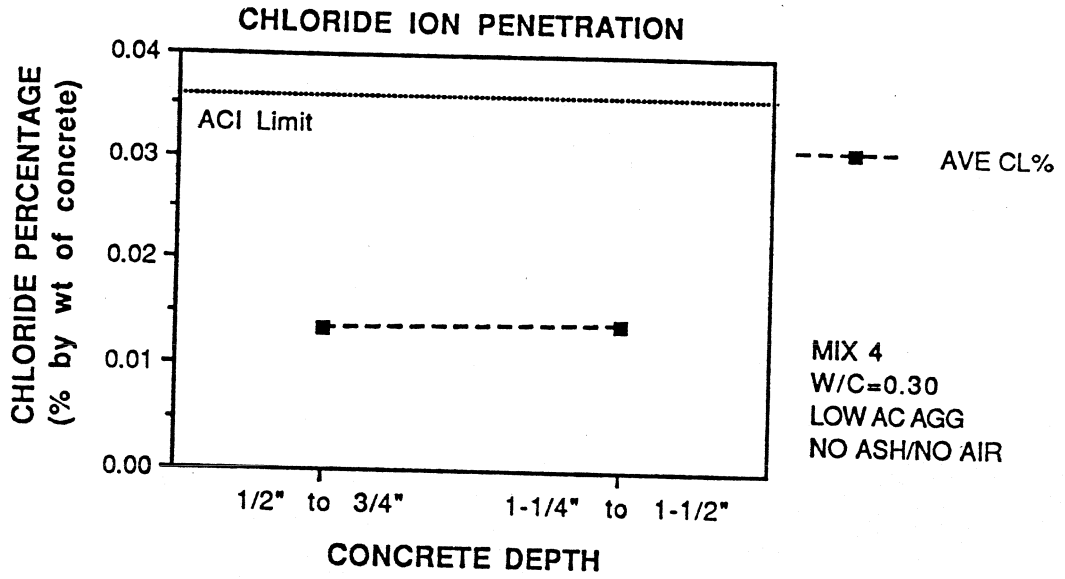


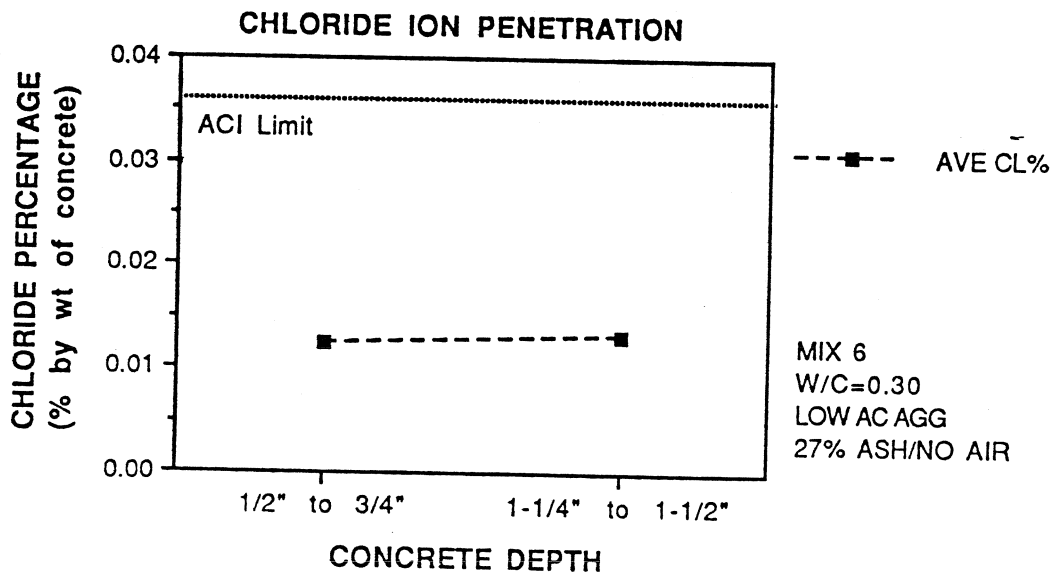
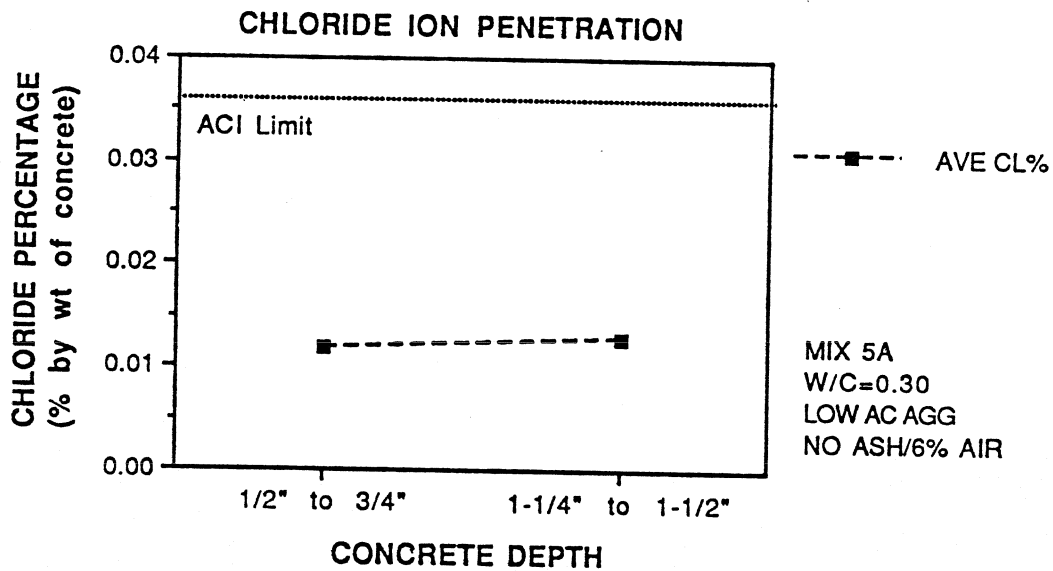


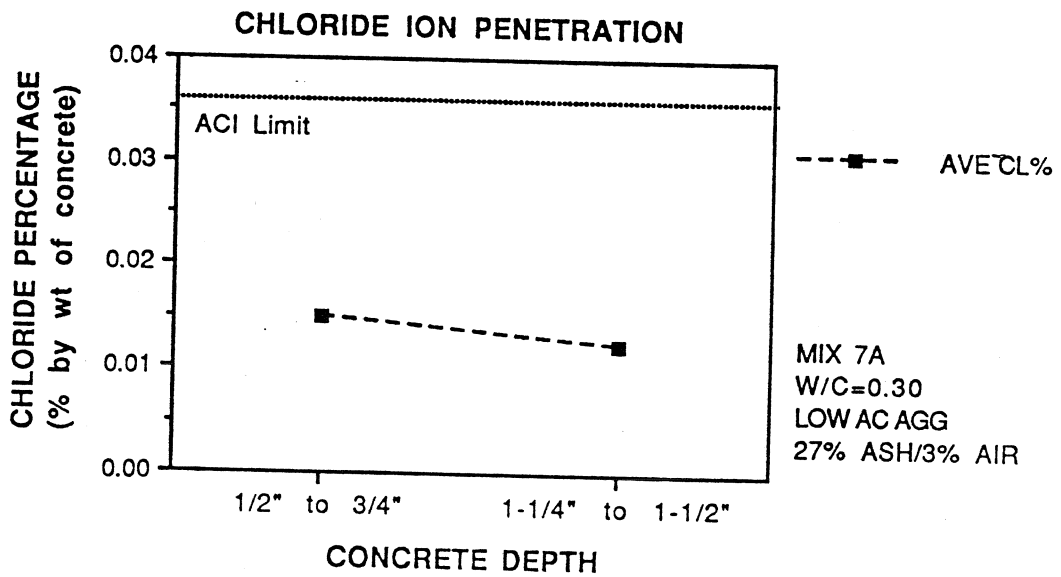
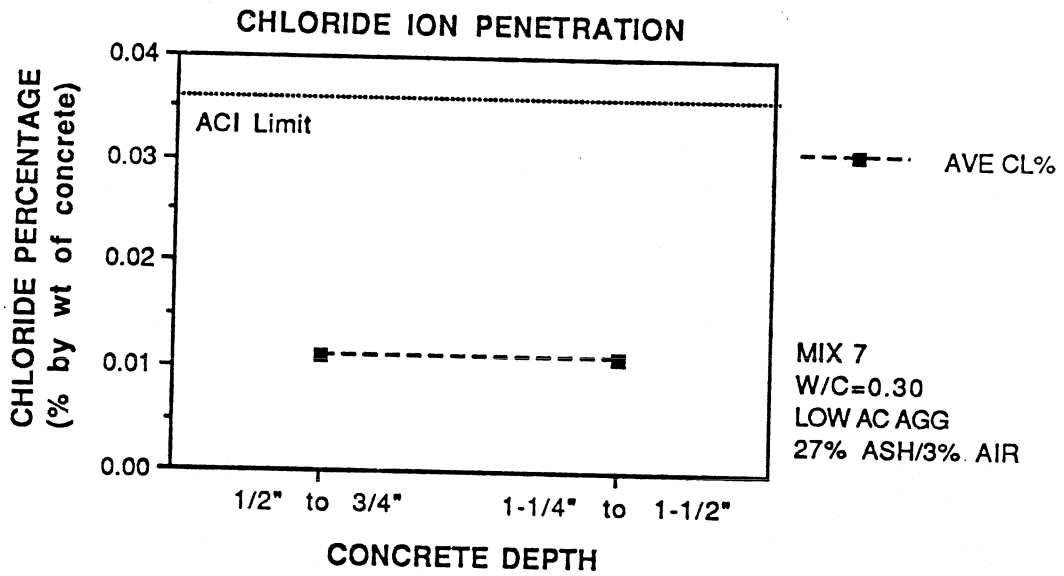


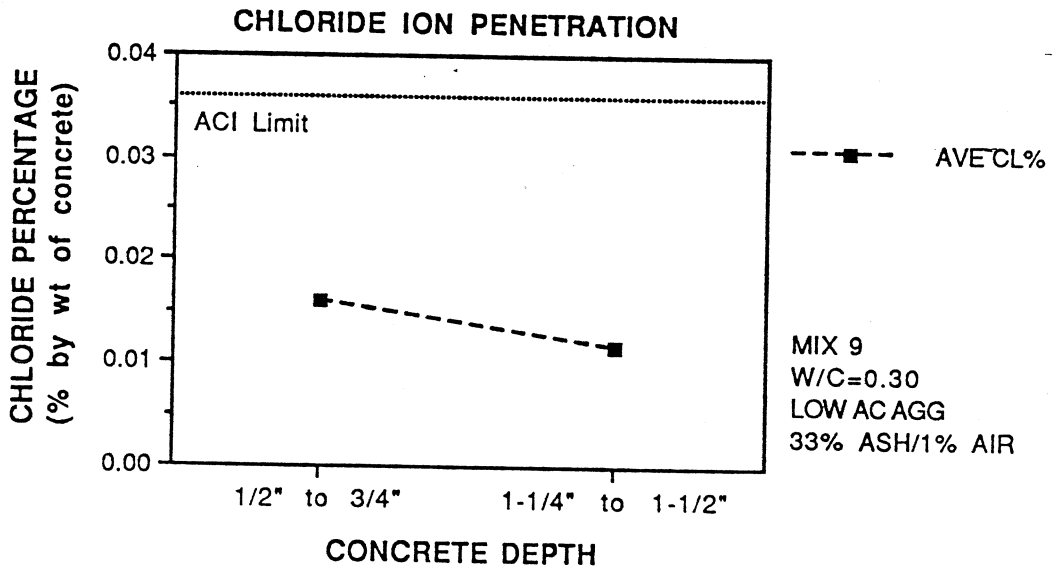
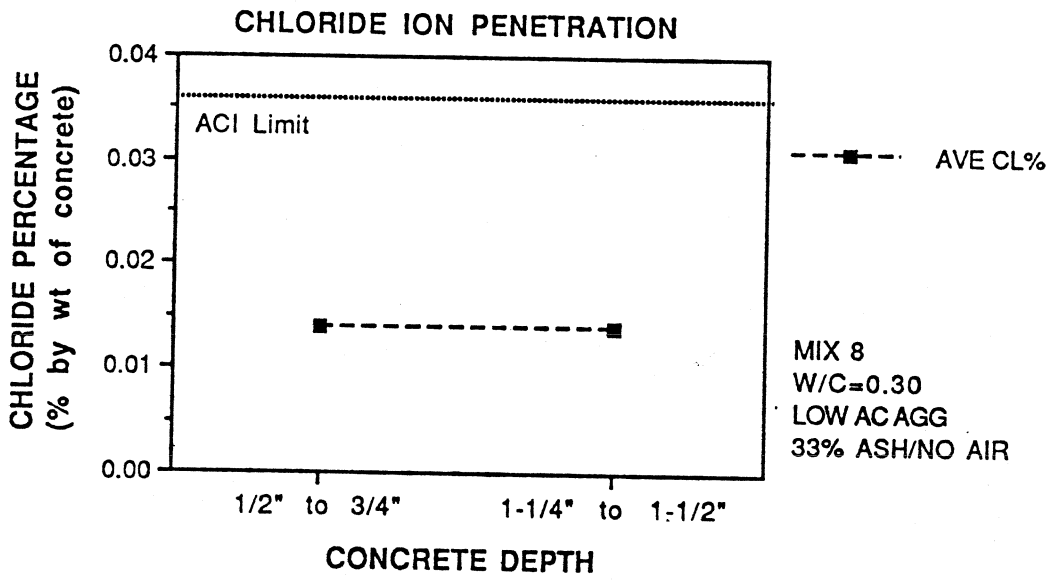


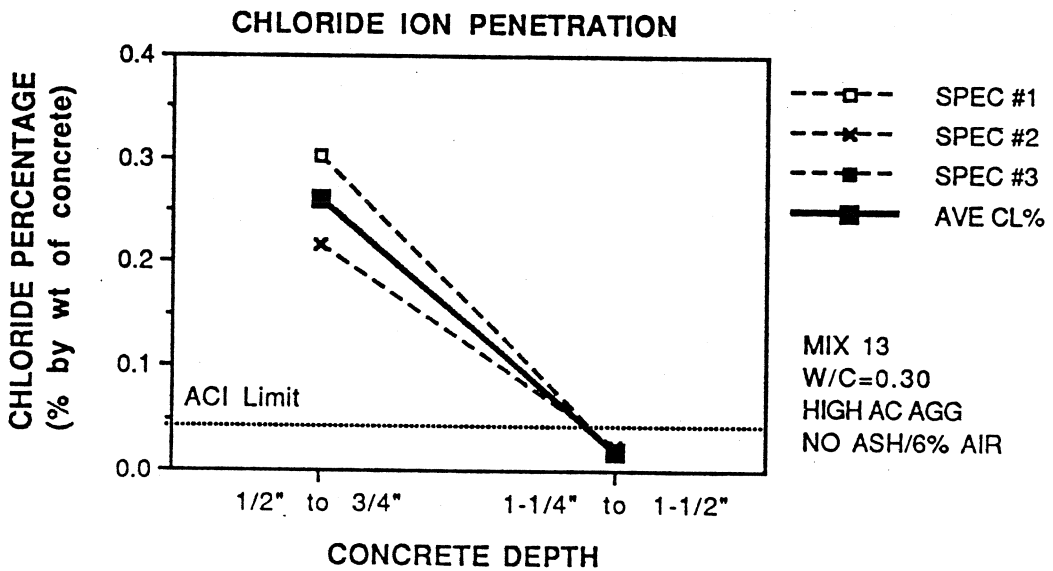
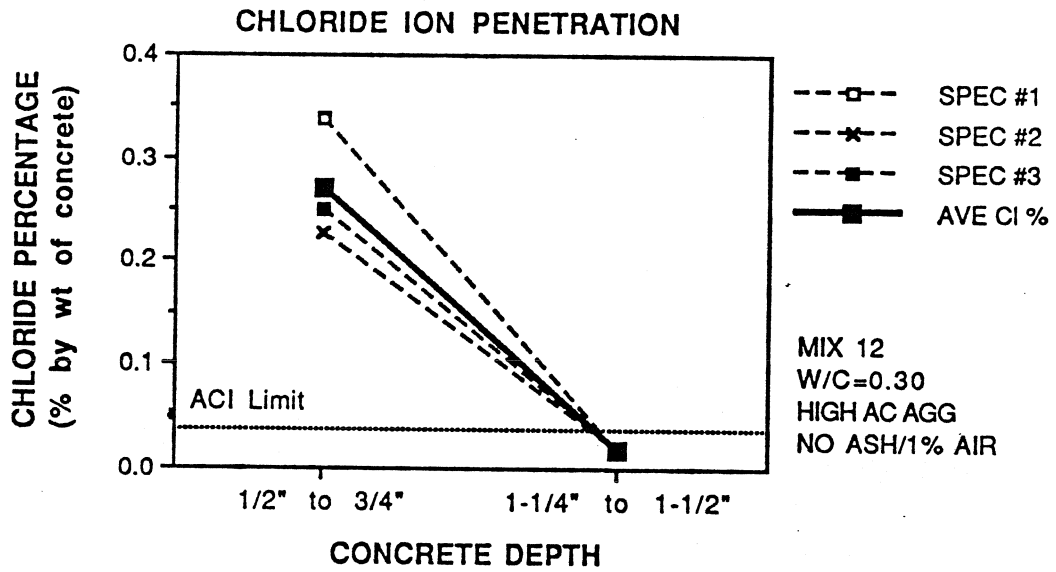
APPENDIX F
CHLORIDE ION PENETRATION DATA

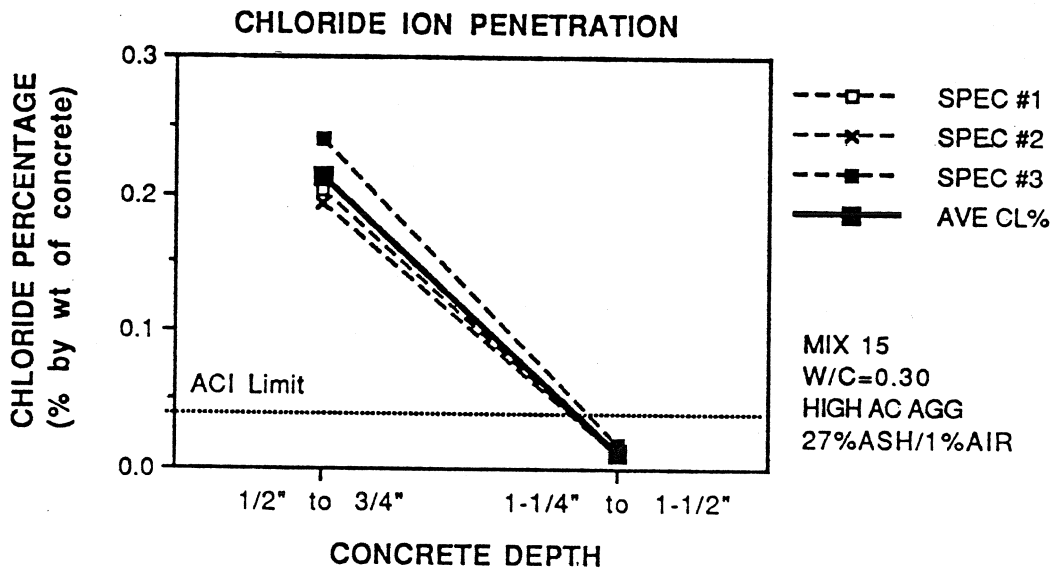
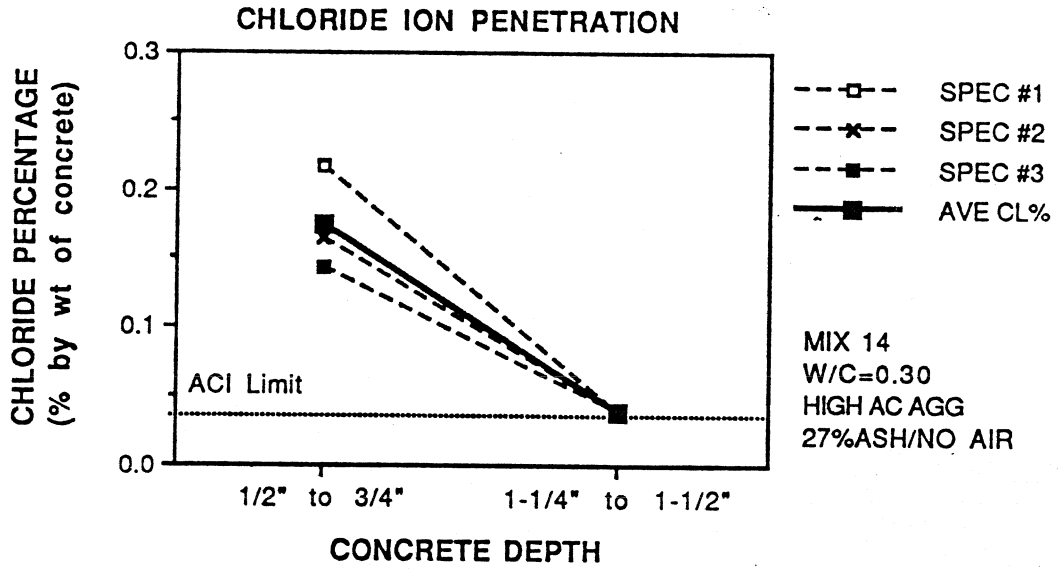


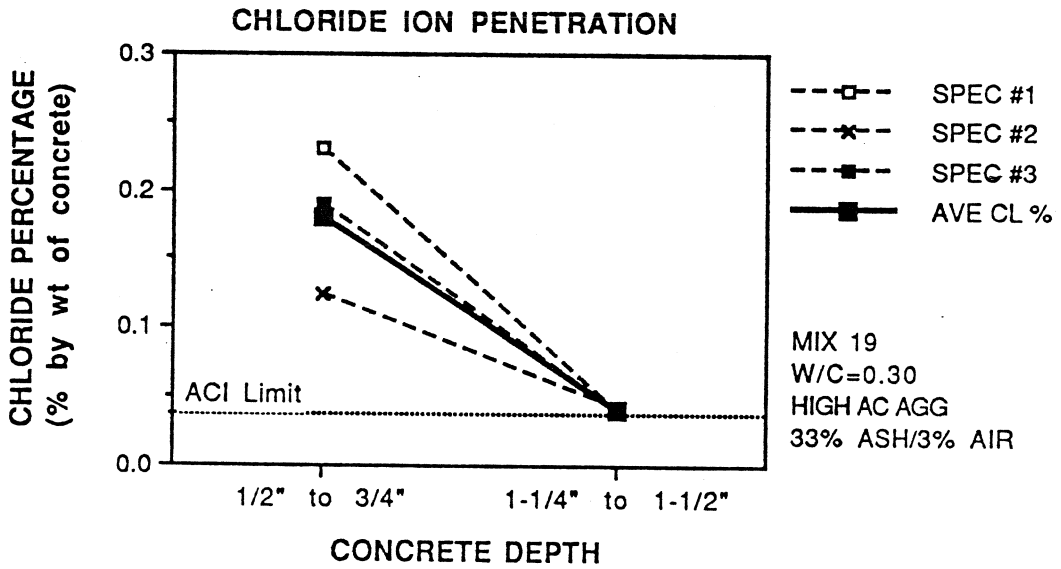
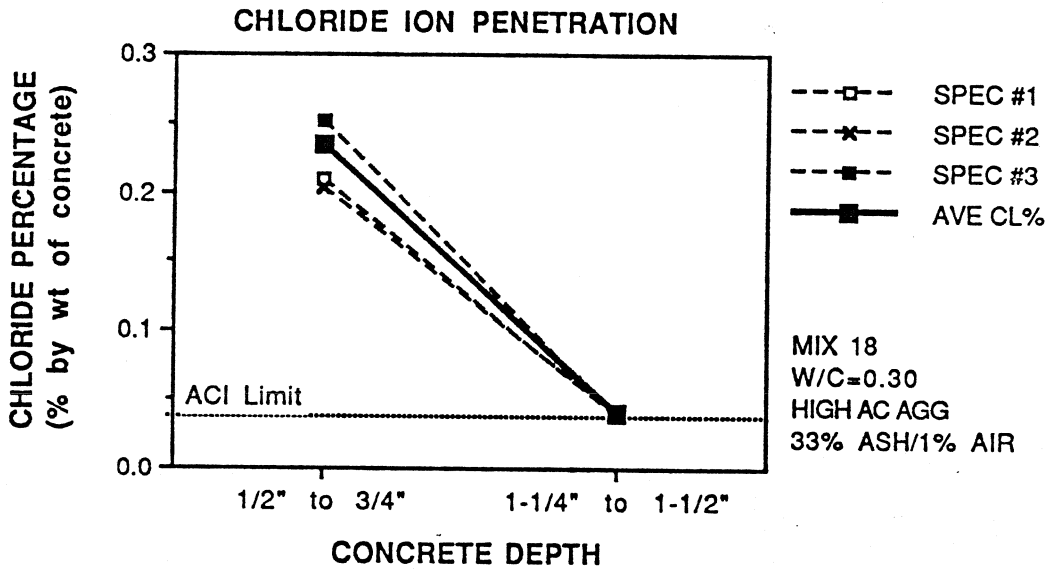


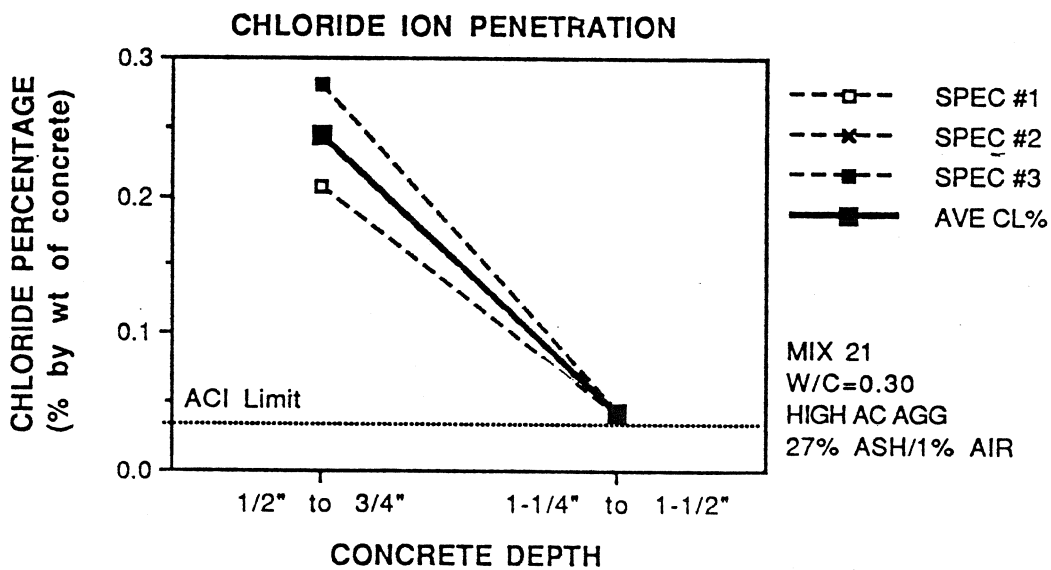
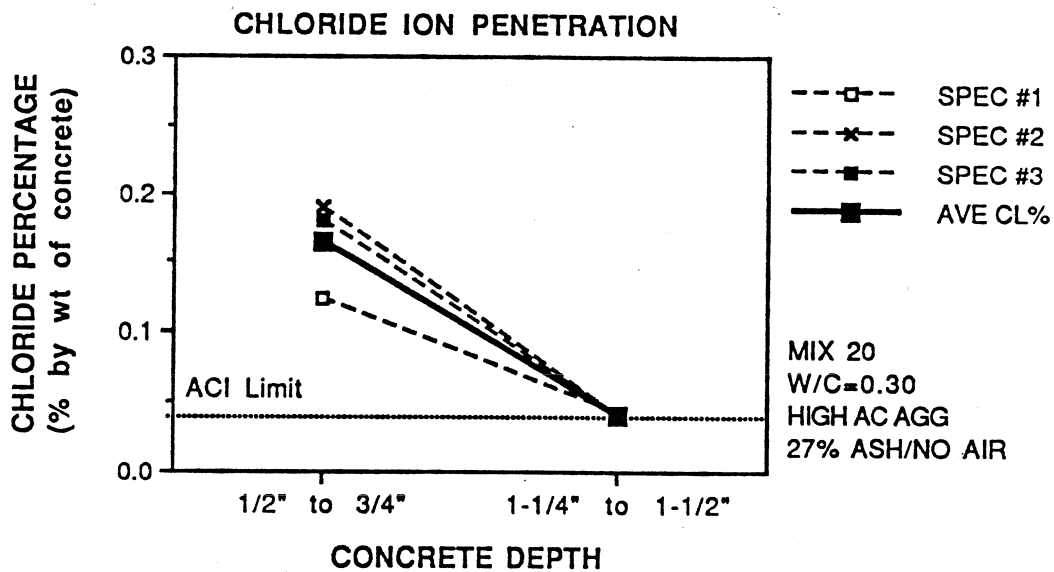


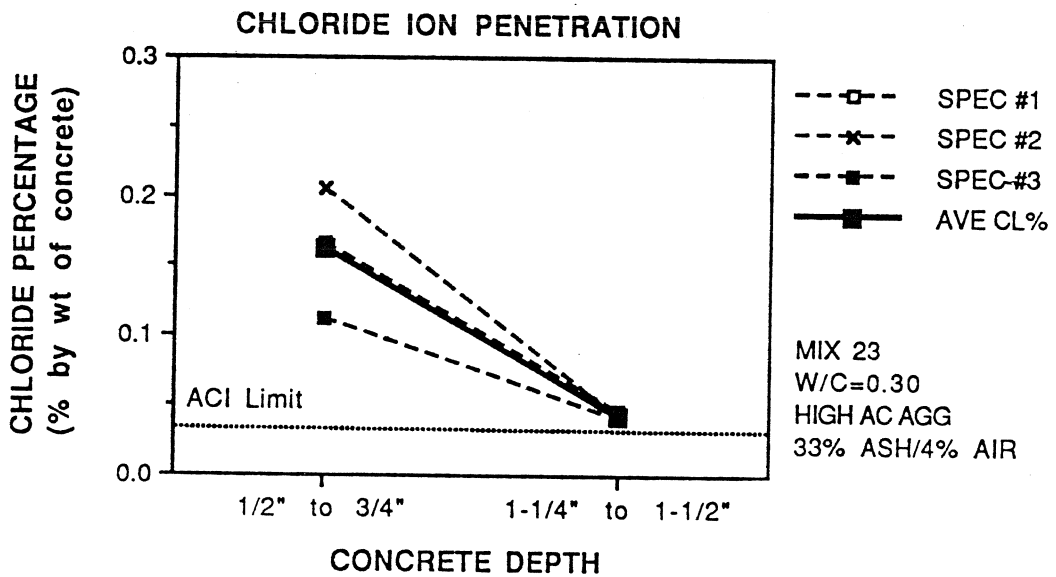
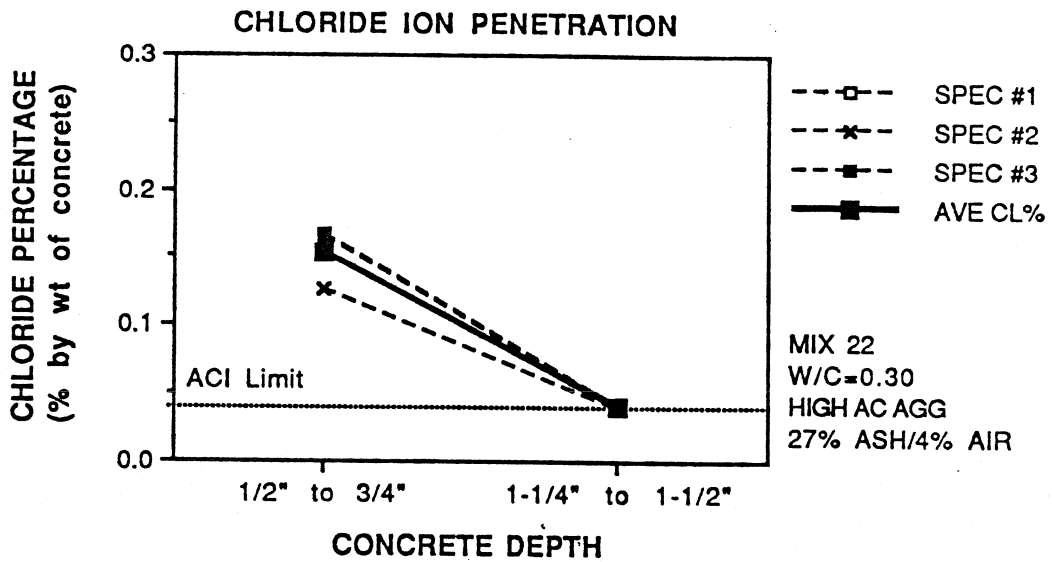


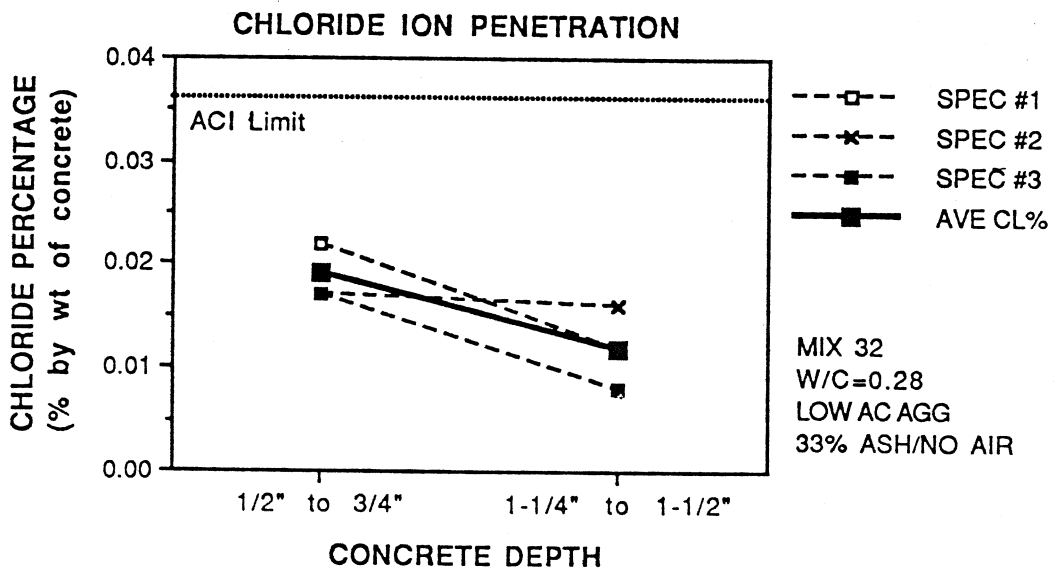
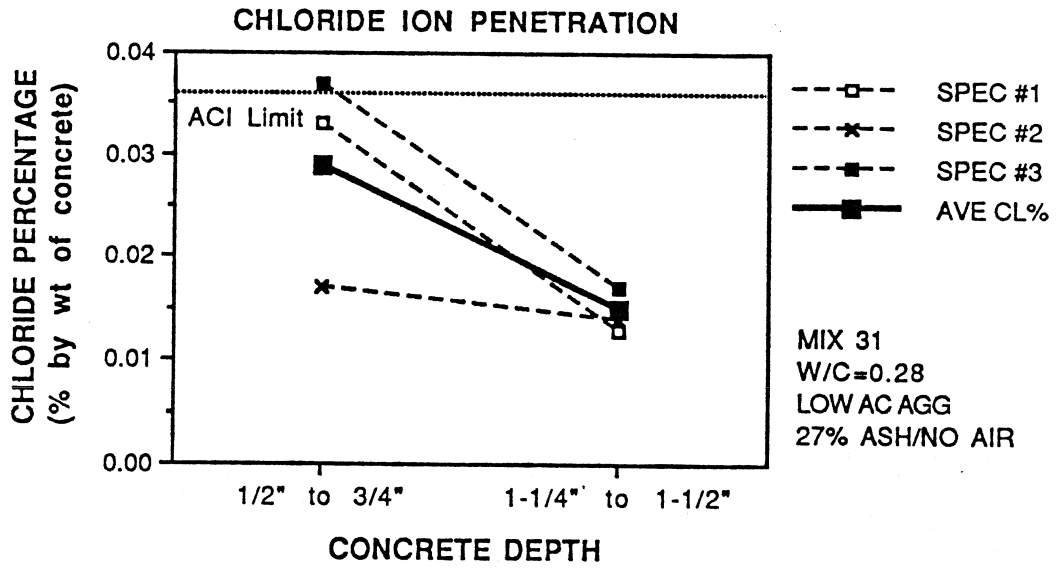


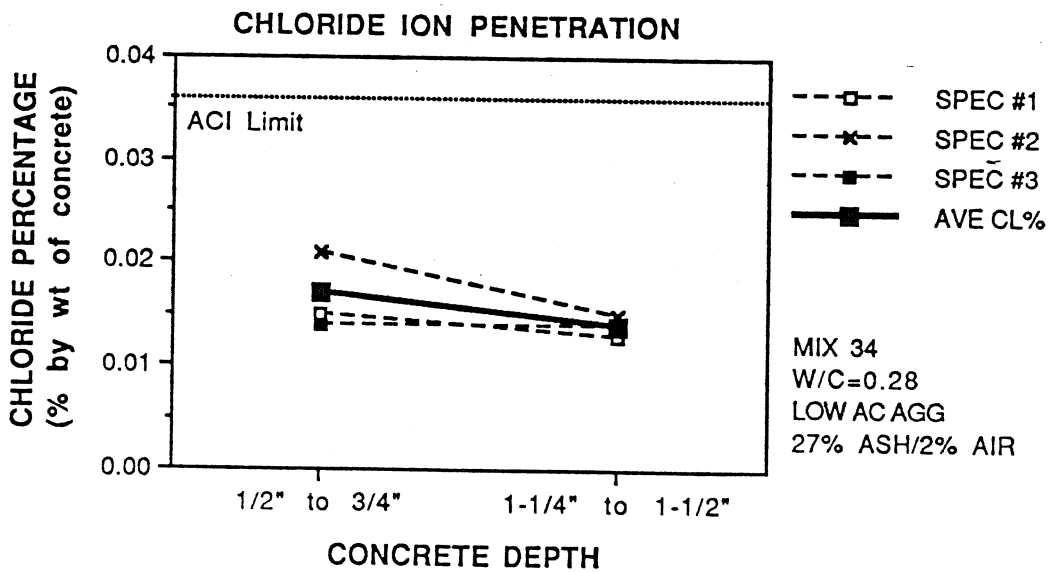
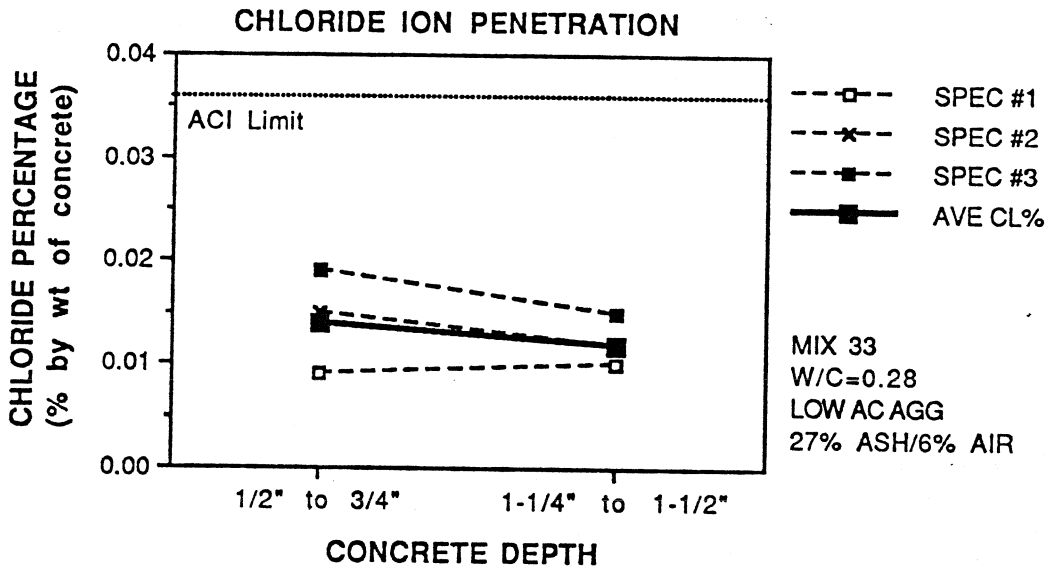


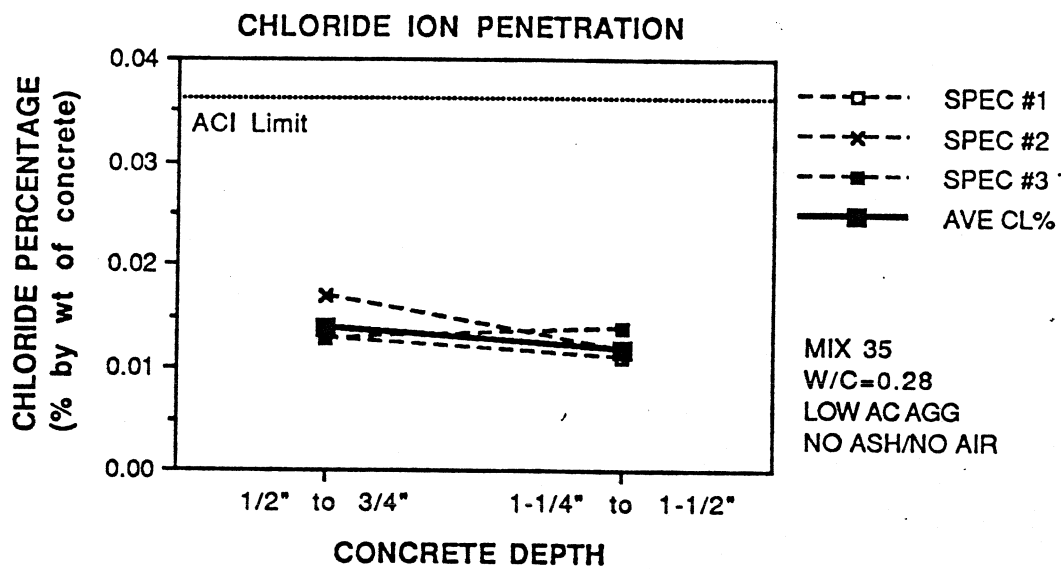


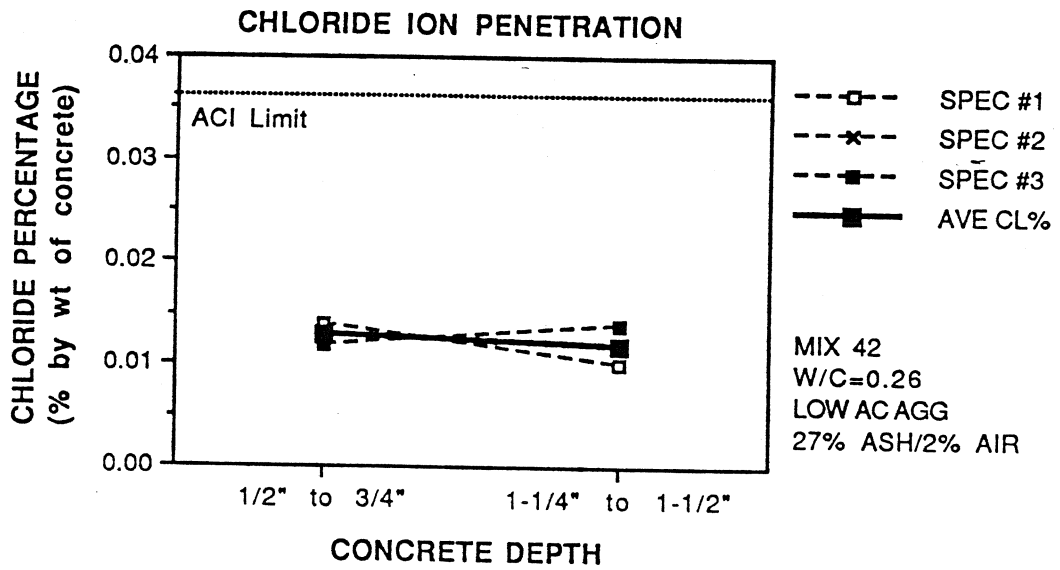
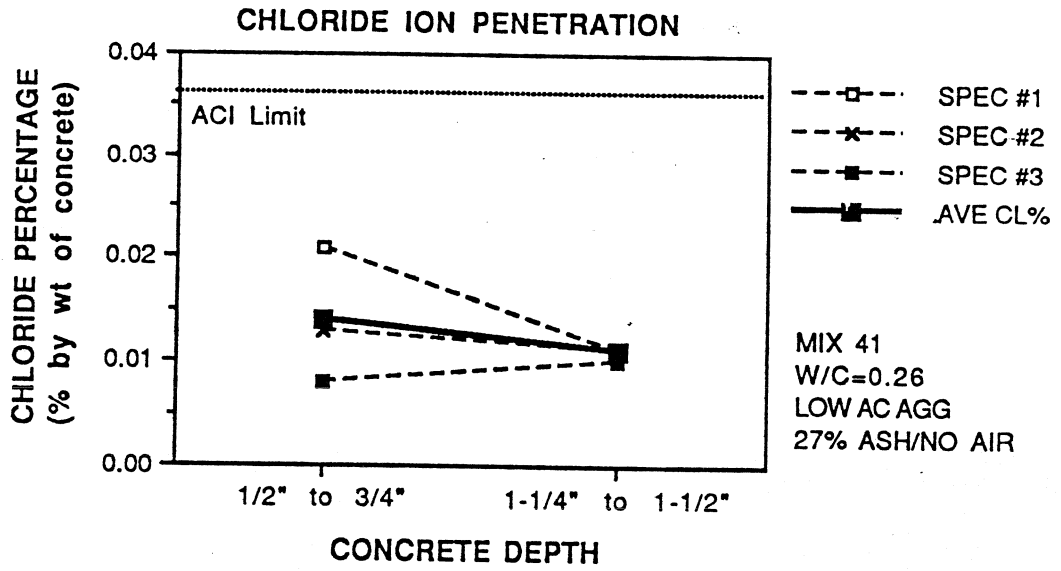


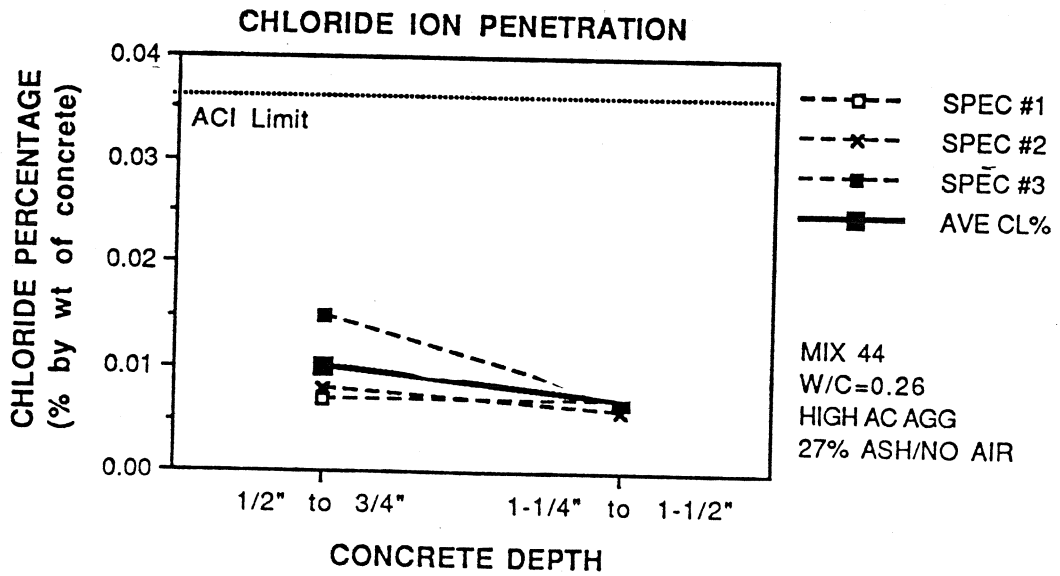
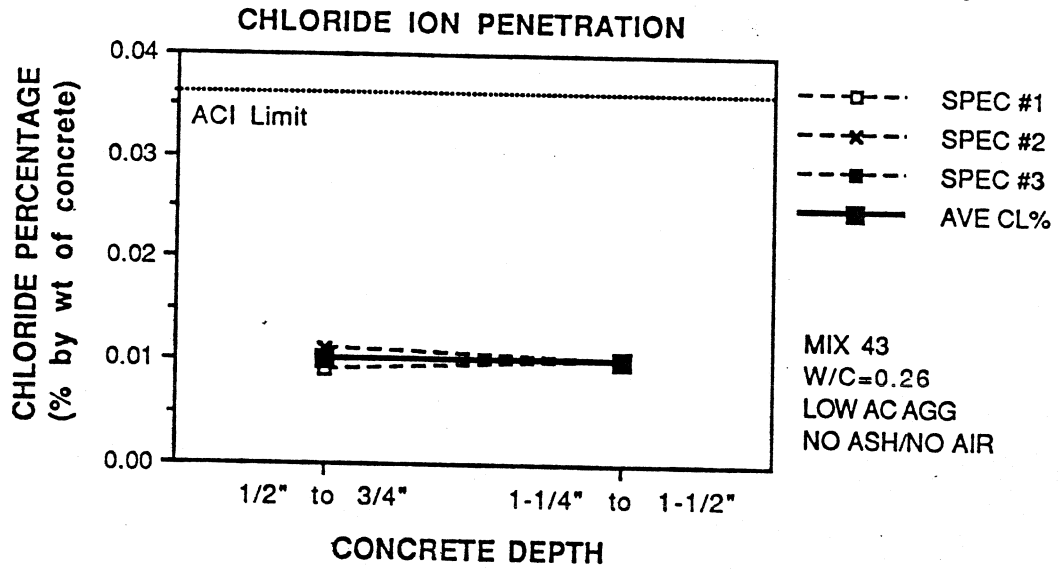


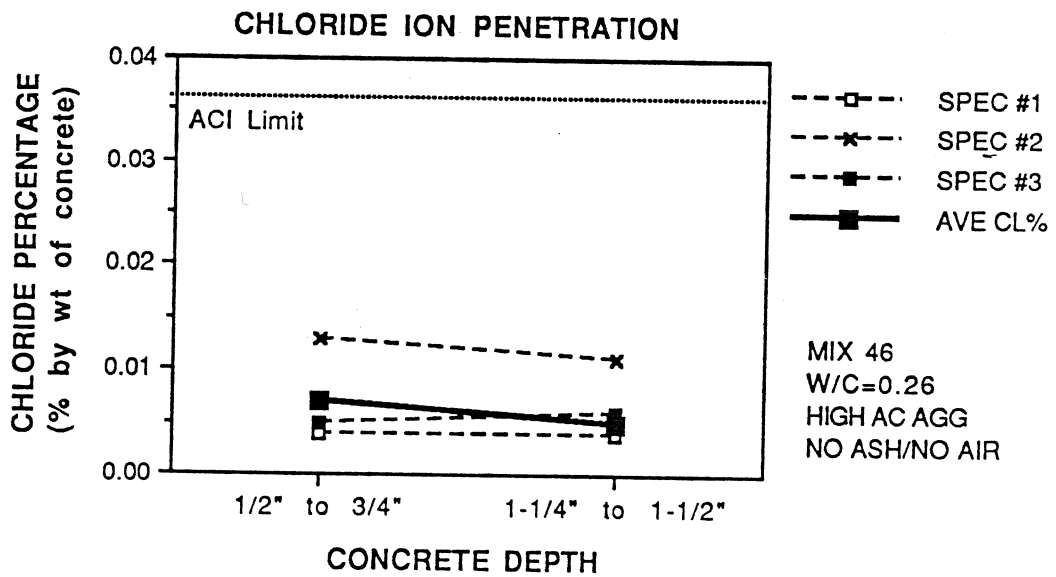
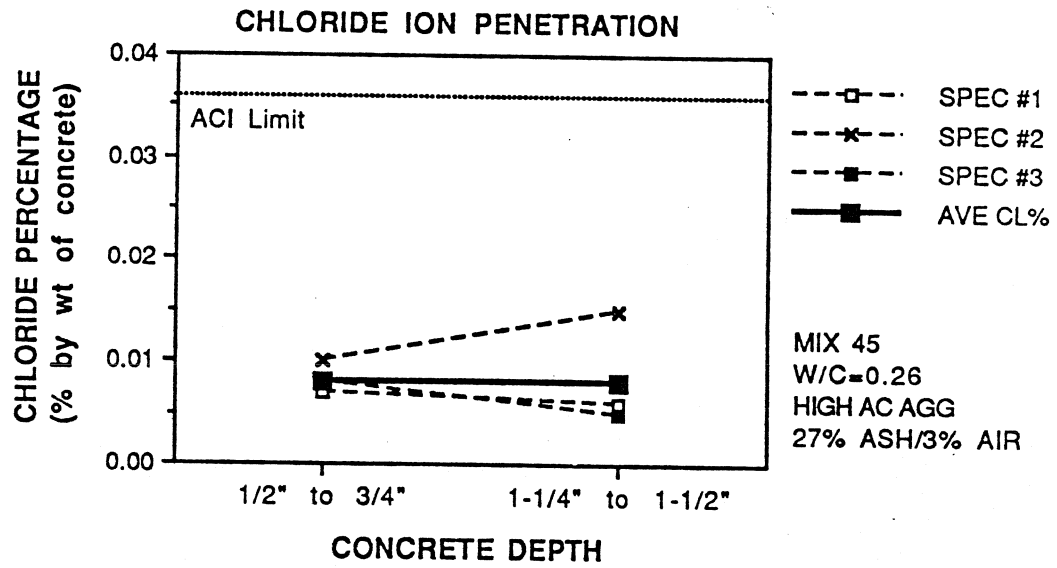


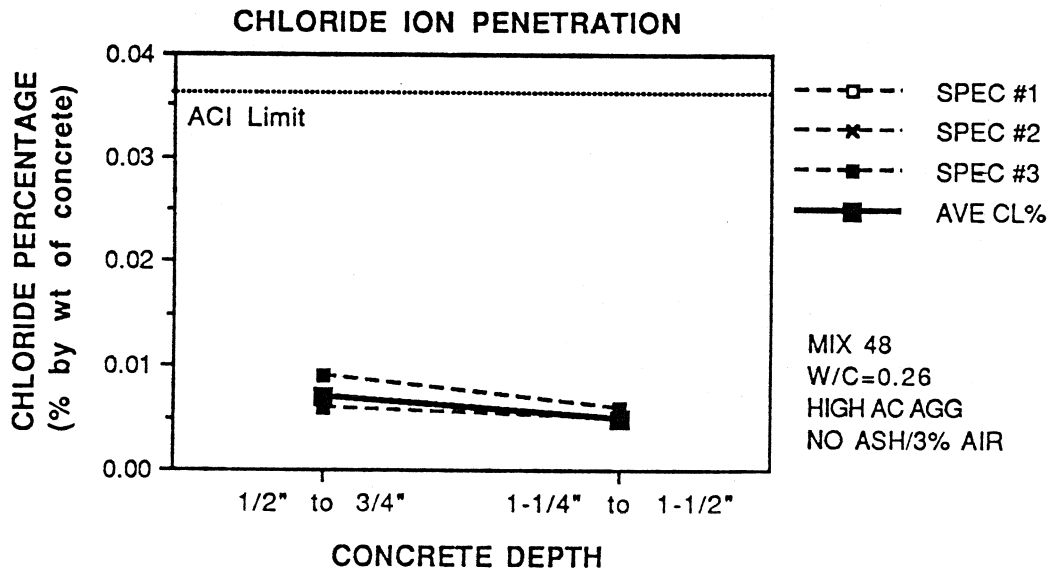
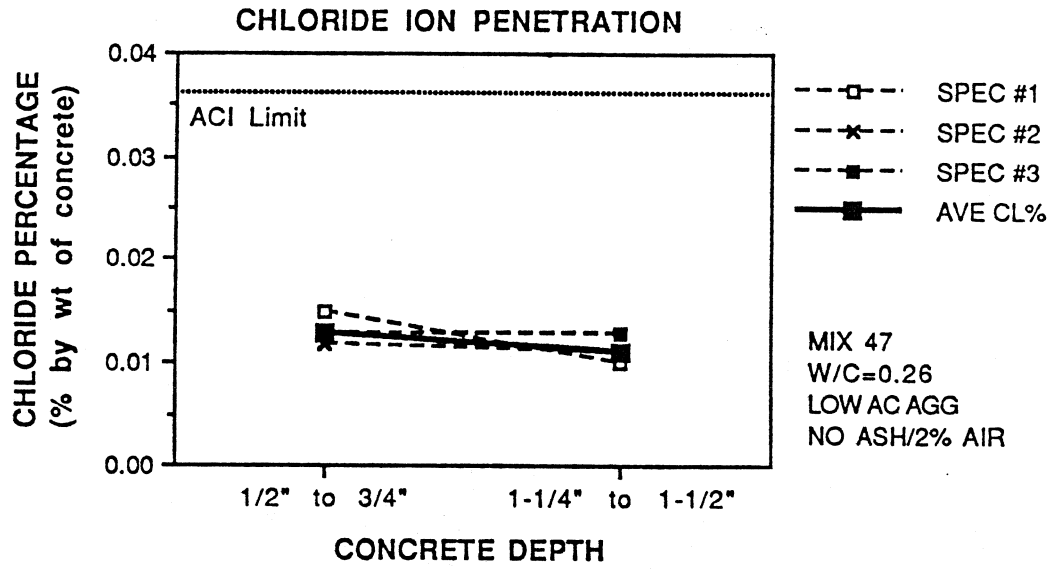


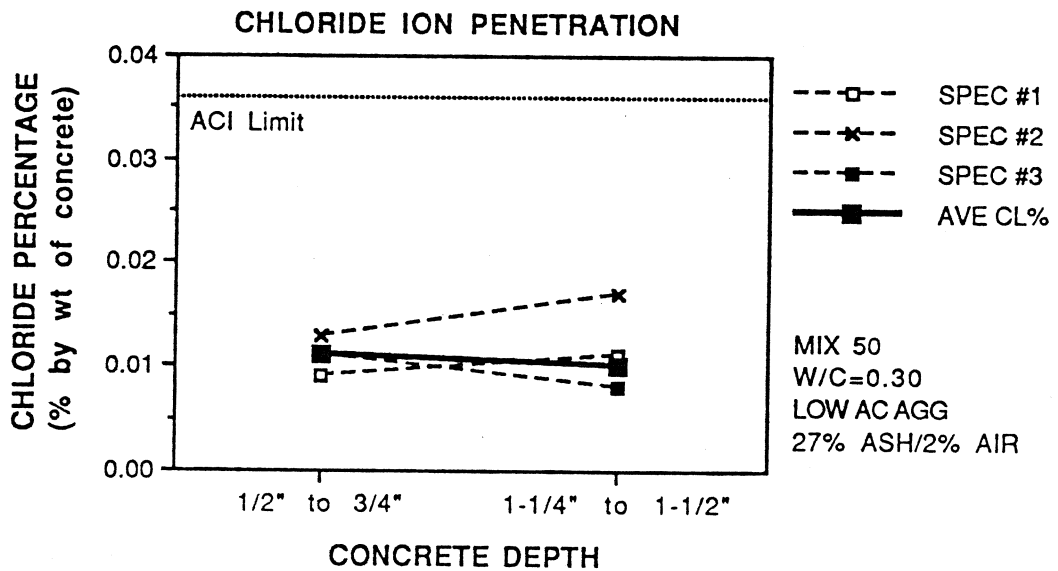
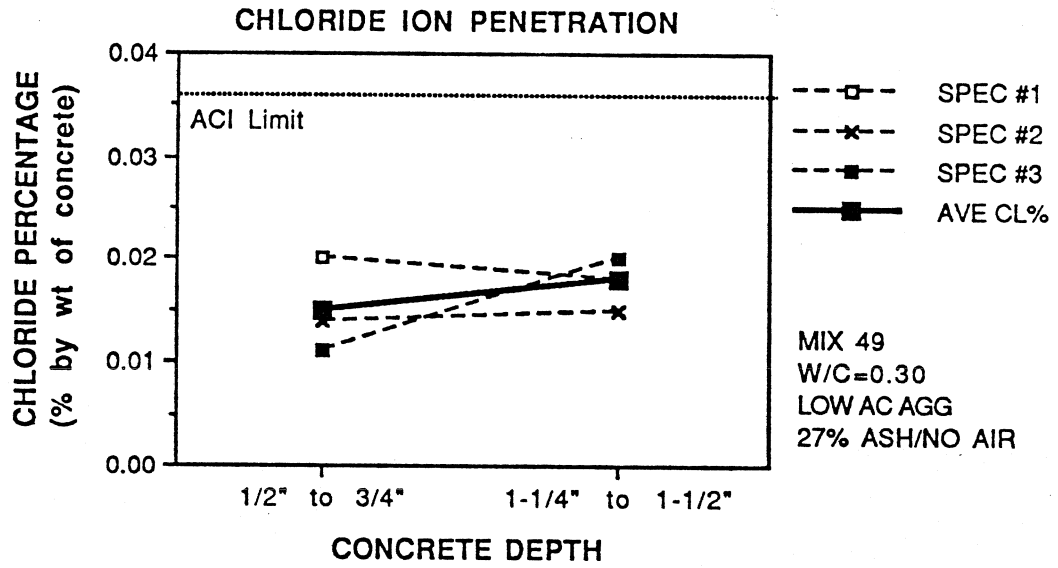


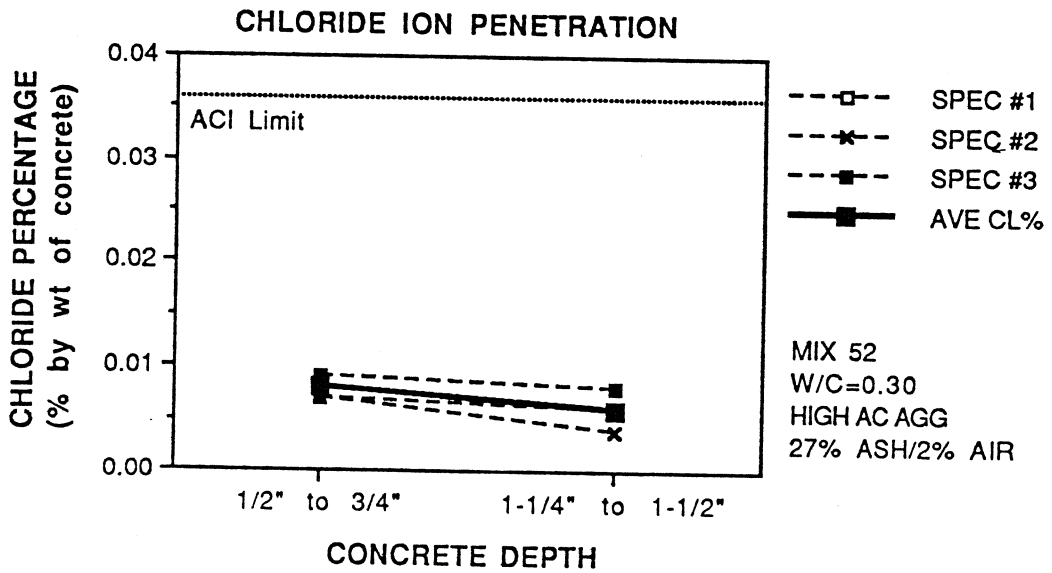
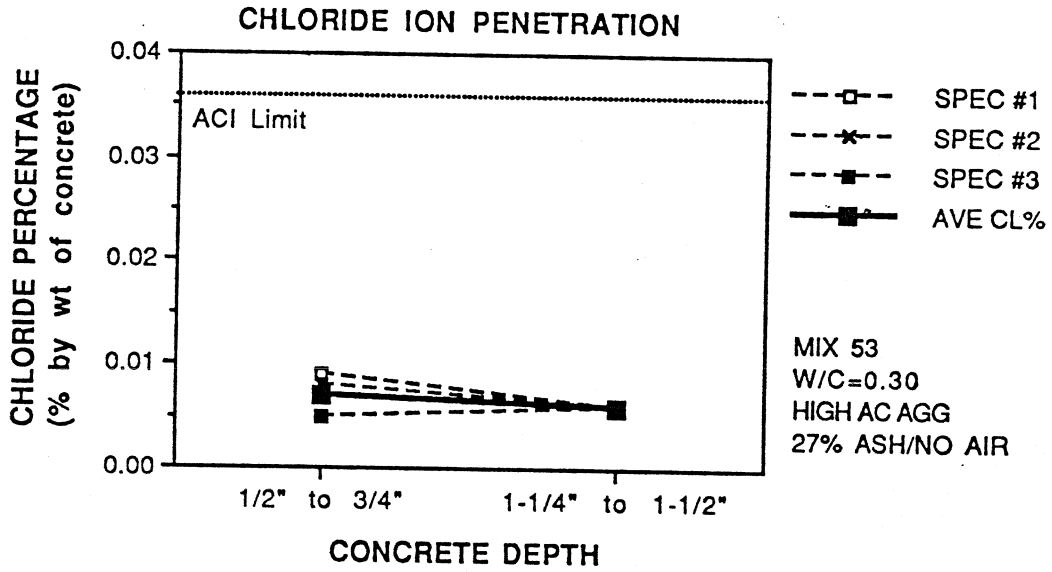


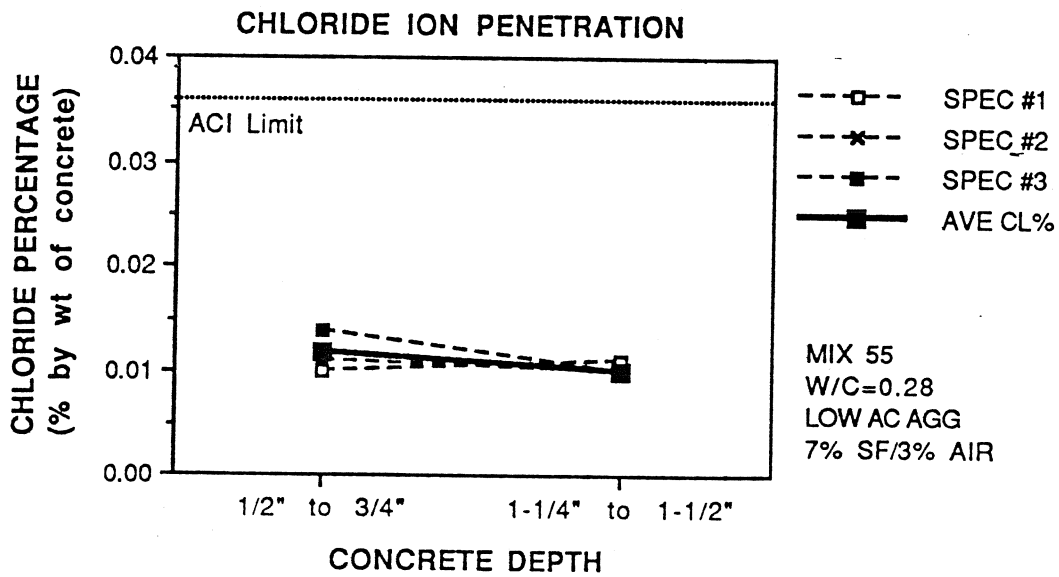
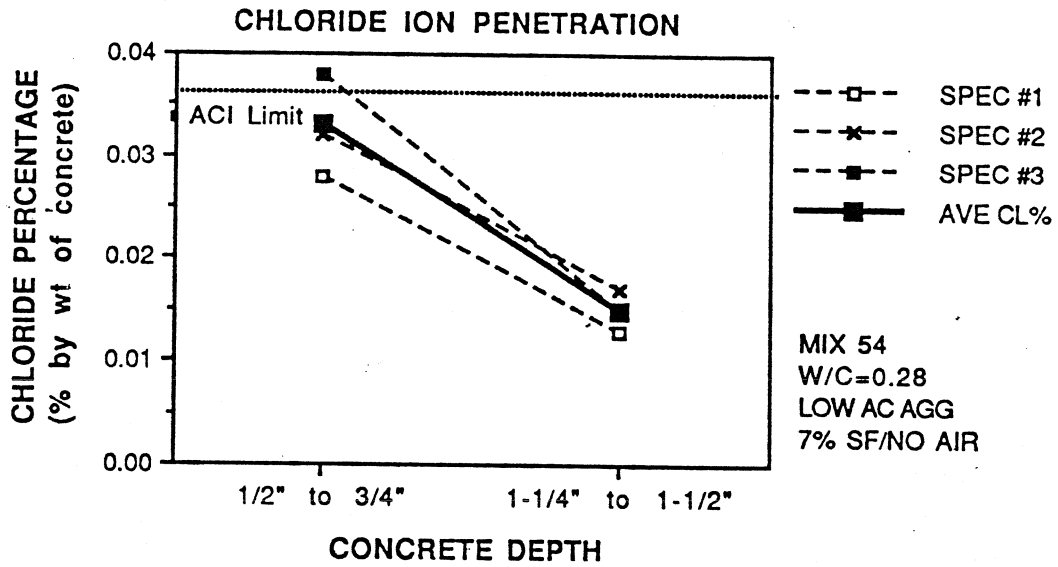


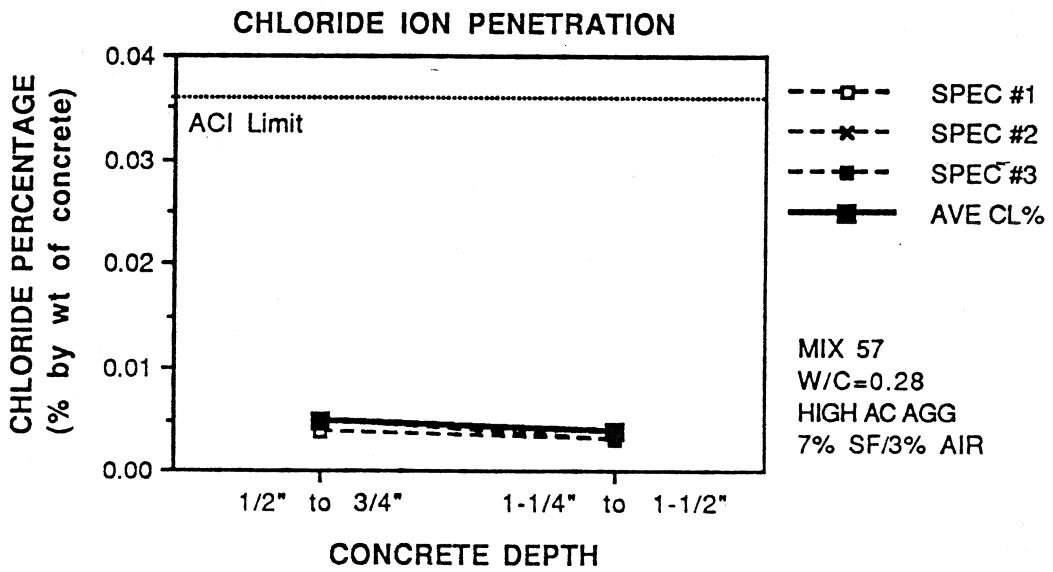
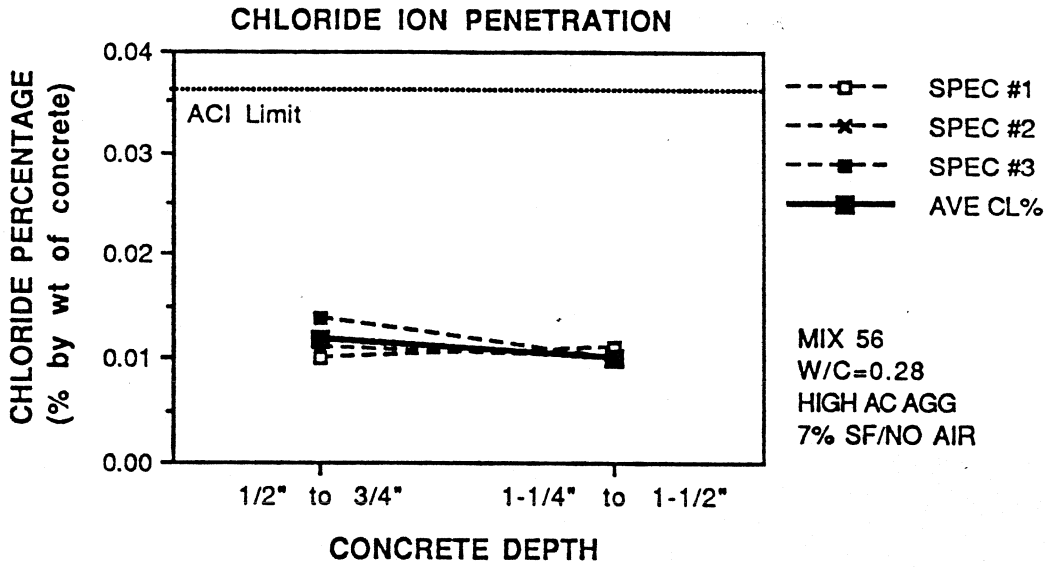


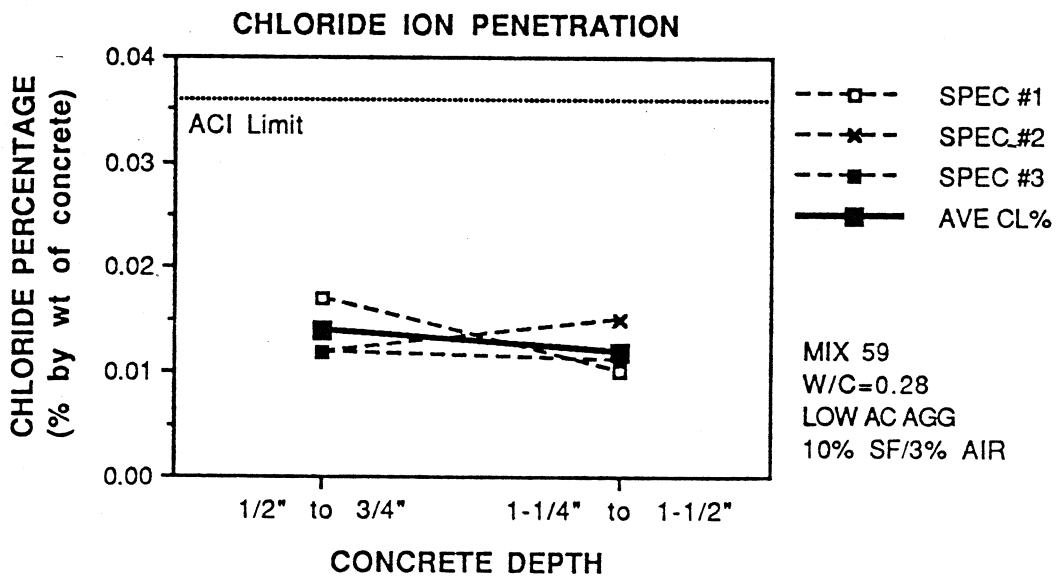
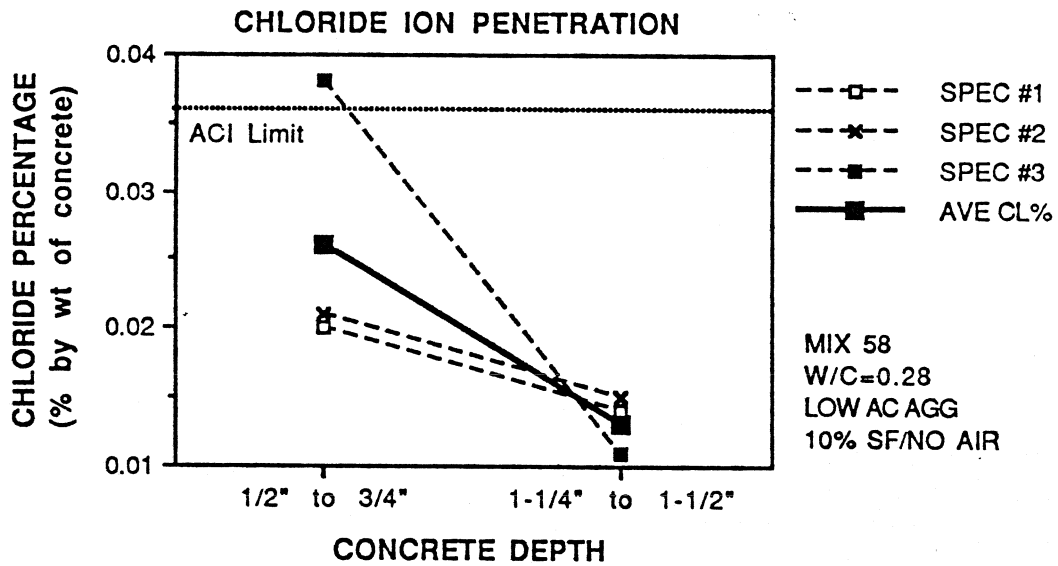


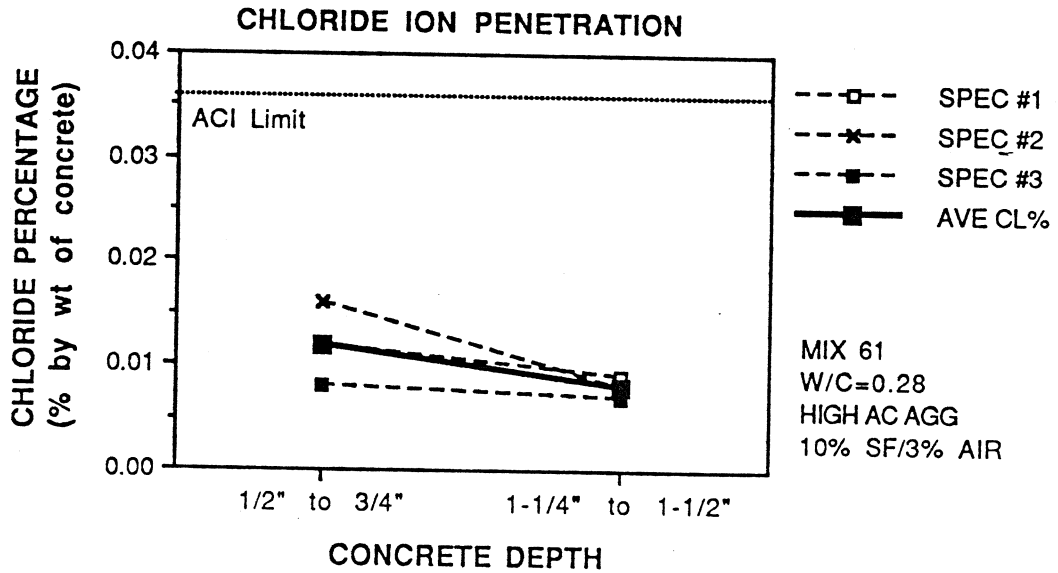
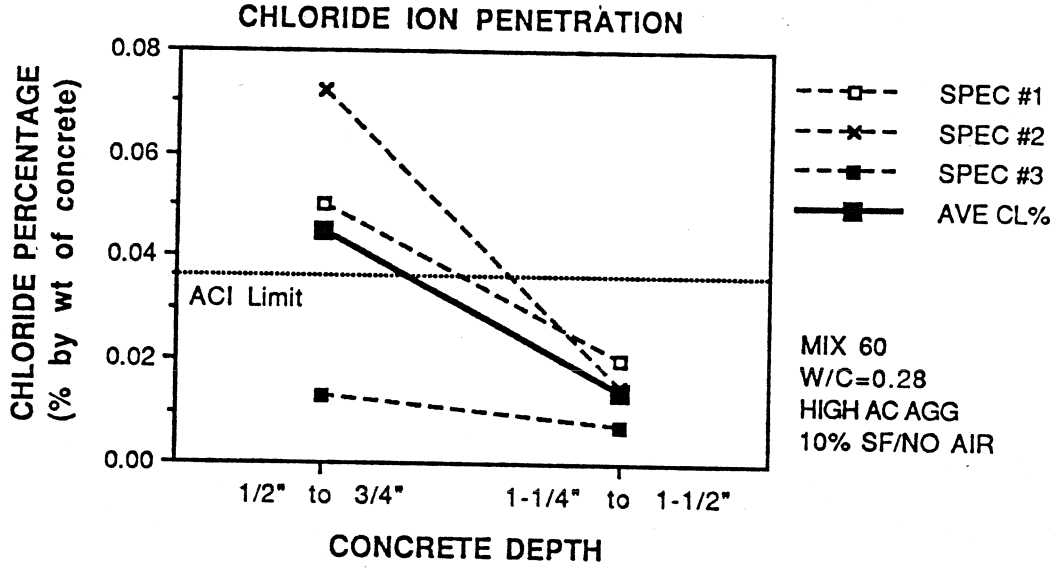


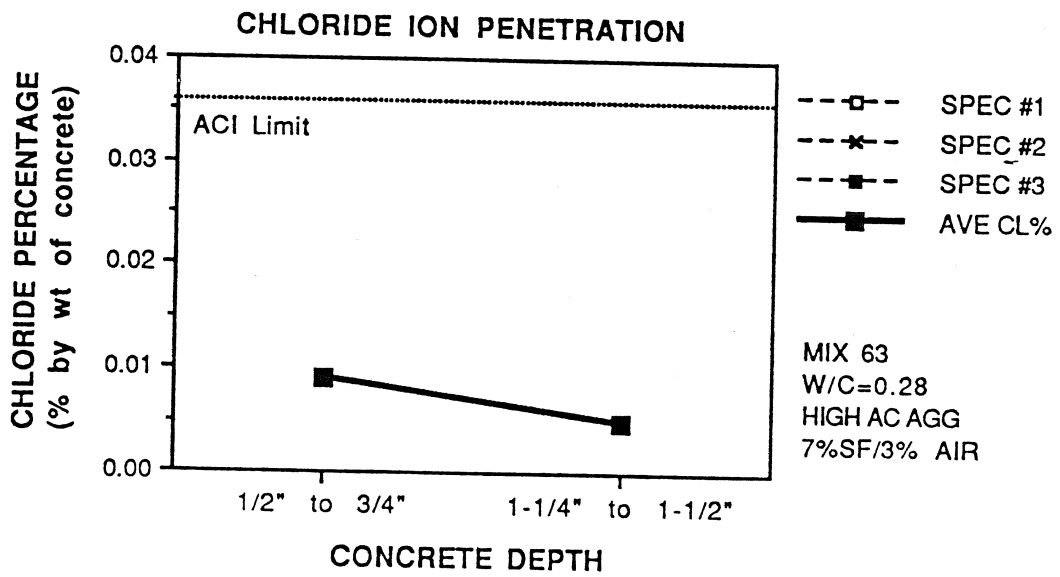
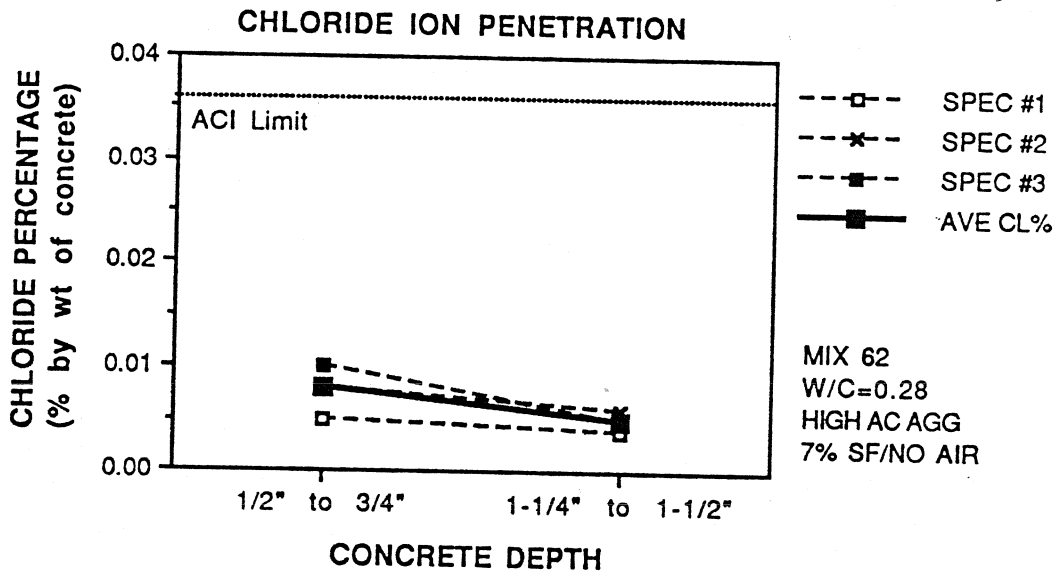


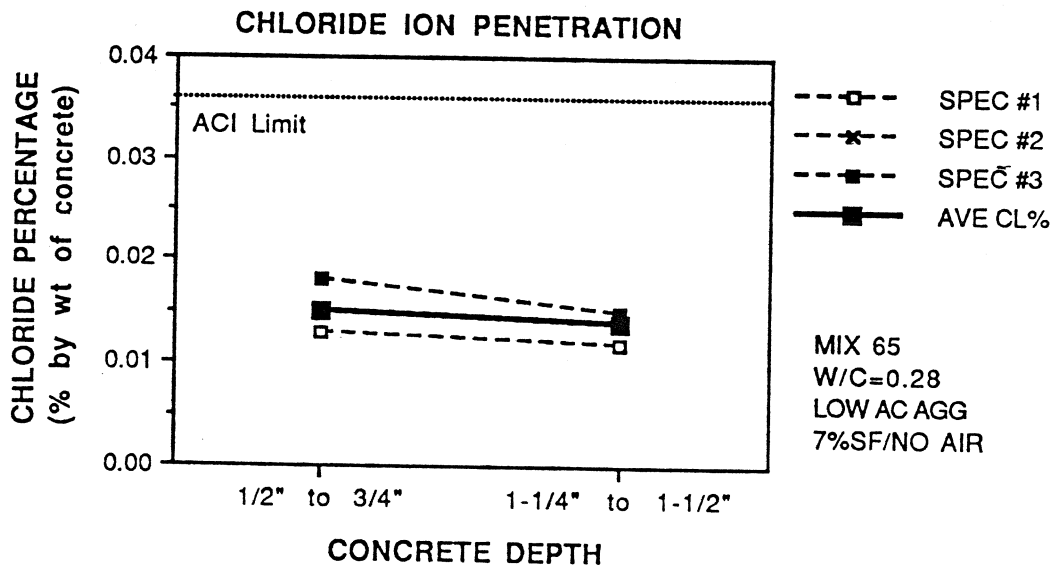
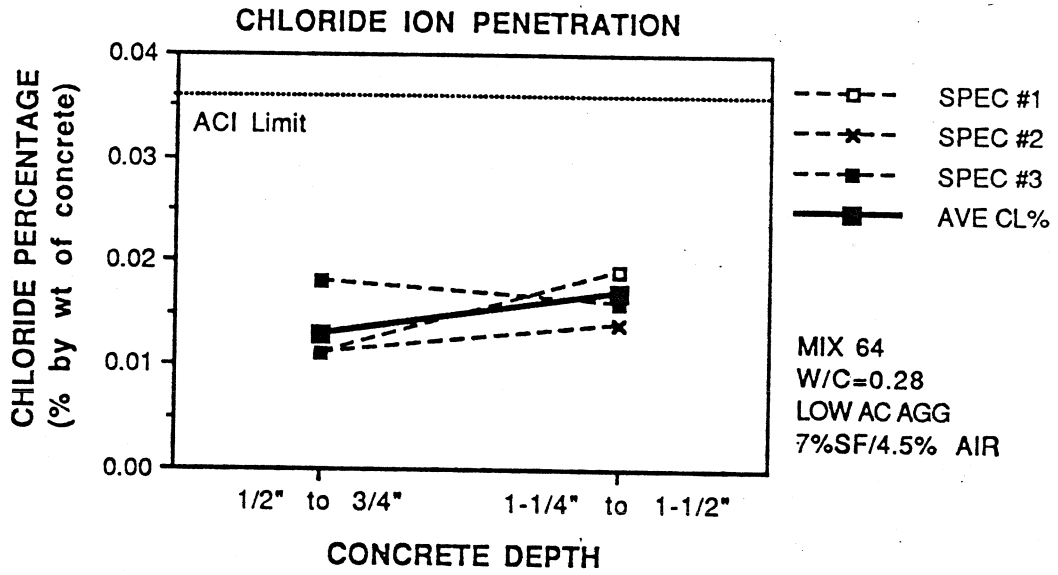


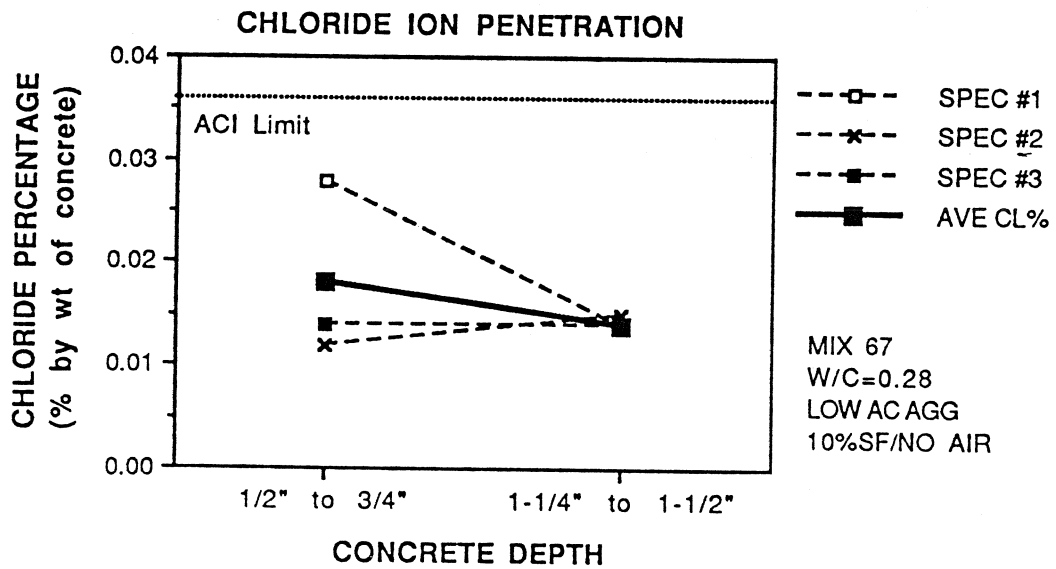
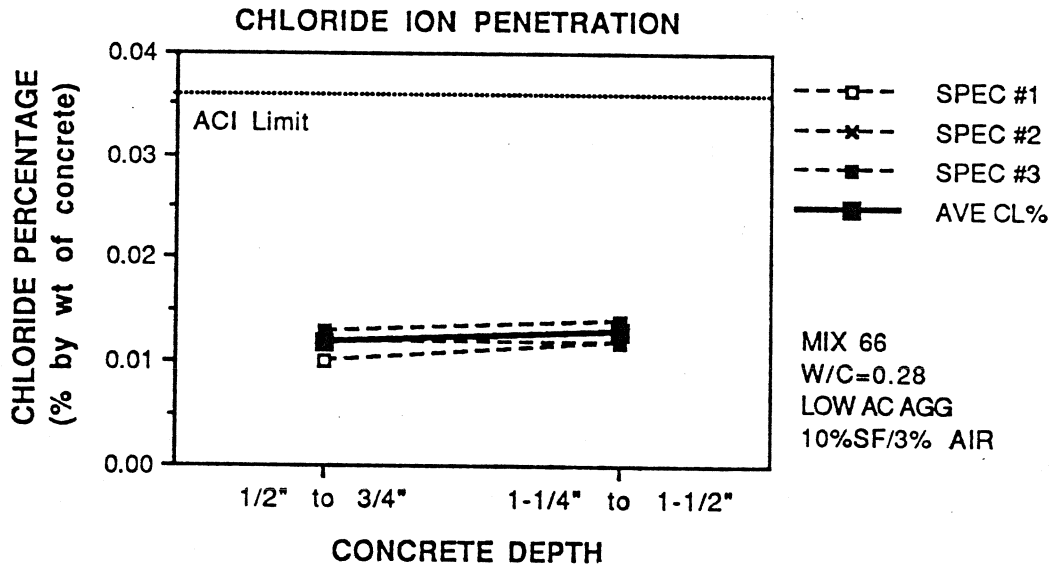


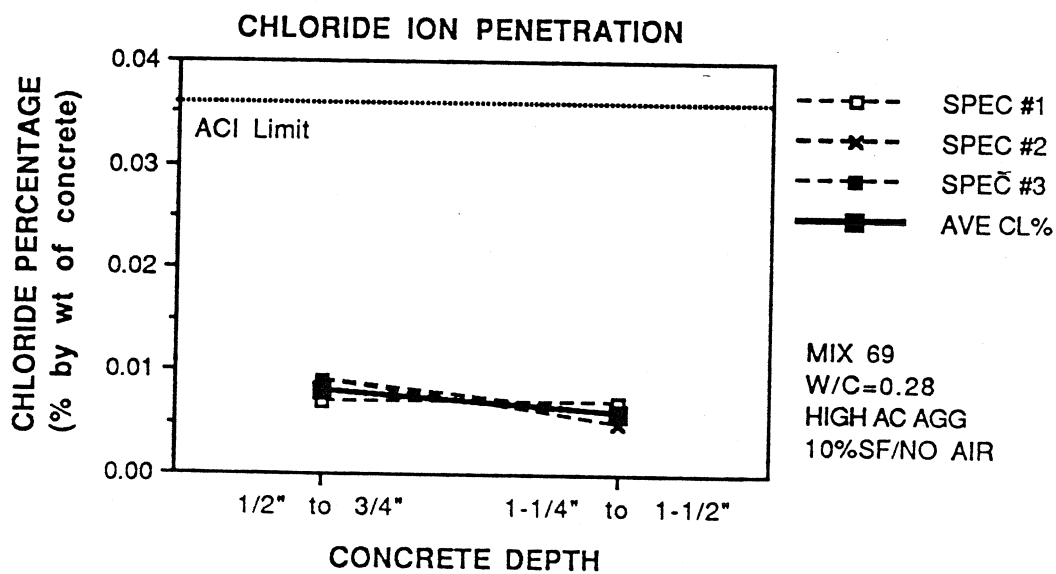
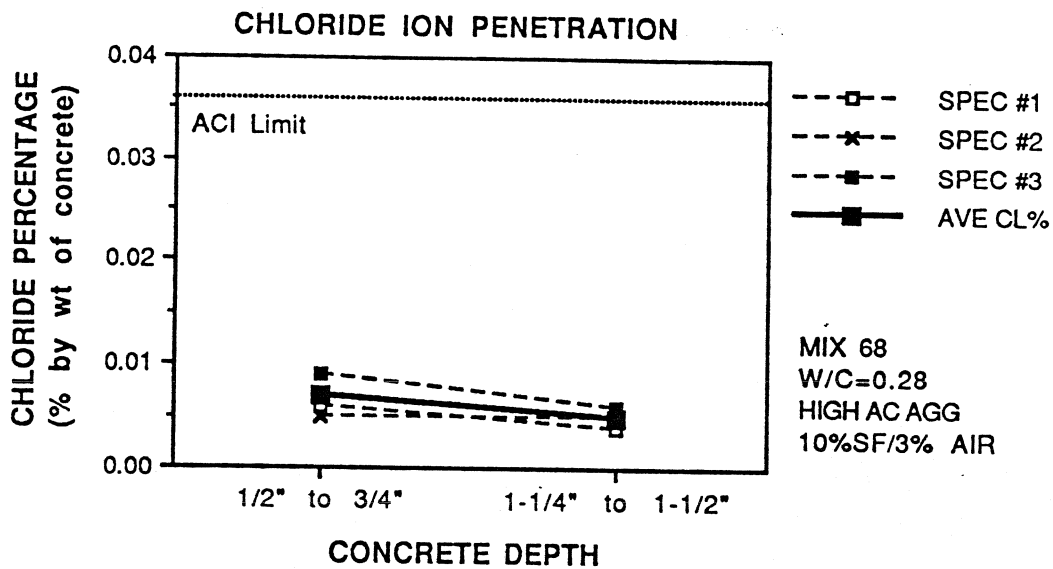




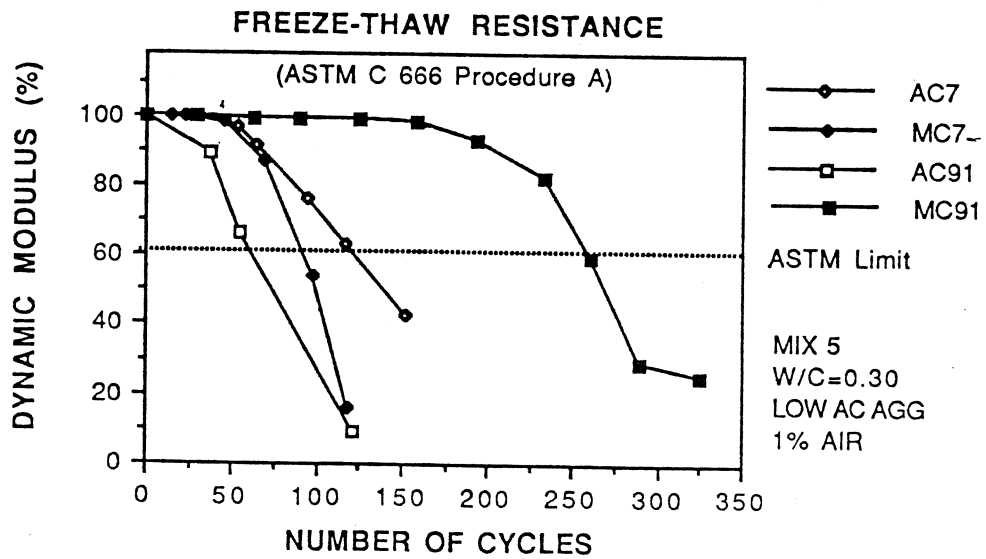
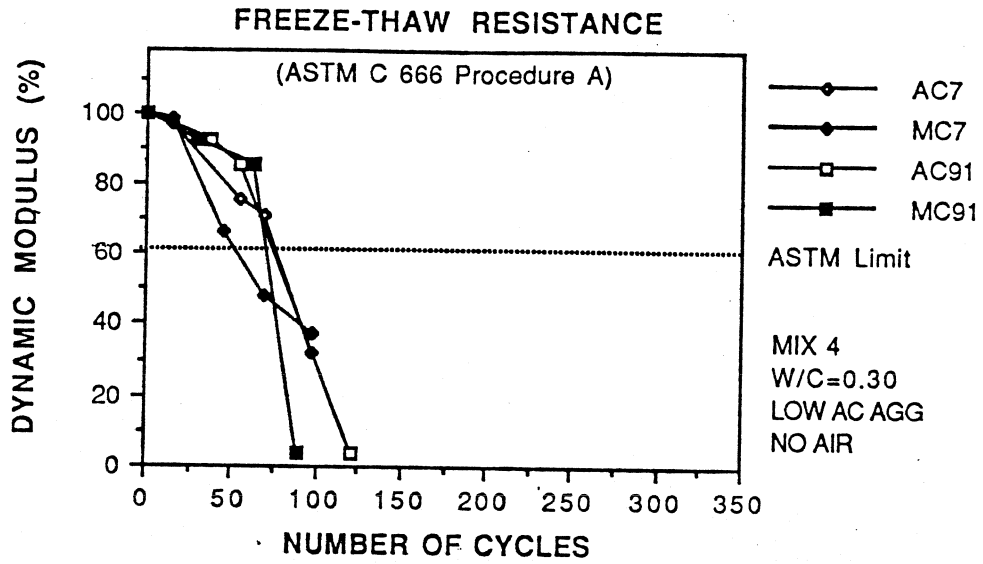


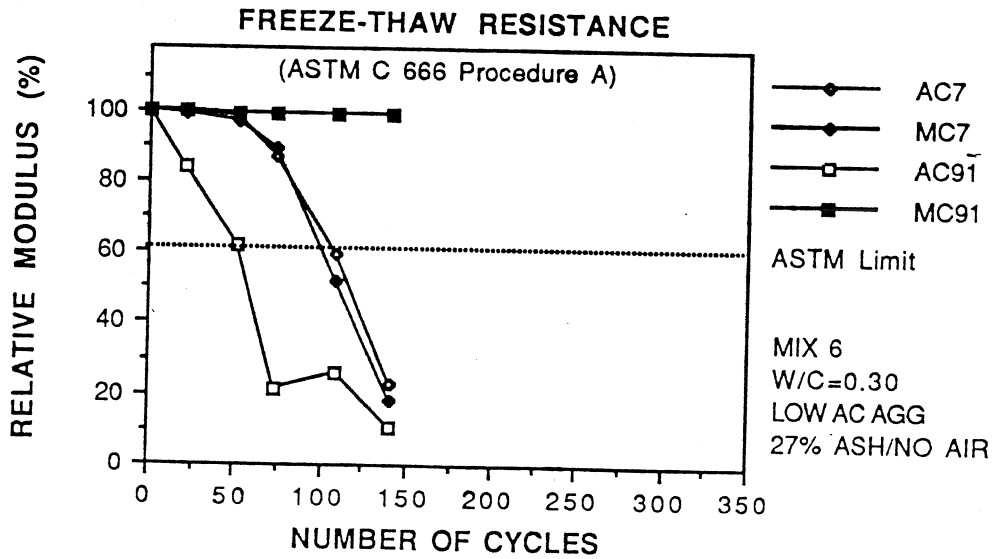
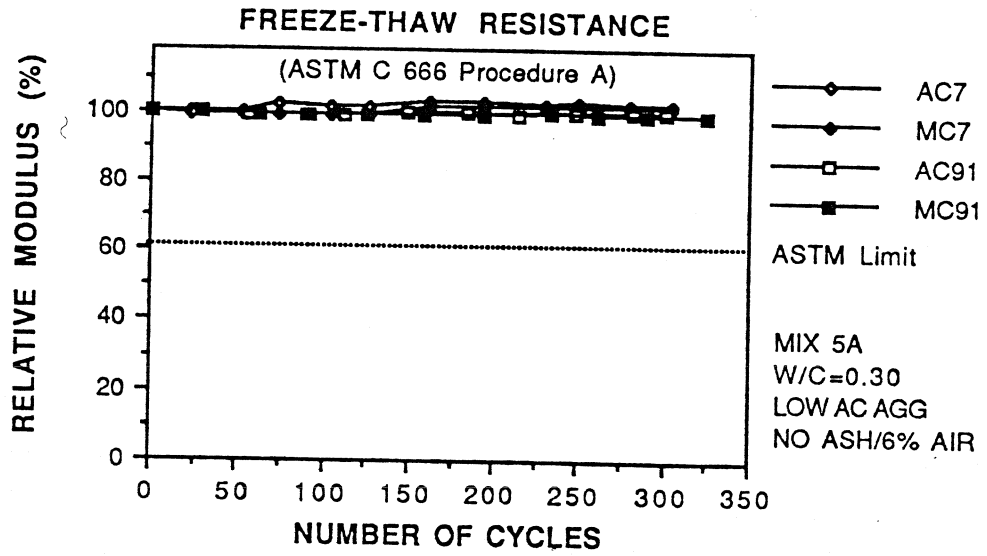


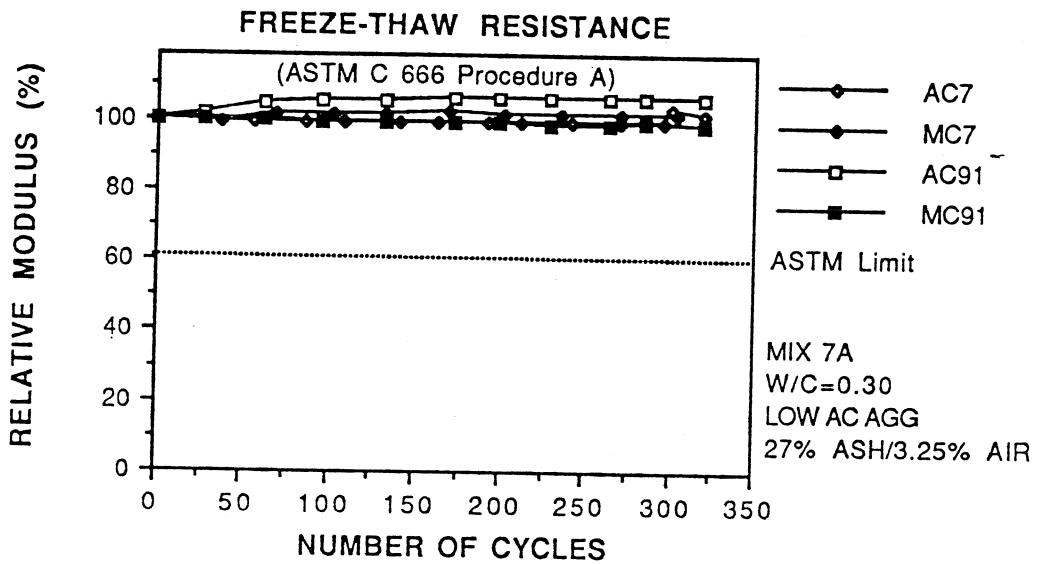
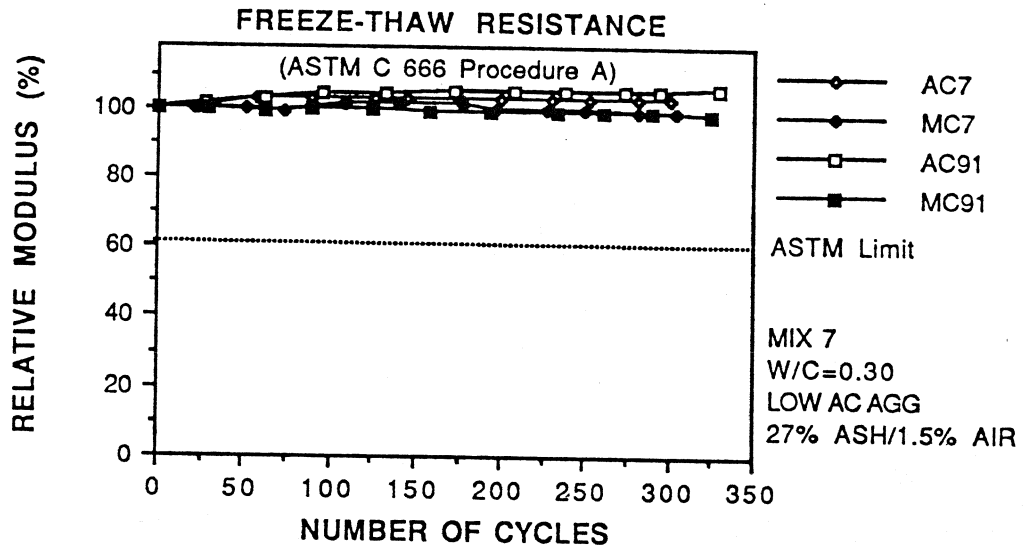


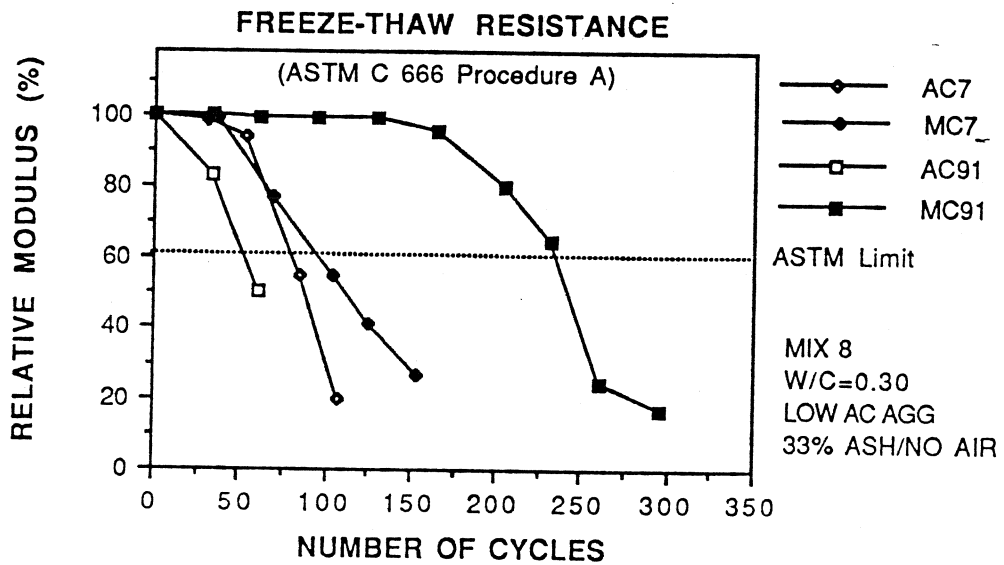
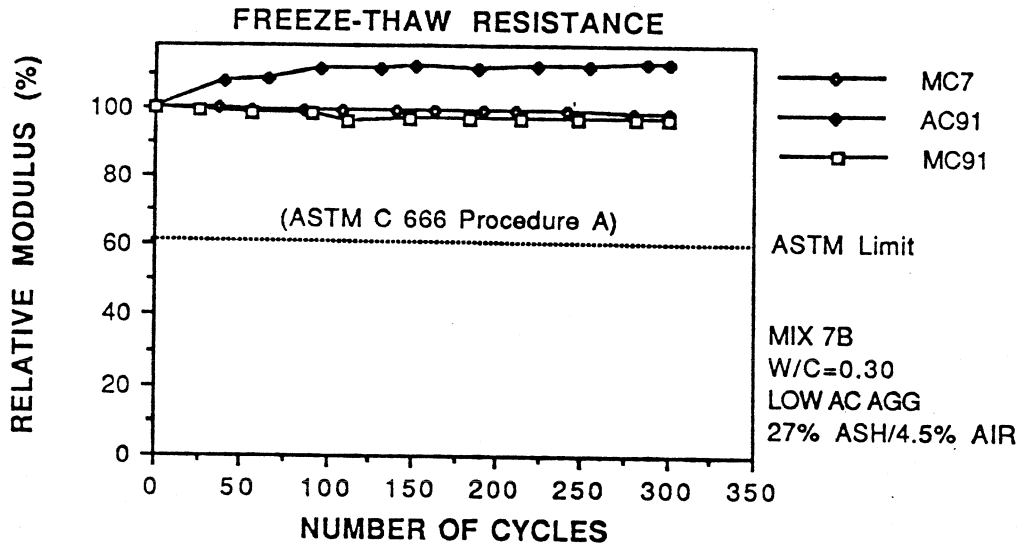


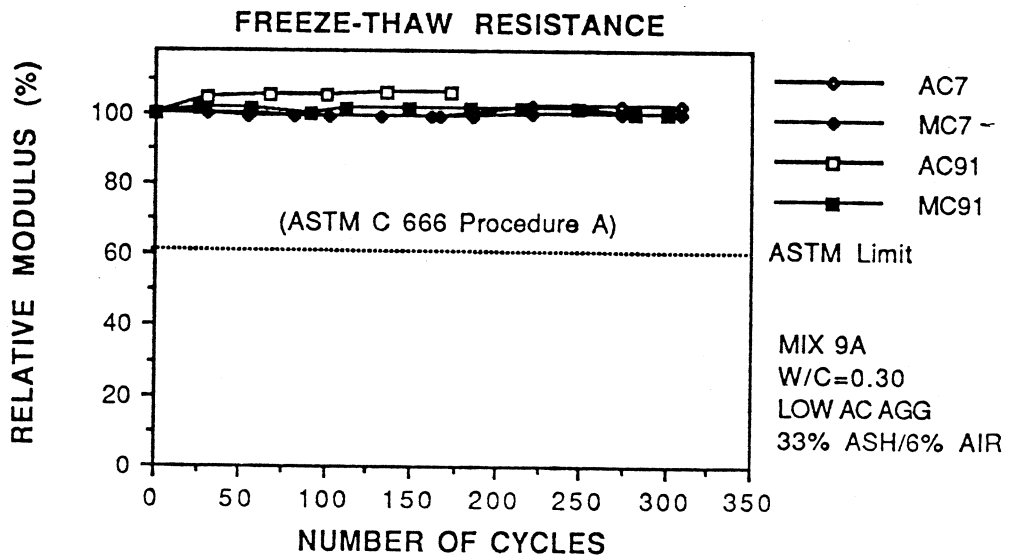
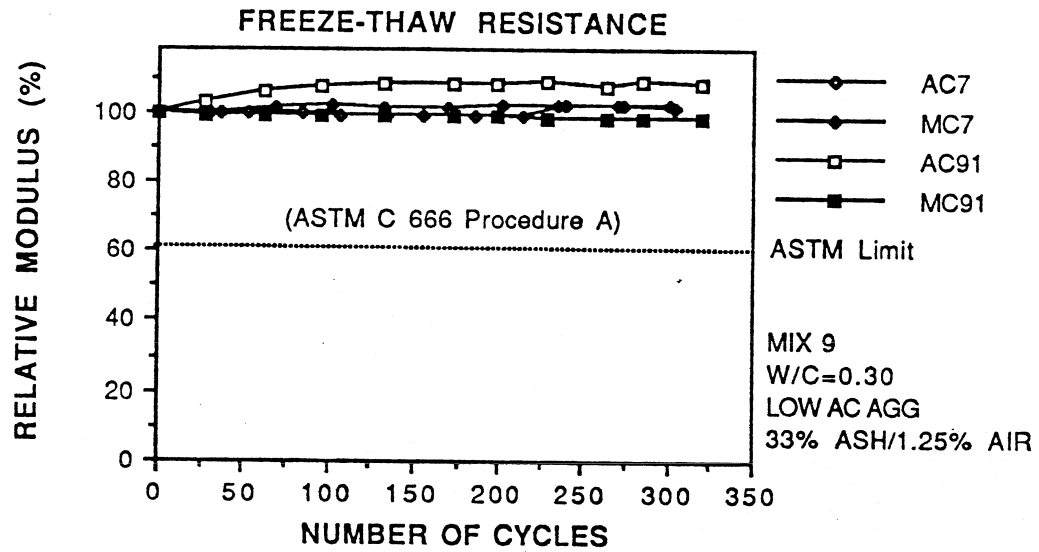
APPENDIX G
FREEZE-THAW RESISTANCE DATA

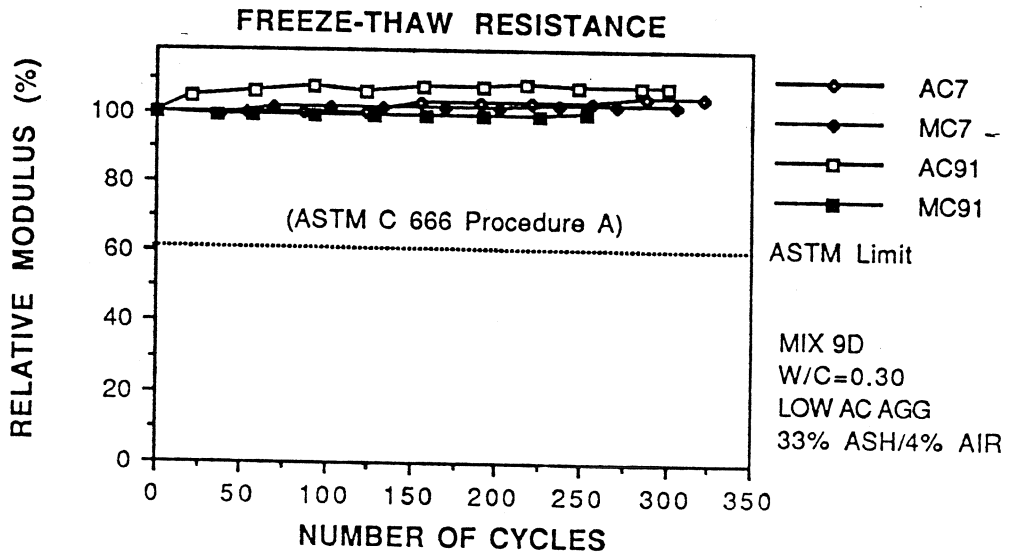
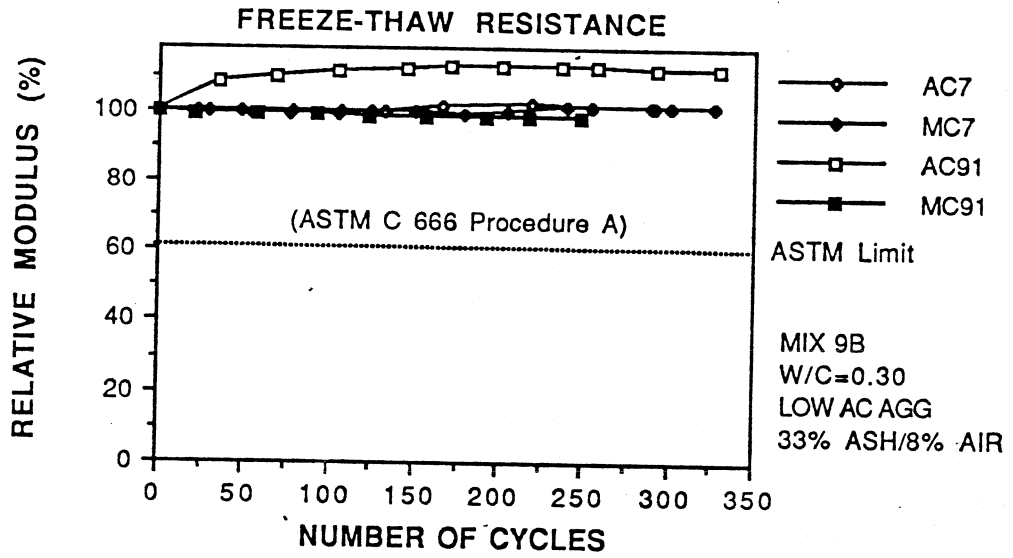


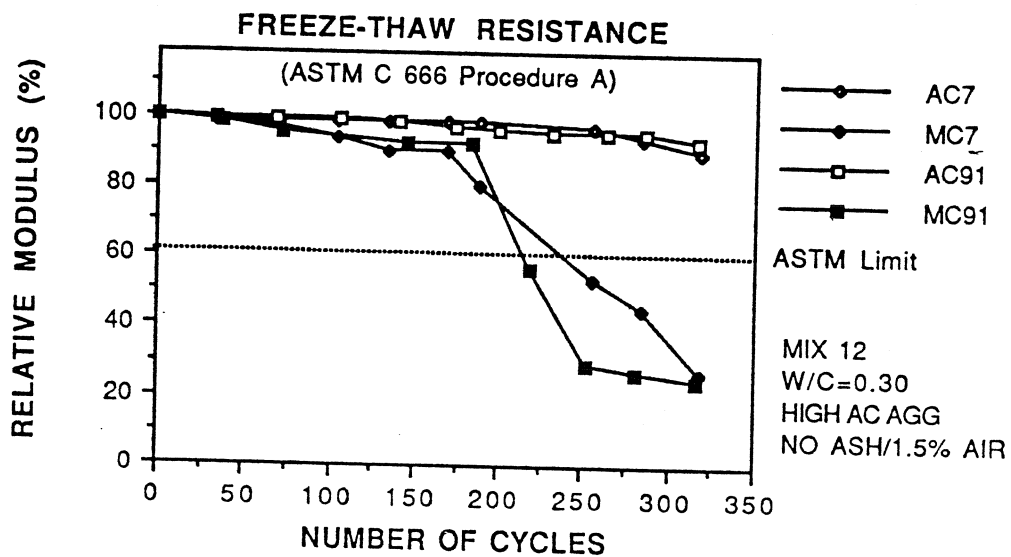
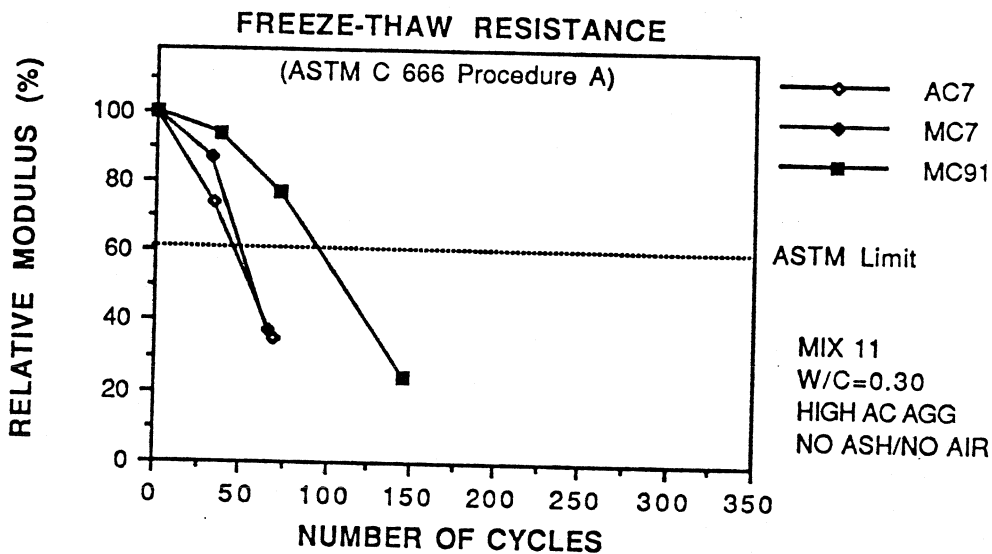


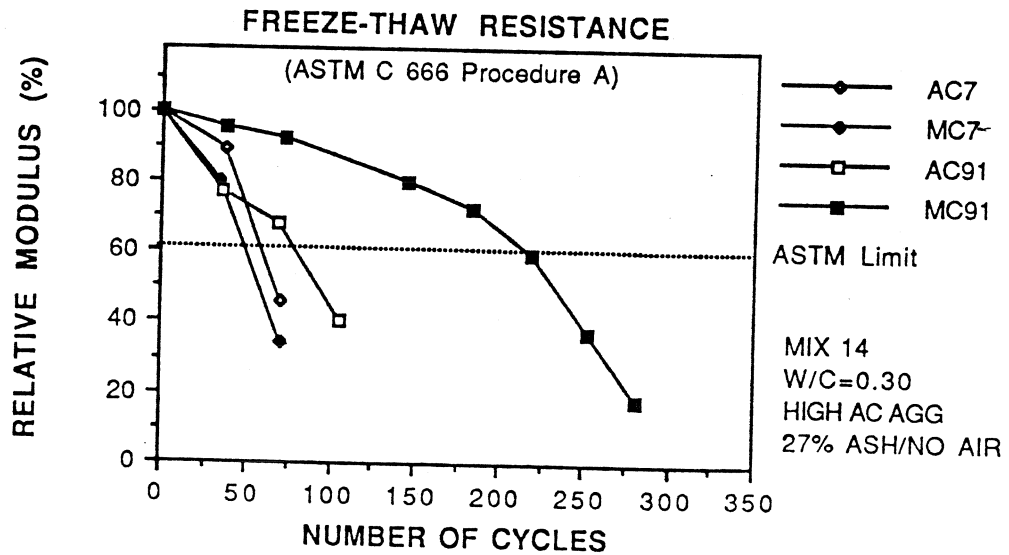
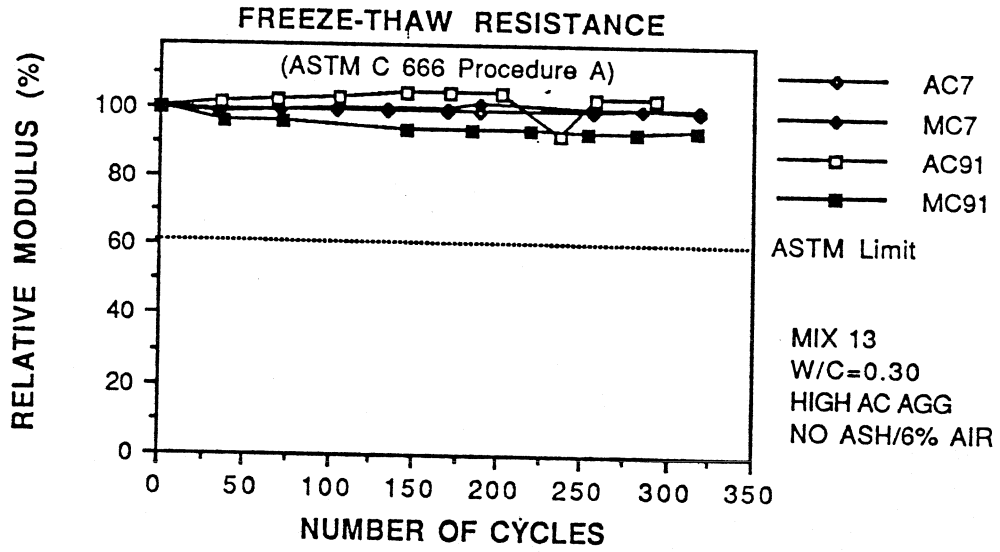


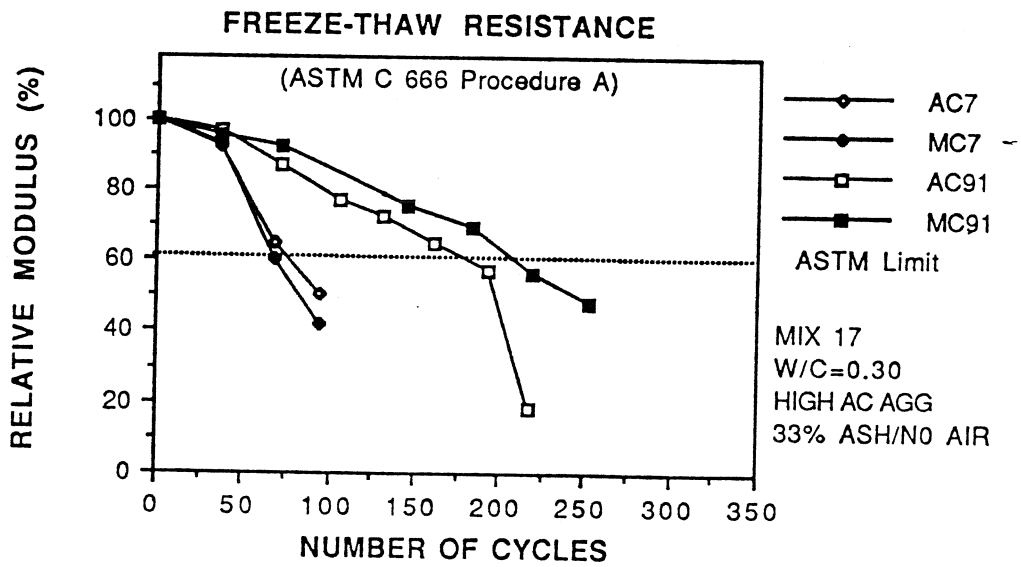
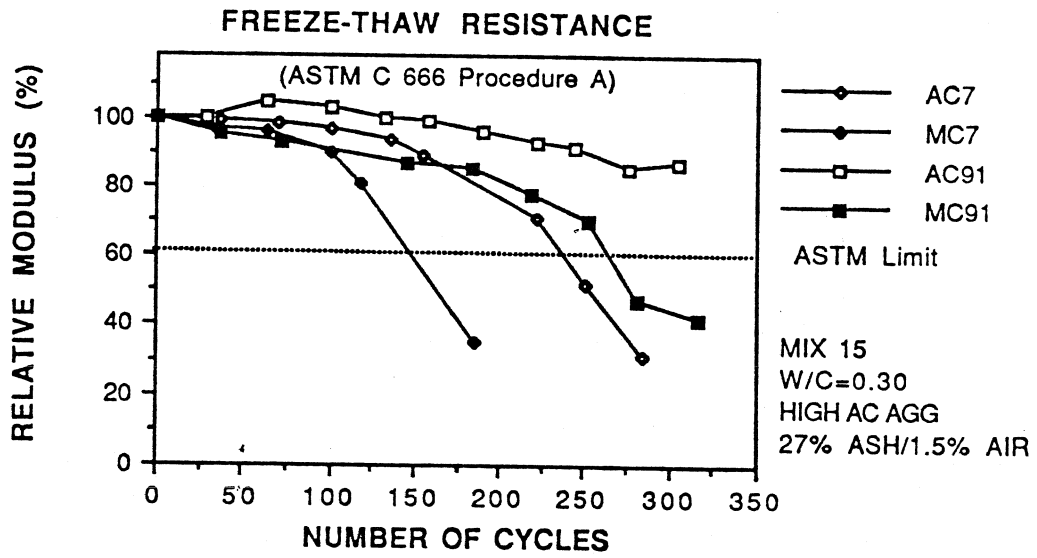


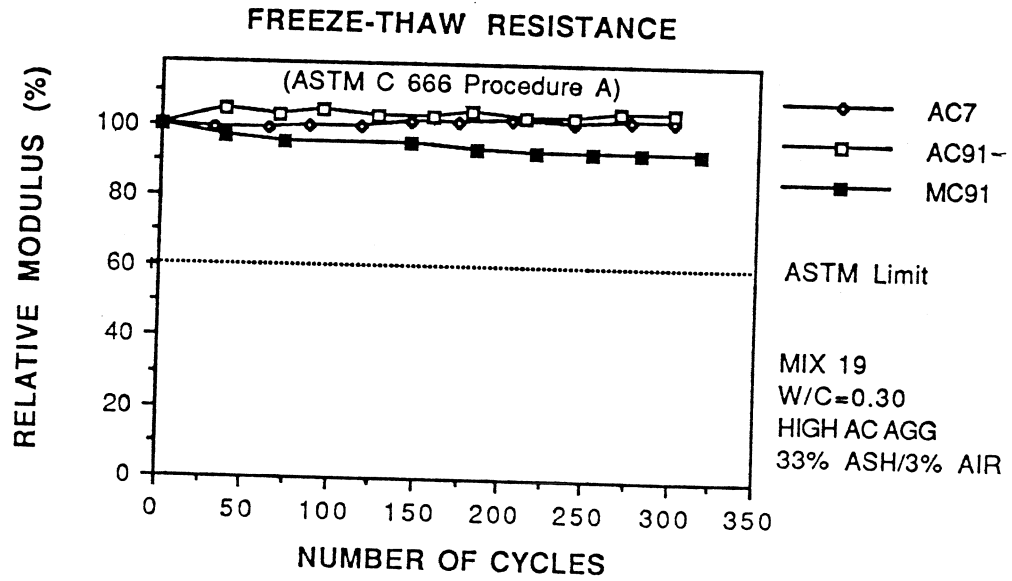
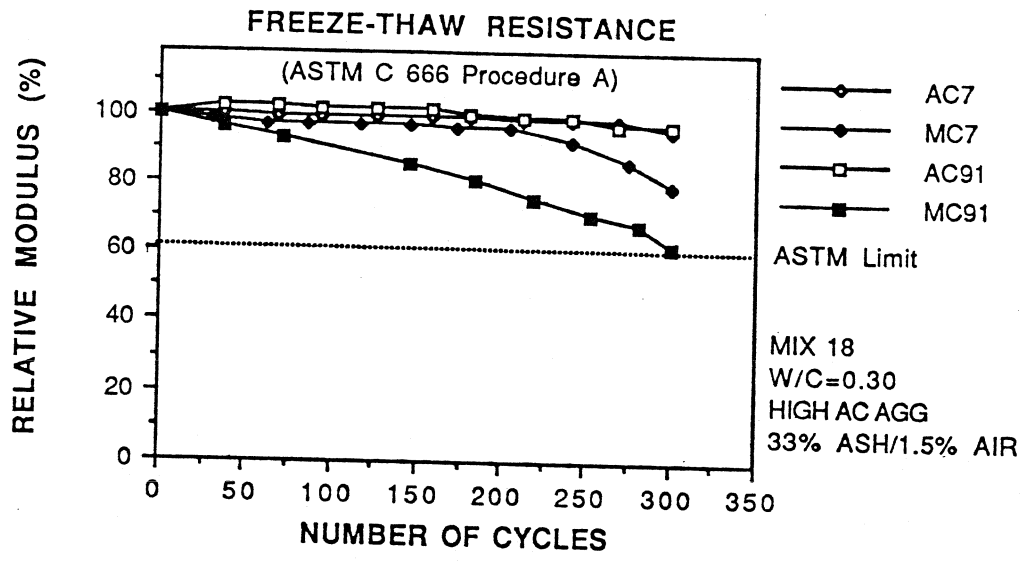


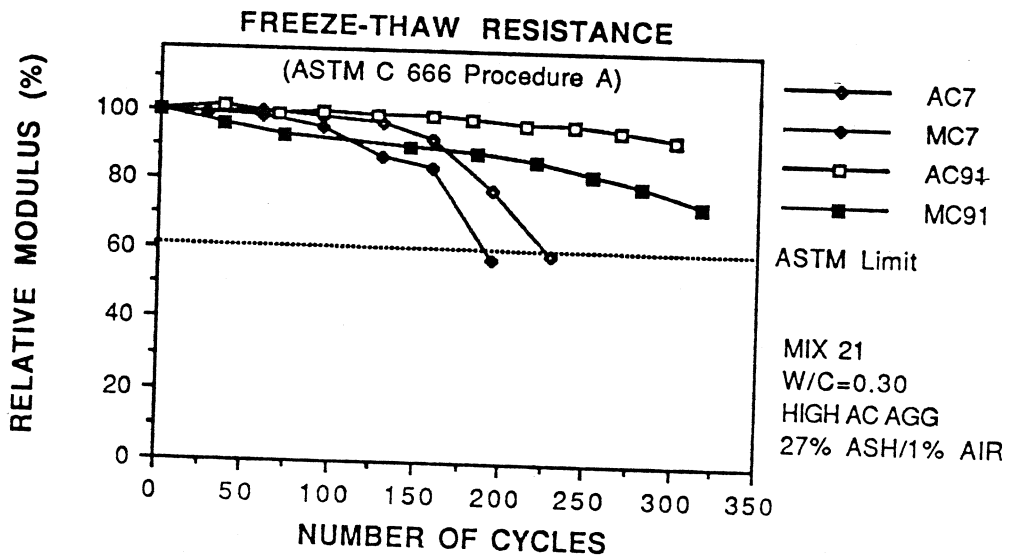
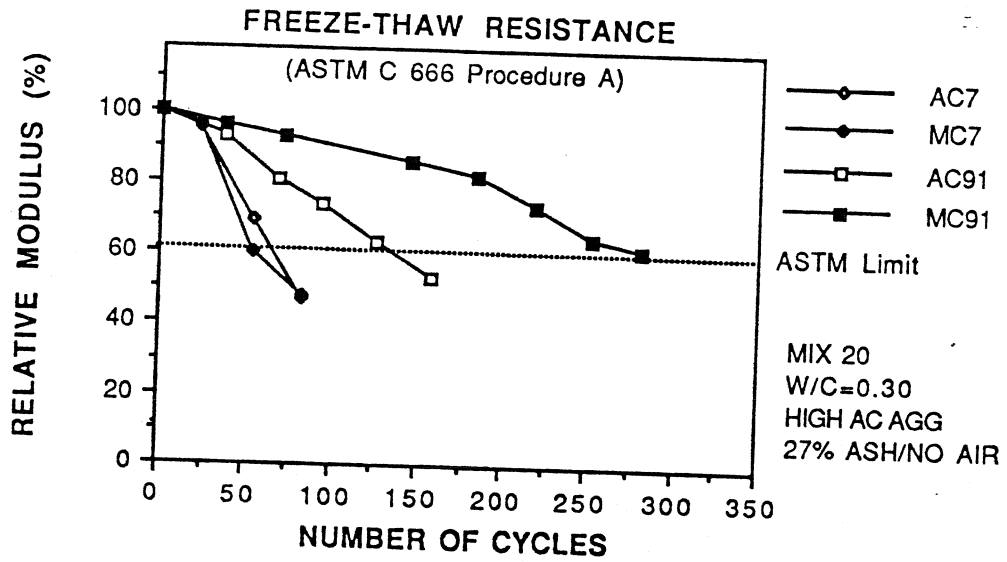


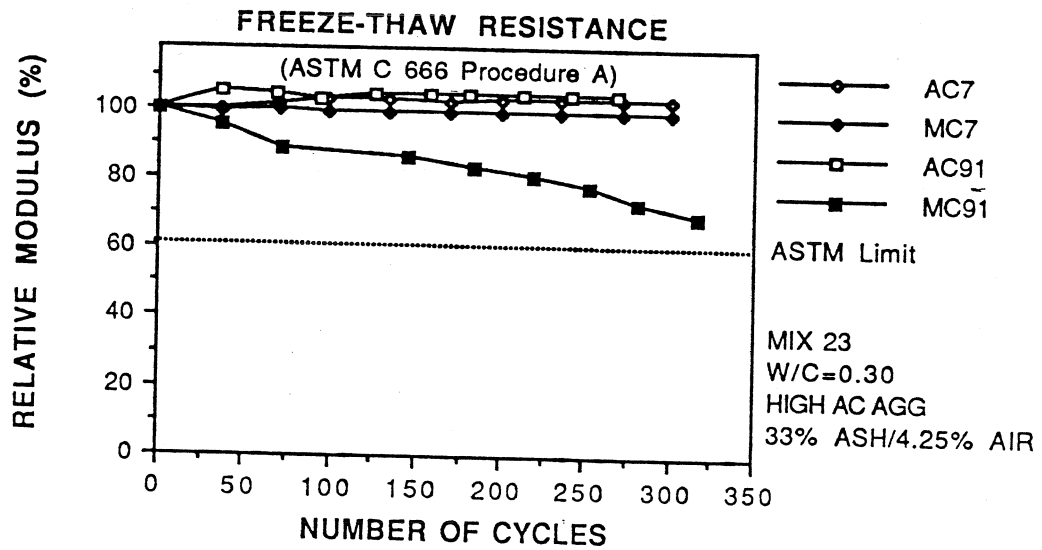
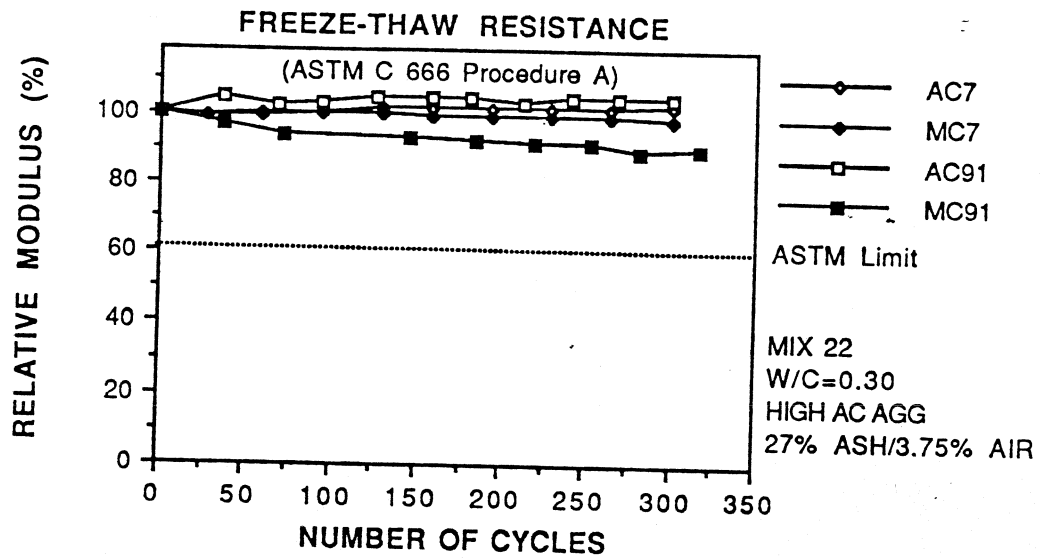


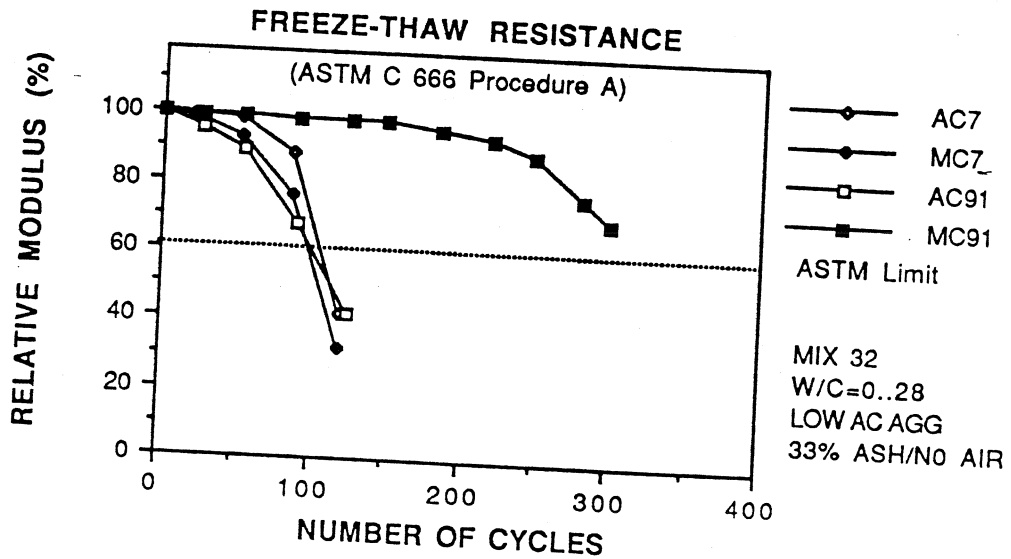
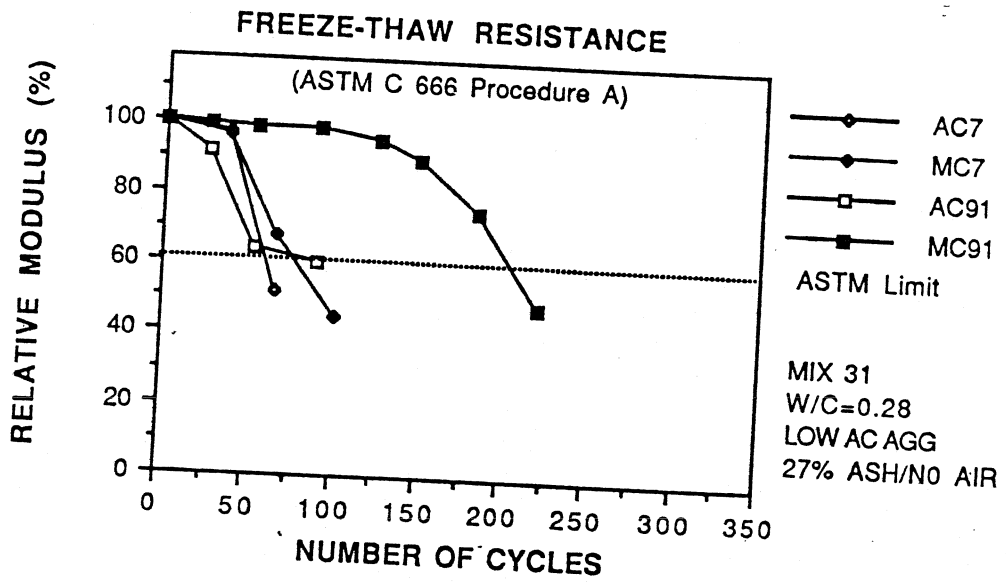


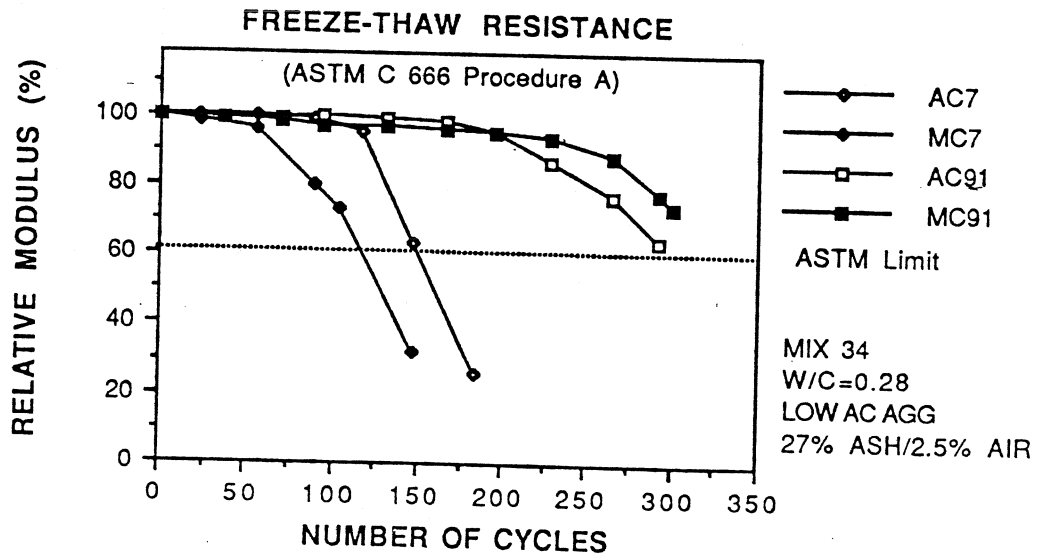
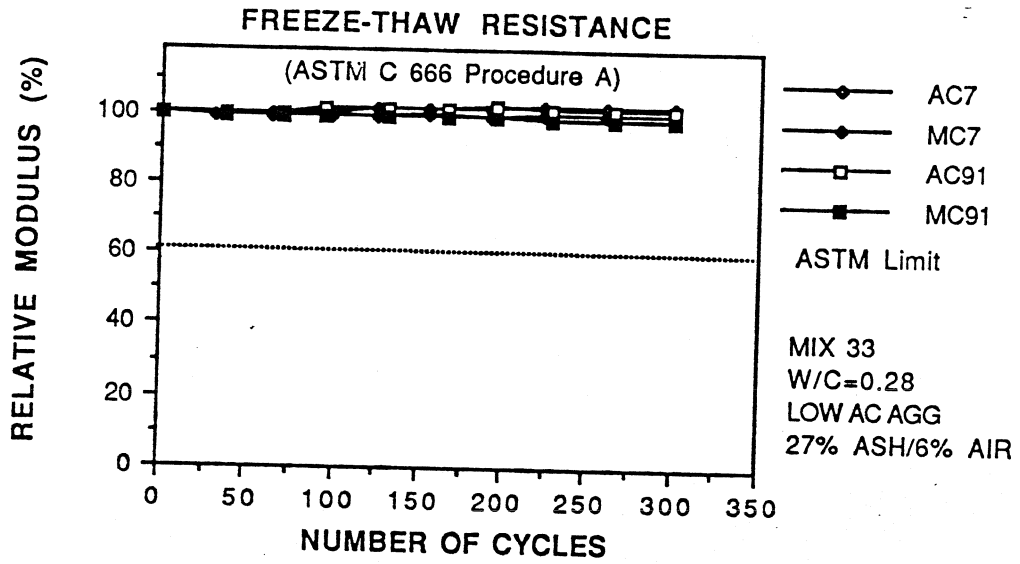


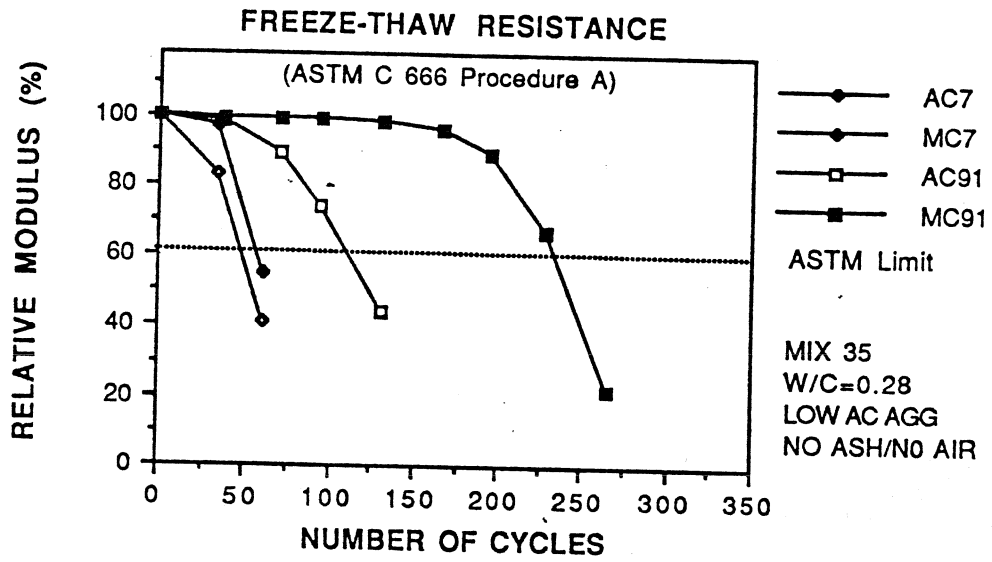


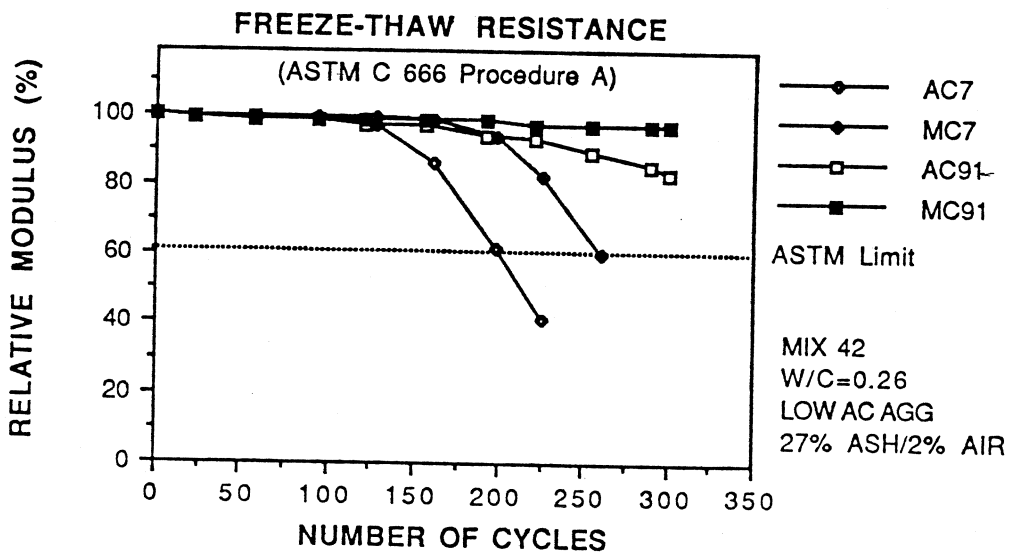
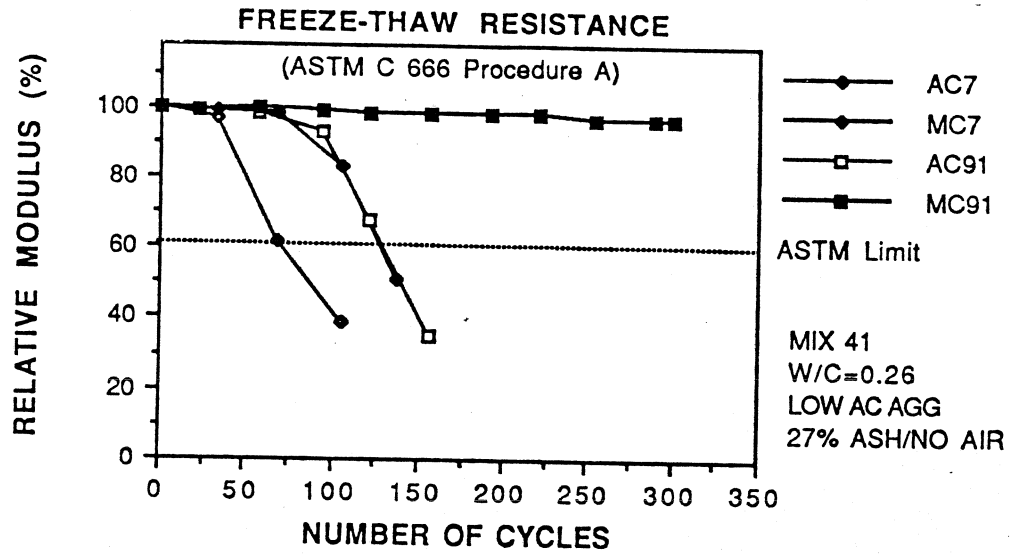


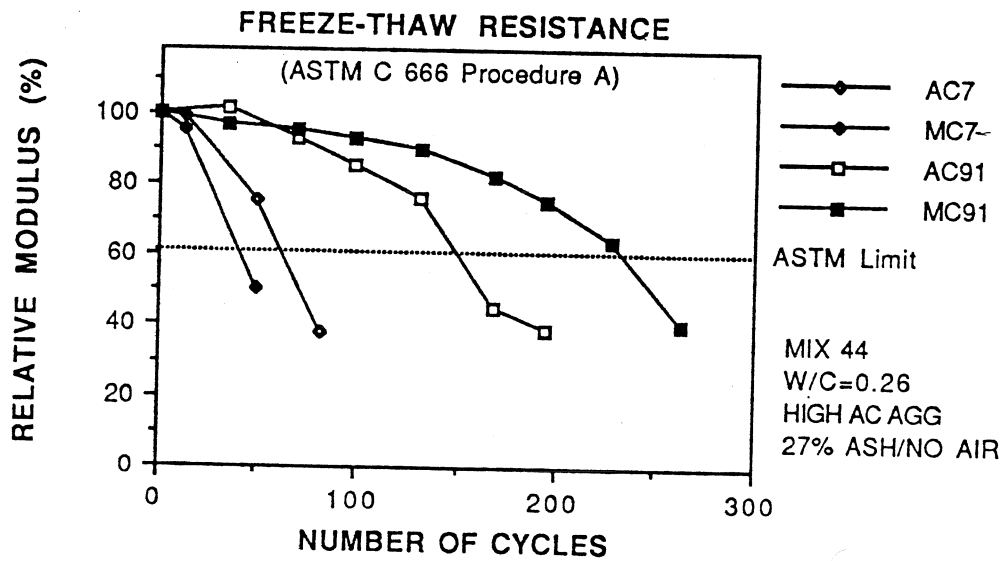
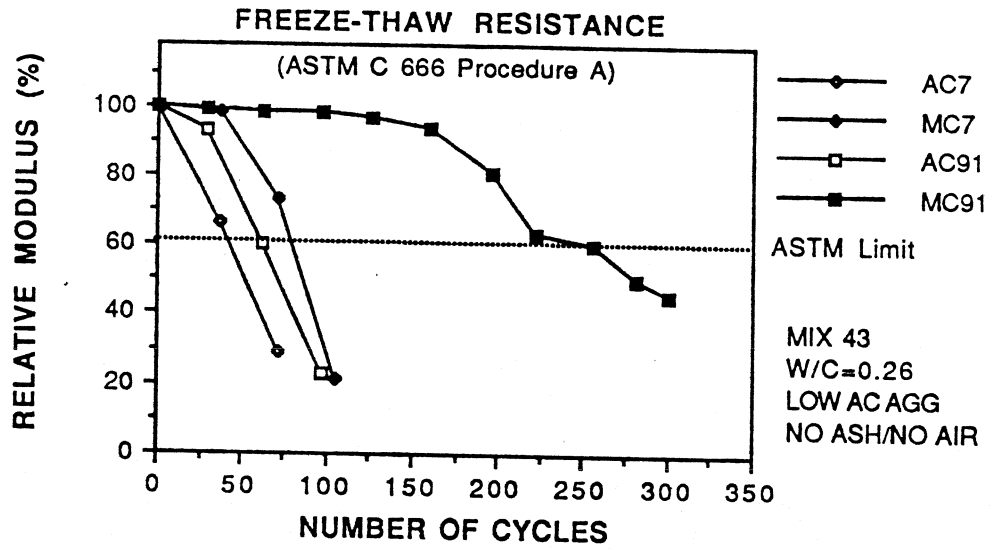


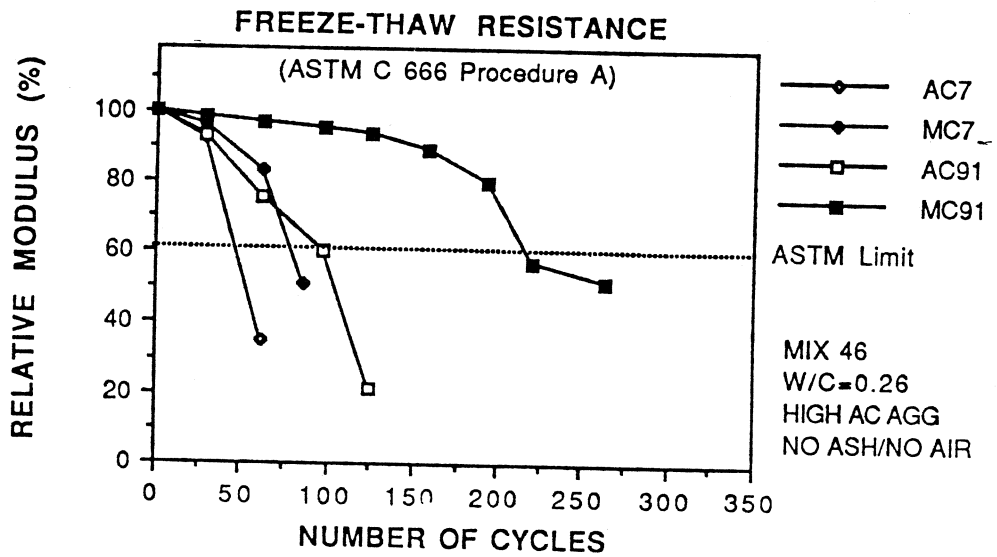
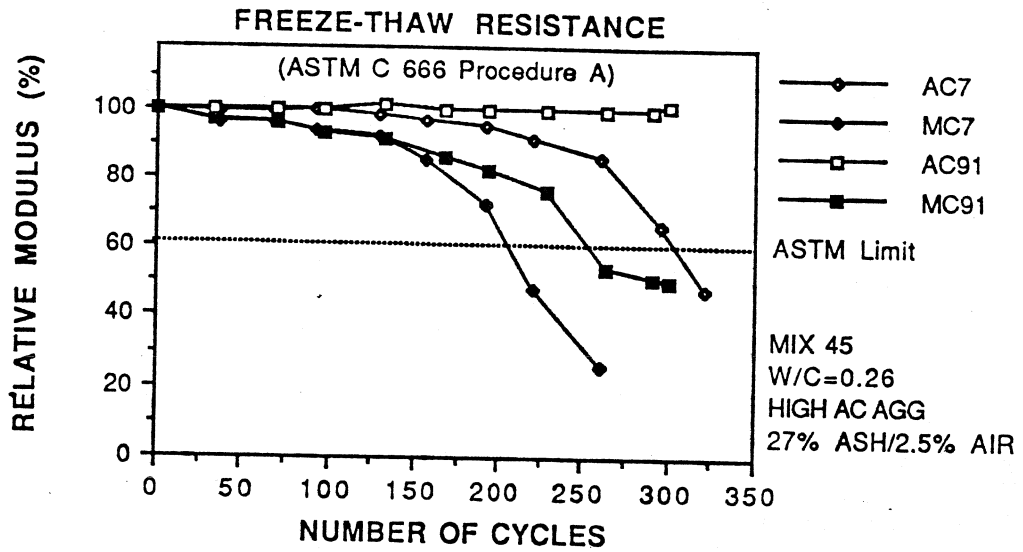


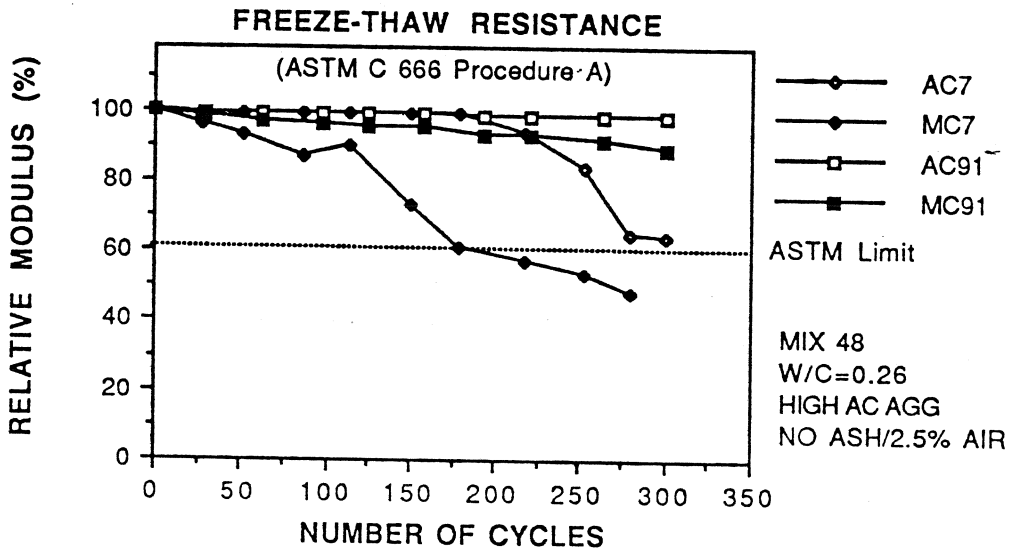
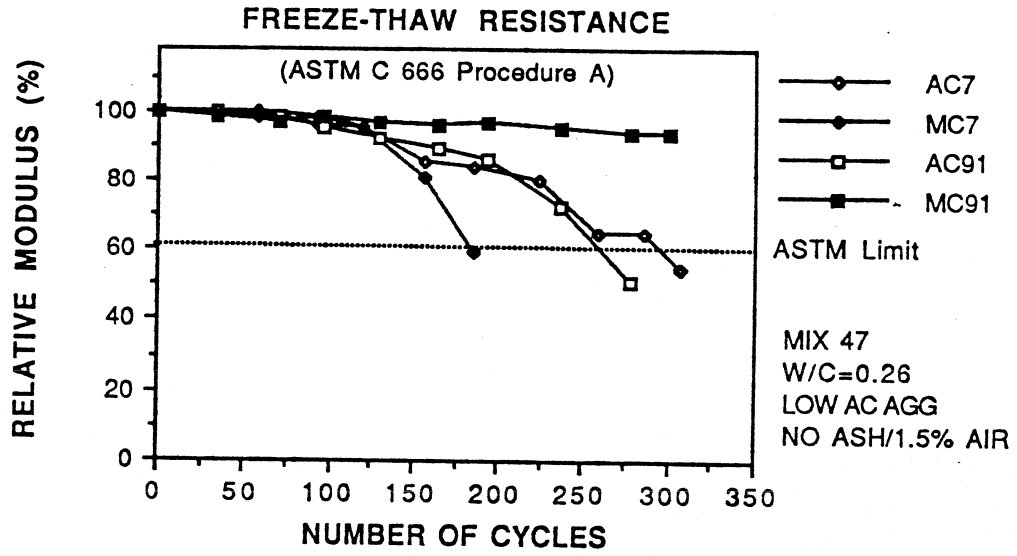


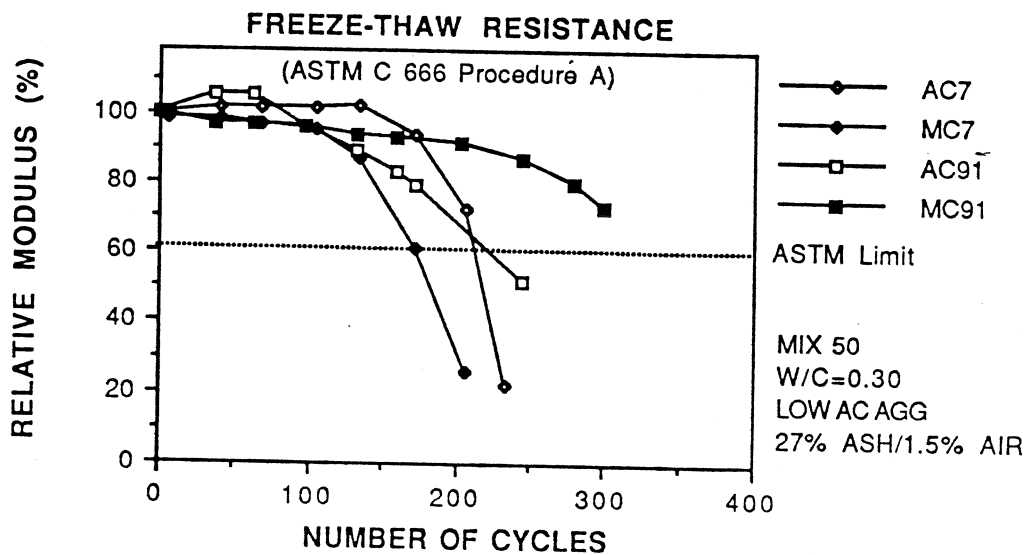
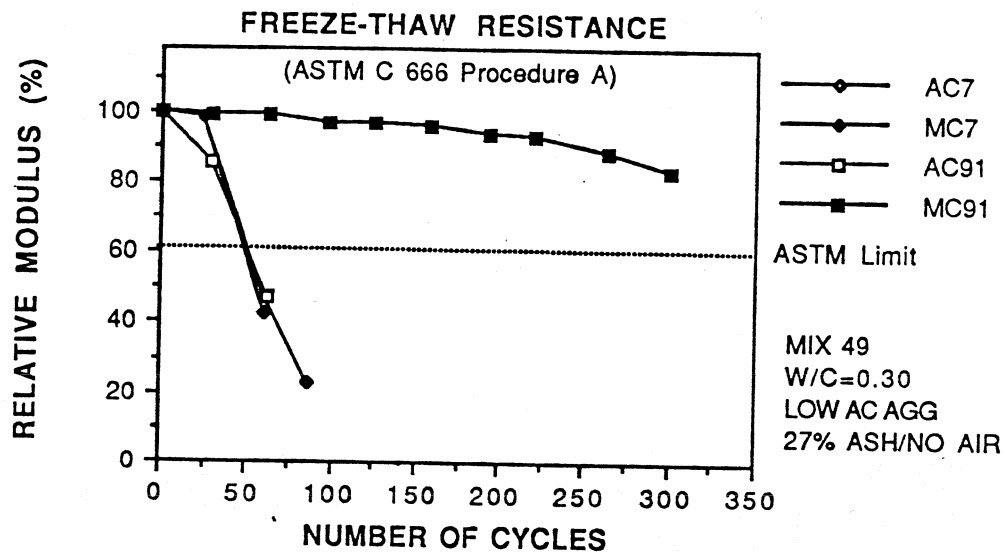


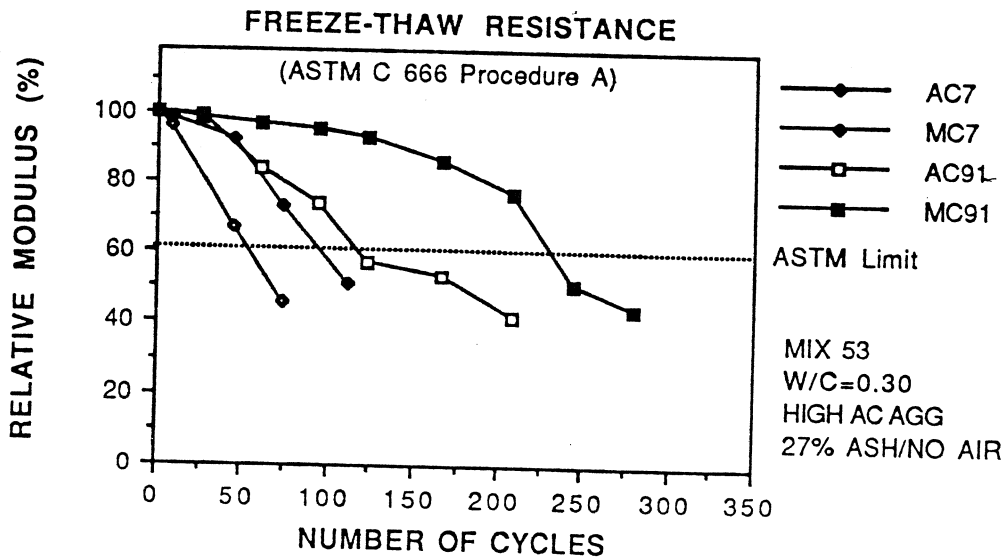
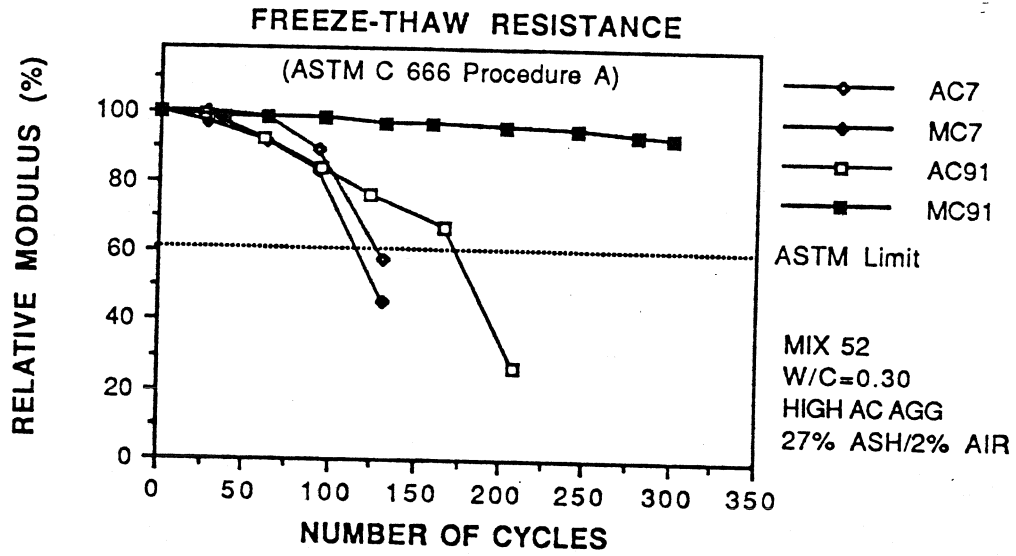


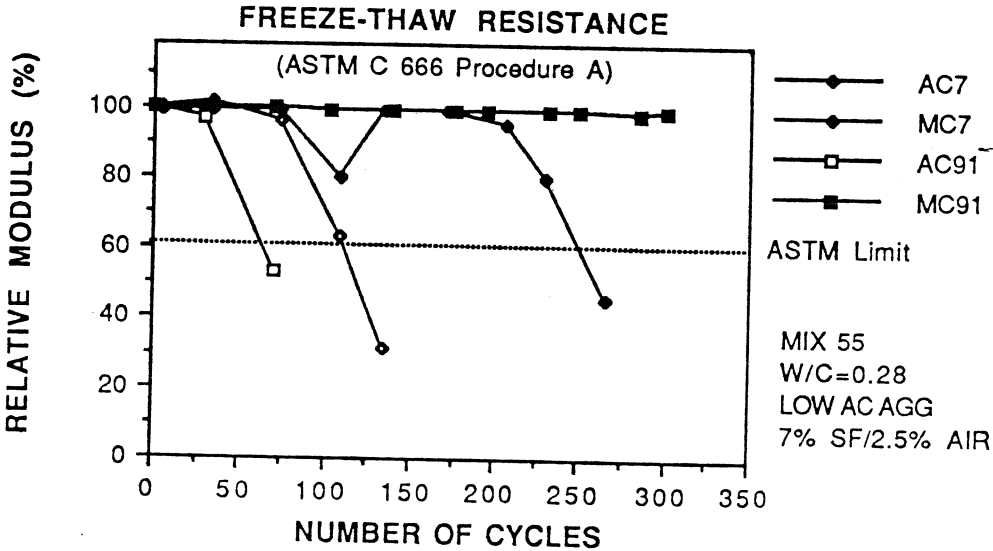
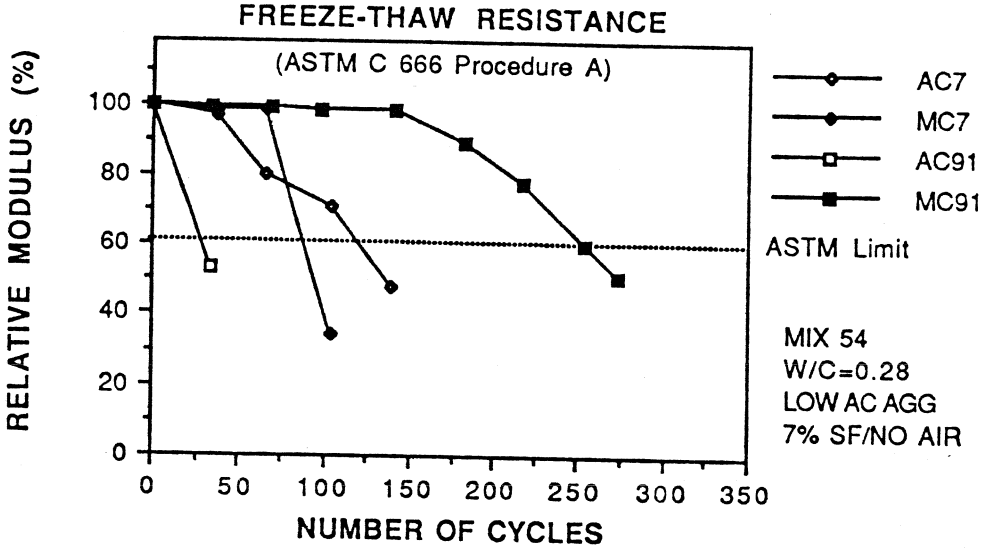


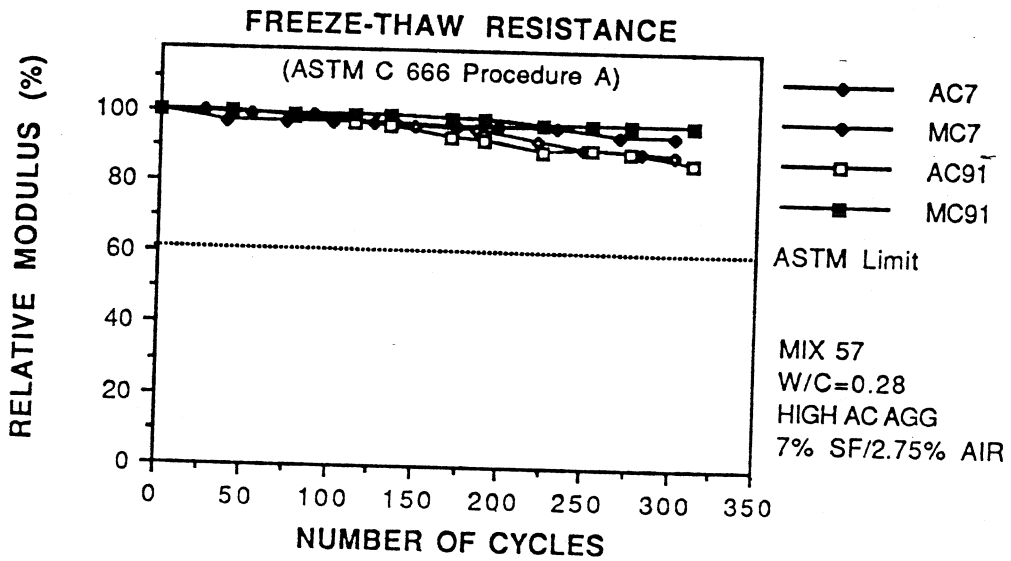
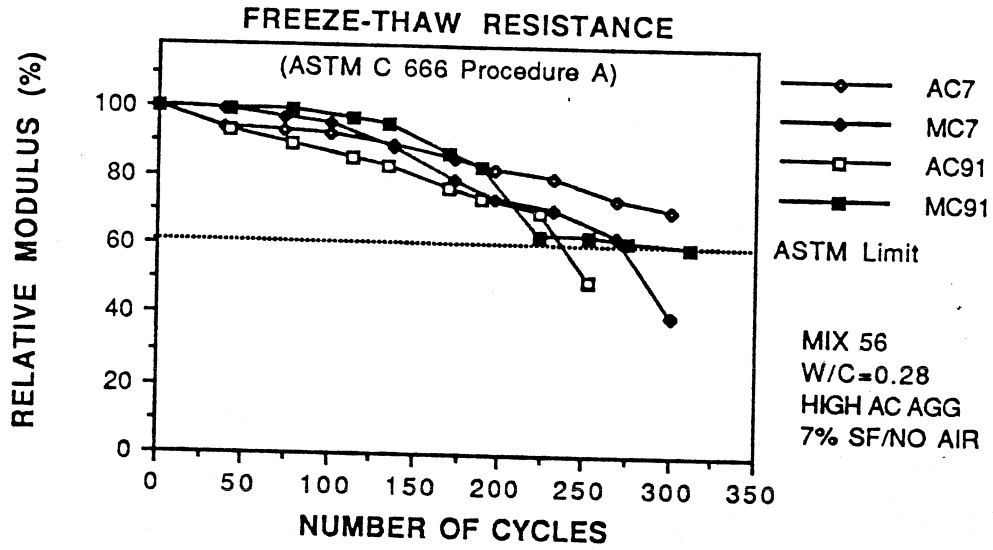


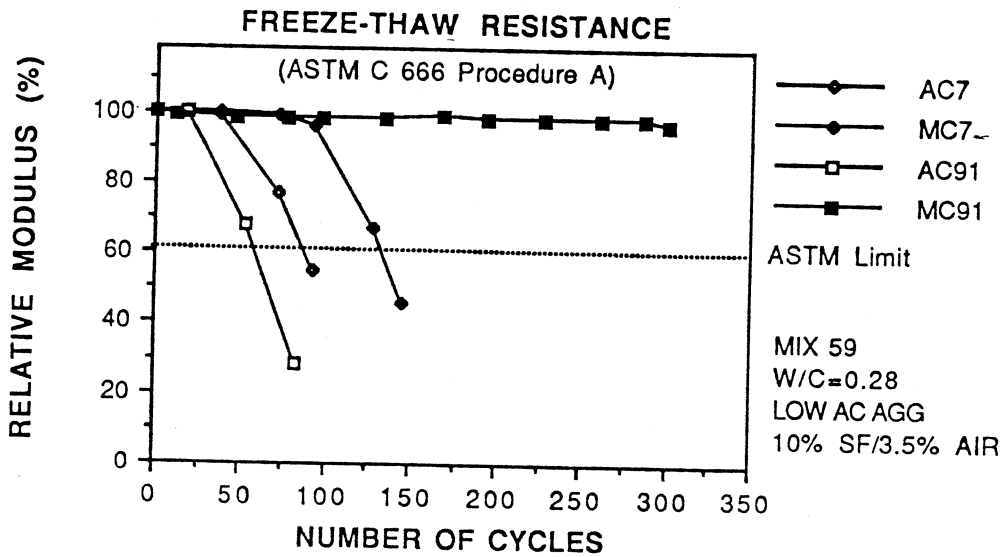
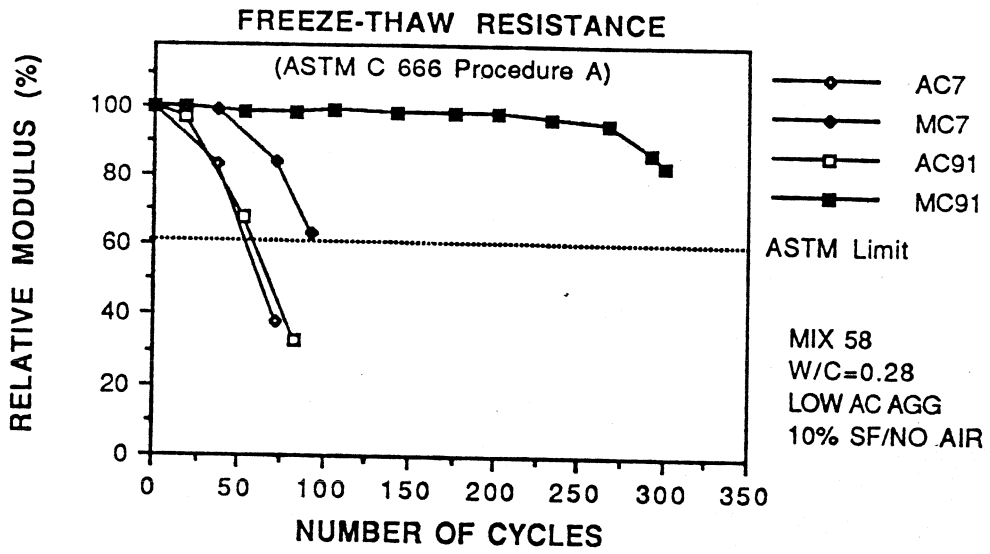


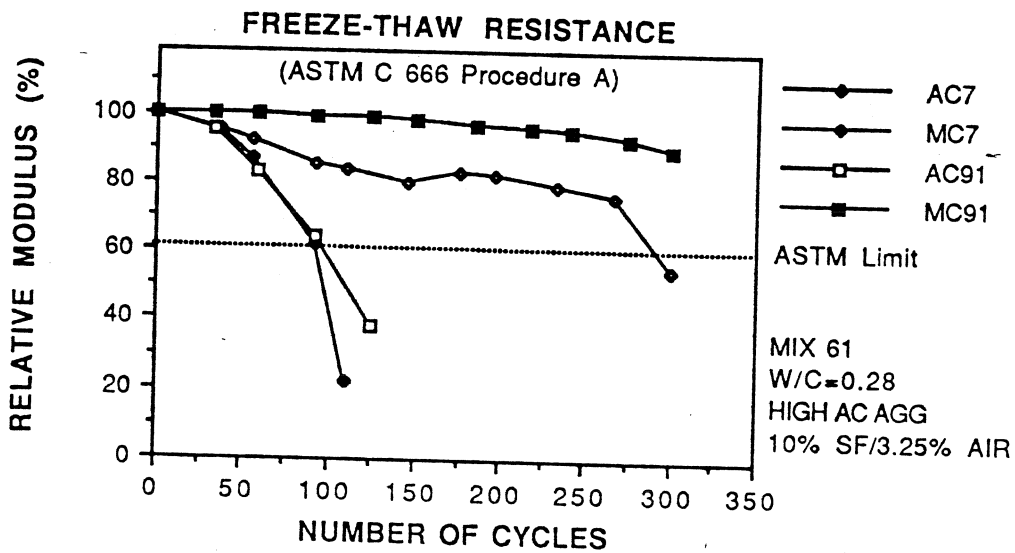
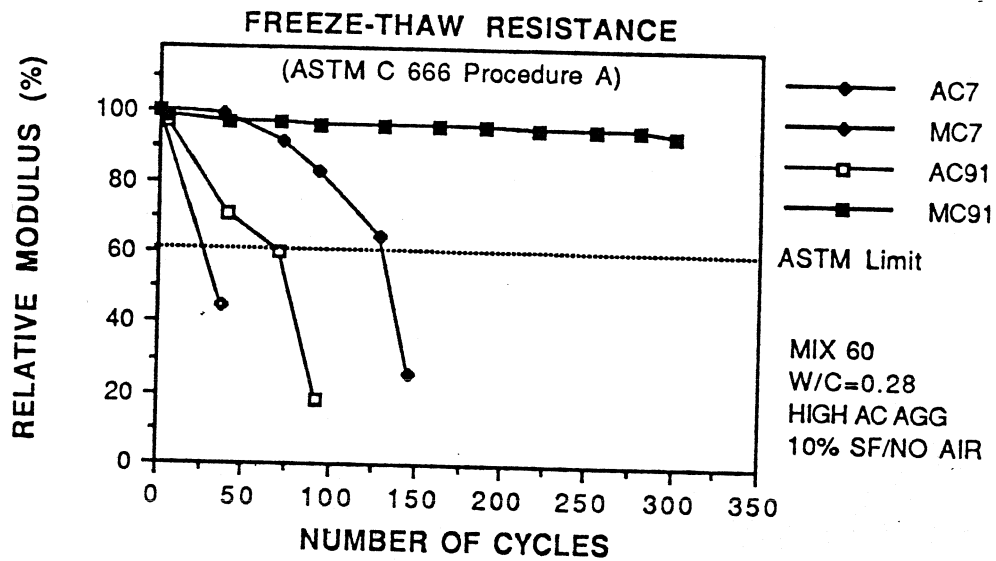


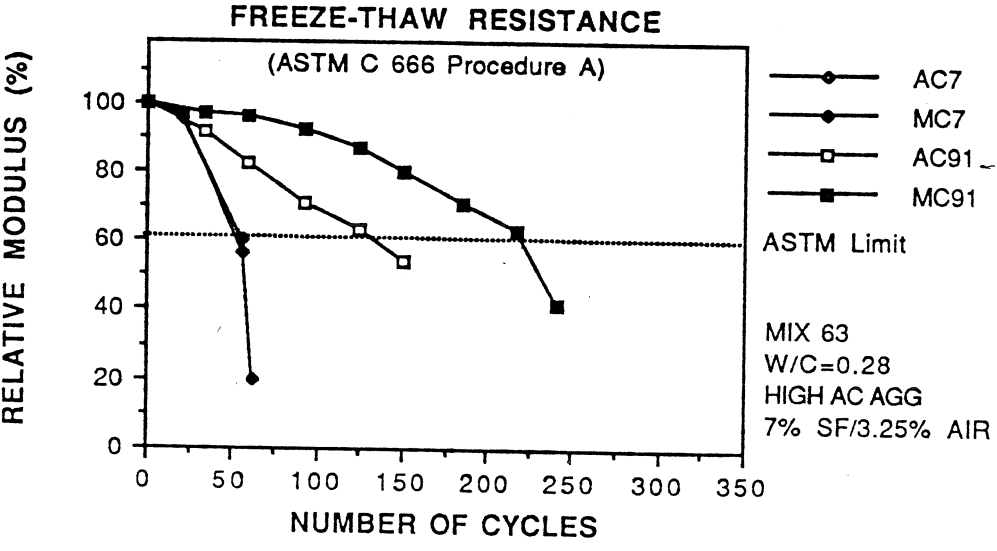
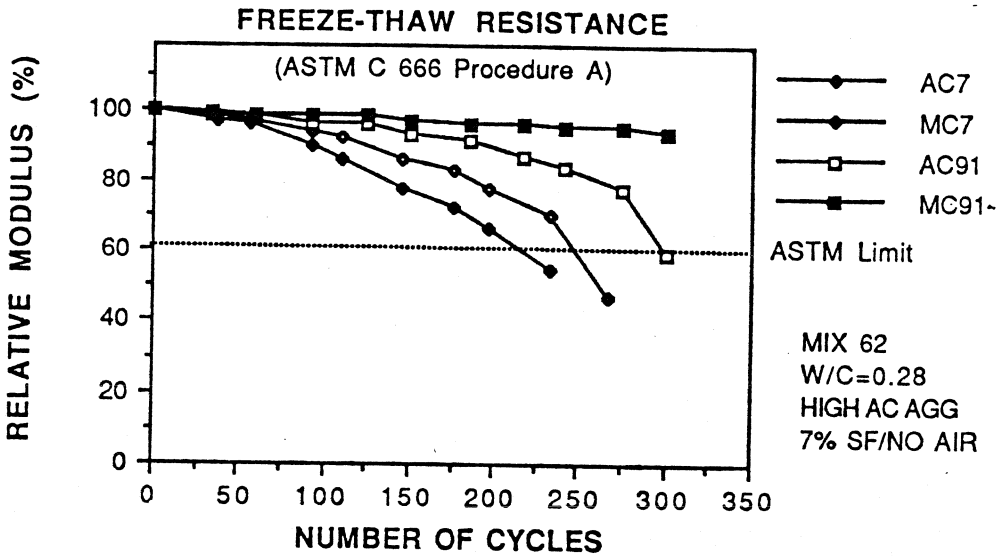


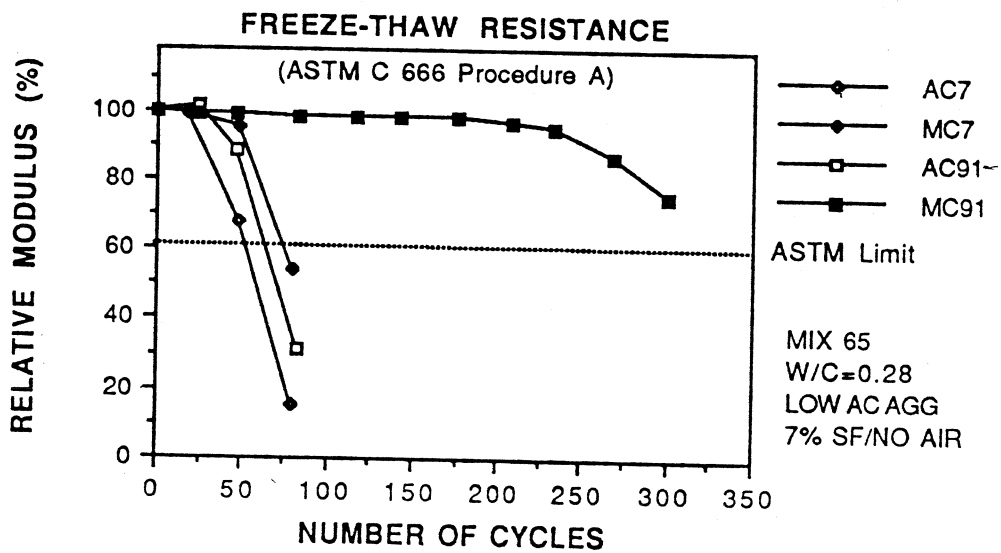
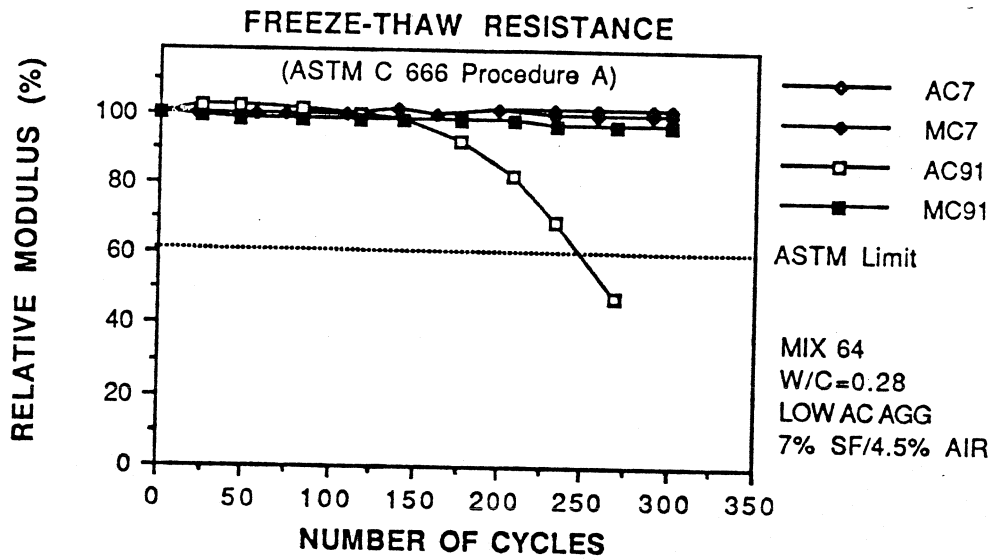


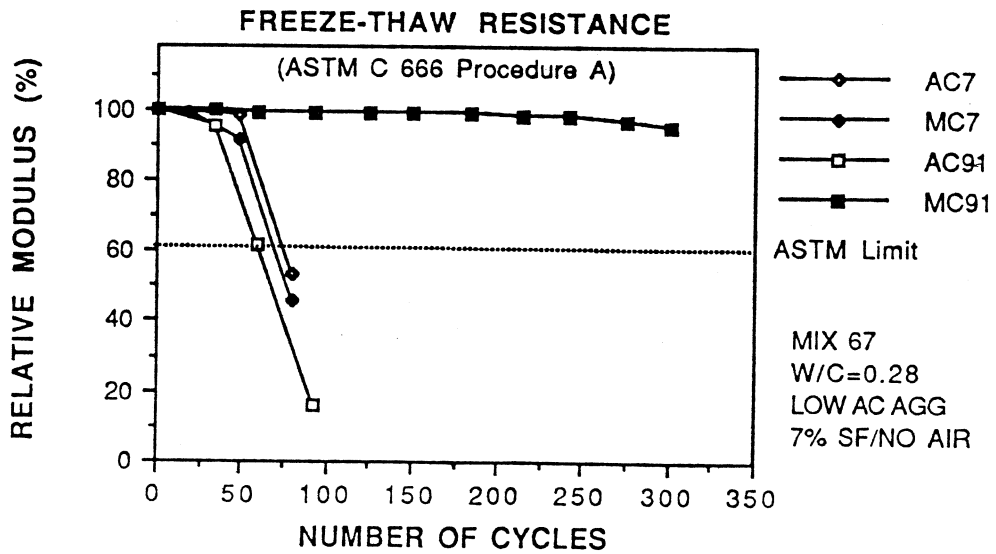
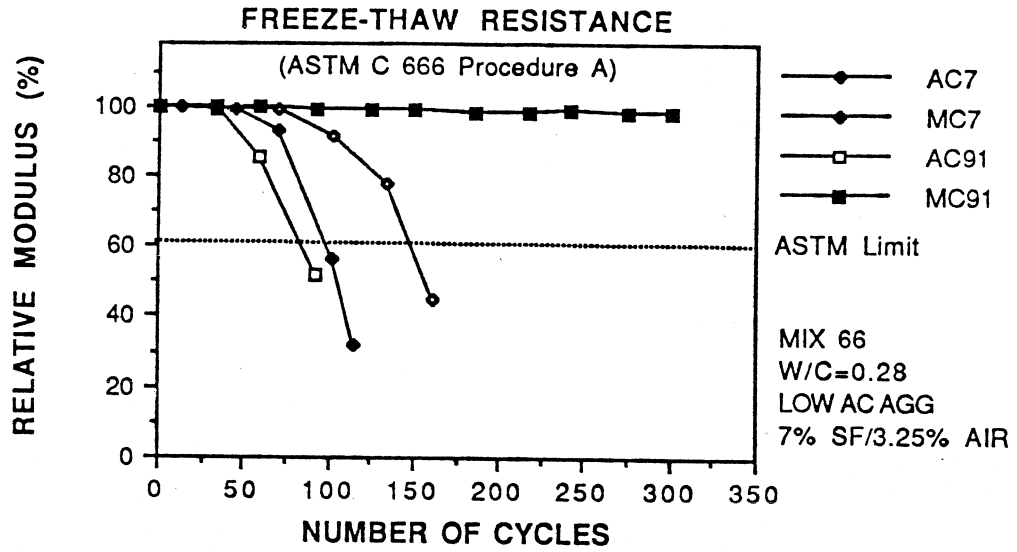


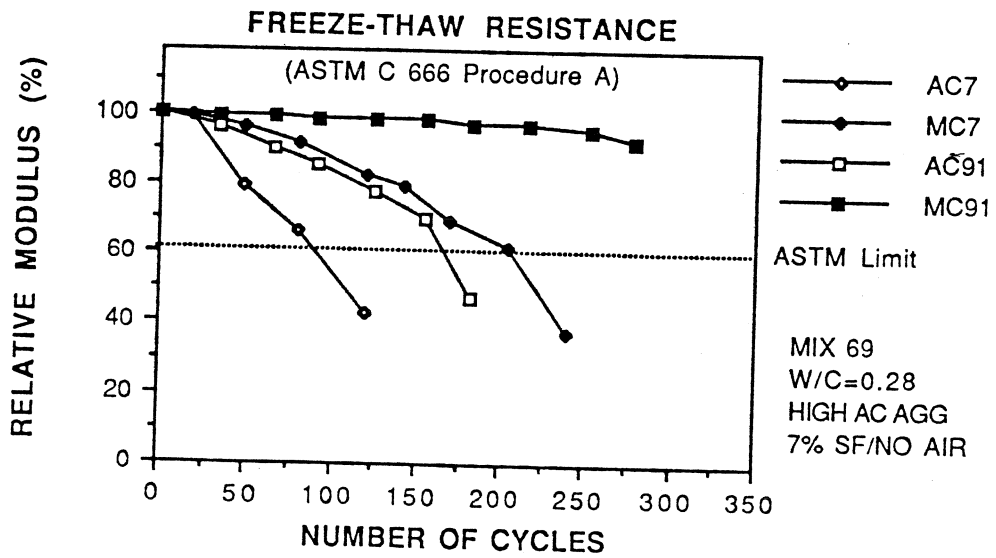
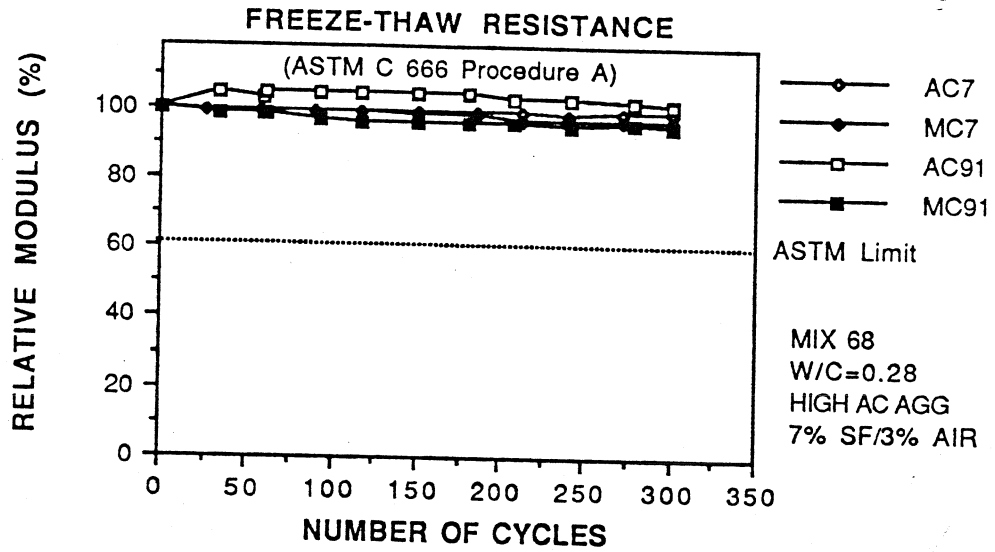












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