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VALUE-ADDED USE OF CLEAN COAL TECHNOLOGY
BY-PRODUCT IN CONCRETE

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Major professor

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VALUE-ADDED USE OF CLEAN COAL TECHNOLOGY BY-PRODUCT IN CONCRETE

By

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ABSTRACT

VALUE-ADDED USE OF CLEAN COAL TECHNOLOGY BY-PRODUCT IN CONCRETE

By

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Coal fly ash and clean coal technology by-products represent major volumes of solid wastes disposed of in landfills. Environmental concerns have led to increased adoption of the clean coal combustion technologies in power plants, substantially increasing the volumes of clean coal technology by-products. This research evaluates the by-products of the calcium spray dryer clean coal technology as a partial replacement for Portland cement in concrete. This by-product possesses higher calcium and sulfur oxide contents, and lower silicon, aluminum and iron oxide contents when compared with the conventional Class F coal fly ash, which is commonly used in concrete.

The clean coal technology by-product, when replacing 15 ~ 30% by weight of cement in concrete, produced concrete materials with performance characteristics comparable to those obtained with conventional coal fly ash. The clean coal by-product concrete possessed better scaling resistance than fly ash conventional concrete. When compared with plain concrete, the clean coal by-product concrete had comparable (or slightly reduced) 28-day compressive strength, improved chloride permeability, and comparable

scaling resistance and freeze-thaw durability. The clean coal technology by-product concrete, like fly ash concrete, responded better than plain concrete to extended moist curing periods.

Capillary pore system characteristics were found to be a fundamental property explaining the effects of the clean coal technology by-product in concrete. There was a general reduction in capillary porosity, particularly after longer moist curing periods, in the presence of the clean coal technology by-product. The pozzolanic reaction of the by-product seemed to block the pores and thus reduce their continuity, which explains the drop in permeability in the presence of the by-product. There was a marked effect of prolonged moist curing on the total capillary porosity and particularly on the volume of larger pores. This explains the highly beneficial effects of extended moist curing on the engineering properties of the clean coal technology by-product concrete. It is my general conclusion that the by-product of calcium spray dryer offers a strong potential for use as a mineral admixture with positive effects on permeability and thus durability of concrete.

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LIST OF ABBREVIATIONS

Abbreviation	Meaning
ASTM	American Standards for Testing Materials
C-S-H	calcium silicate hydrates
mm	millimeter
MPa	million pascal
nm	nanometer
W/C	water-cement ratio
Å	angstrom
μm	micron

CHAPTER 1

INTRODUCTION

Environmental concerns have led to increased use of clean coal combustion technologies in coal-burning power plants. This has led to the generation of tremendous volumes of clean coal technology by-products which are largely disposed of in landfills. These by-products generally comprise conventional coal fly ash, the unreacted sorbent used to react with the sulfur oxide present in emissions, and the sorbent reaction products. Since conventional coal fly ash has found a large-volume market in concrete construction, it seems prudent to evaluate the potential of clean coal technology by-products for use in this market.

This research evaluates the by-product of the calcium spray dryer (clean coal) technology for use as mineral admixture (to partially replace Portland cement) in concrete. The research compares the effects of the clean coal by-product and conventional Class F coal fly ash on the structure and properties of concrete materials with diverse mix proportions which are subjected to different moist curing durations. Both short-term mechanical properties and long-term durability characteristics are considered.

Chapters 2, 3, 4 and 5 present literature surveys on the scaling resistance of fly ash concrete, air void system characteristics of fly ash concrete, clean coal technology by-products, and microstructural characteristics of concrete. The experimental program statistical analyses of results are presented in Chapter 7. The results of microstructural studies and the structure-property relationships are given in Chapter 8. Chapter 9 presents a summary of the research project and its conclusions.

CHAPTER 2

FLY ASH EFFECTS ON THE SCALING RESISTANCE OF CONCRETE: A LITERATURE REVIEW

2.1 INTRODUCTION

The use of salt on concrete pavements to remove ice may cause an accelerating surface disintegration of pavements in the form of scaling. Concrete that is adequately air-entrained for frost resistance may nevertheless be damaged by repeated application of deicing salts; freezing and thawing of concrete in combination with salt action present one of the most aggressive influences on concrete.

Concrete pavements commonly use fly ash as a partial substitute for cement. Concerns have, however, been raised regarding the scaling resistance of fly ash concrete. The properties of the surface layer of concrete play an important role in the scaling phenomenon.[1] Scaling is most likely to occur on surfaces that have been overvibrated, trowelled too early and too long, subjected to plastic shrinkage, or where excessive bleeding has occurred. In these conditions a weak layer of paste or mortar tends to form either at the surface or just below it, and there may exist microcracks or bleeding channels through which surface solutions can be transported to lower levels. Careful mix design, placing and finishing should eliminate many potential problems. If adequate moist curing is followed by a period of drying before deicing chemicals are applied, tendencies towards scaling should be reduced substantially.[1]

2.2 SCALING MECHANISMS

A number of physical and chemical mechanisms have been proposed to cause scaling, as discussed below.

2.2.1 Physical Mechanisms

The consumption of heat required to melt ice when deicer is applied causes a rapid drop in the temperature of concrete just below the surface, which may cause differential thermal strains. Deicing chemicals may accumulate in concrete just below the surface to form relatively concentrated solutions. When rain water accumulates on the surface, the phenomenon of osmosis occurs, whereby water flows to equalize concentration differences. Considerable osmotic pressure can be created by this effect, causing rupture of cement paste. The additional free moisture present at concrete surfaces may also encourage the growth of microscopic or macroscopic ice lenses near the surface.

Scaling often occurs in the form of small flat flakes breaking away from the pavement mass. The flakes appear to be sound; this is also true for the mass of concrete. Quite likely, the reason for this phenomenon lies in deicer gradient and the degree of saturation. Above the failure plane of the scale, the solution of deicer in concrete pores is too concentrated to produce sufficient freezing to cause failure (antifreeze effect). Saturation at the surface is determined by the vapor pressure of the solution present. Strong calcium chloride solutions have a much lower vapor pressure than pure water. These solutions draw moisture from concrete, lowering the surface saturation. The background saturation is determined by the original mix proportions, curing conditions, and the environment. The higher this background level, the more vulnerable the concrete is to deicer scaling. The concentration gradient and the degree of saturation together produce scaling in the form of flakes.

A variable which has to be considered with respect to its possible contribution to the scaling process is temperature. Every freeze-thaw cycling process inherently involves a temperature cycling process. The influence of temperature cycling on the absorption of deicer solutions plays a role in deciding the scaling of concrete materials.

2.2.2 Chemical Mechanisms

While salt scaling is generally believed to be a physical action, there are some chemical phenomena which may pronounce the effect. The pH of pure calcium chloride solutions can vary from 6.0 in dilute solutions to 4.0 in saturated solutions. It is likely that these acid solutions react directly with the cement paste in concrete to yield readily soluble salts.

It has been shown that saturated solutions of calcium chloride, without freeze-thaw cycling, can be deleterious to concrete. The mode of attack depends on the water-cement ratio of concrete. It has been hypothesized that at low water-cement ratios, leaching is the key deterioration mechanism under exposure to saturated calcium chloride solutions, while at higher water-cement ratios (0.7 by weight), degradation results mainly from deposition and crystallization.

An interesting property of the attack on concrete by saturated calcium chloride is its dependence on temperature. The specimens cycled from 45 to 75°F (6.2 to 24.0°C) deteriorate much faster than those cycled from 15 to 45°F (-9.4 to 6.2°C). This increase in reactivity with increasing temperature is characteristic of a chemical reaction.

The effect of strong solutions of sodium chloride, the other common deicing chemical, in the absence of freeze-thaw cycling has received little attention.

2.3 FLY ASH EFFECTS

A combination of different factors influence the scaling resistance of concrete.[1,2] These factors include mix proportions (cement content, water-cementitious ratio, level of cement substitution with fly ash, etc.), cement type, finishing and curing procedures, and exposure conditions after the placement of concrete.

Fly ash may change the scaling resistance of concrete through its effects on: (a) reduction of water requirements for fresh mix workability; (b) reduction of permeability and filling of large capillary pores with relatively insoluble calcium silicate hydrates; [3,4,5,6,7] (c) causing slower rates of strength gain at early ages; (d) increase in the influence of temperature on the rate of reactions in concrete; (e) destabilizing the entrained air void system in fresh concrete; and (f) changing the chemical composition of concrete and pore water. These factors are expected to have opposing effects on the scaling resistance of concrete. The specific effects of fly ash on surface characteristics of concrete have not been fully investigated.

While the mechanisms through which fly ash influences the scaling resistance of concrete are not well understood, a number of investigators have performed experimental studies on the scaling resistance of fly ash concrete. The reported test data dealing with the effects of curing procedures, fly ash type, fly ash content and water-cement ratio on the scaling resistance of fly ash concrete are summarized below.

Gebeler et al.(1989)[3] conducted scaling tests on five sets of air-entrained concrete slabs cured in the following conditions: moist-cured at 73°F (23°C); air-cured at 73°F (23° F); membrane-cured at 73°F (23°C); membrane-cured at 40°F (4.4°C); and moist-cured at 40°F (4.4°C). Concrete mixtures with Class C or Class F fly ash as well as control mixtures without fly ash were investigated. Five replications were made in scaling tests with each class of fly ash under each curing condition. Mixtures with fly ash had total binder contents of 517 lb/cu.yd. (307 Kg/cu.m.) and 474 lb/cu.yd. (282 Kg/cu.m.), and fly ash-binder ratios between 0.4 and 0.45; those without fly ash had cement contents of 517 lb/cu.yd. (308 Kg/cu.m.) and 474 lb/cu.yd. (283 Kg/cu.m.). The fresh mix air contents were almost constant in all mixtures, ranging from 6 to 6.5 percent.

Following curing, the slabs were ponded with a 1/4-in. (6-mm) layer of water on the test surface for 3 days, after which the freeze-thaw deicer test cycles commenced. Freezing took place in a room maintained at $0 \pm 3^{\circ}F$ ($-18 \pm 1.7^{\circ}C$); thawing was accomplished in a room maintained at approximately $70^{\circ}F$ ($21^{\circ}C$). To start the thawing, flake calcium chloride was applied to the 1/4-in. (6-mm) layer of ice on the top surface at the rate of 2.4 lb/yd^2 (1.40 Kg/M^2). After thawing, the slabs were washed and 1/4-in. (6-mm) layer of water was replaced. Slabs were subjected to one freeze-thaw cycle per day. The amount of scaling was determined visually at selected intervals of 100, 200 and 300 cycles.

A summary of the scaling test data at 300 cycles reported by Gebeler et al.(1989)[3] is presented in the Table 2.1.

Table 2.1 Average Deicer Scaling Test Results for Various Curing Conditions (Gebeler et al., 1989).[3]

Class of fly ash	Scale rating at 300 cycles[a]				
	73°F (23°C)			40°F (4.4°C)	
	Moist cure	Air Cure	Membrane Cure	Moist Cure	Membrane cure
C	3-	3	2	2-	2-
F	3	3-	2+	2	2+
Control Mixtures 517 pcy[b]	2-	2	2-	1+	2
474 pcy[b]	1+	2+	2	1	2-

(a) Where: 0 = No scaling
1 = Slight scaling
2 = Slight to moderate scaling
3 = Moderate scaling
4 = Moderate to severe scaling
5 = Severe scaling
(b) To convert pounds per cubic yard to kilograms per cubic meter, multiply by 0.594.

Analysis of the data presented in Table 2.1, disregarding the observed experimental errors, have led Gebeler et al.(1989)[3] to make the following conclusions:

- Under moist curing at 73°F (23°C), air-entrained concretes with fly ash showed somewhat less resistance to deicer scaling than the control concretes, and there was essentially no significant difference in deicer scaling performance between either class of fly ash.
- Air-entrained concretes with fly ash, when air-cured at 73°F (23°C), showed somewhat less resistance to deicer scaling than either of the control concretes. The lack of moisture during curing did not have significant effects on the deicer scaling resistance of concretes with fly ash. However, the control concretes did show slightly

less deicer scaling resistance after air curing as compared to moist curing. This was particularly noticeable for the control mix with lower cement content. Overall, the lack of moisture during curing had relatively small effects on the deicer scaling resistance of concretes with or without fly ash. Some test data reported in the literature, however, suggest that air-drying may have beneficial effects on deicer scaling resistance.[8]

- Membrane curing at 73°F (23°C) improved the deicer scaling resistance of fly ash concrete as compared to moist curing or air curing at 73°F (23°C). For the control air-entrained concretes (without fly ash), the effect of membrane curing on deicer scaling resistance was minor.
- Air-entrained concretes without fly ash which were moist cured at 40°F (4.4°C) showed slightly better resistance to deicer chemicals than air-entrained concretes with fly ash.
- For specimens that were membrane cured at 40°F (4.4°C), concretes with Class C fly ash had essentially the same deicer scaling resistance as control concretes. However, concretes with Class F fly ash showed slightly less resistance to deicer chemicals than concretes with Class C fly ash or those without fly ash.
- Examination of the overall performance of air-entrained concretes cured at moderate and low temperatures, and subjected to deicer chemicals during freezing and thawing, indicates that low-temperature moist curing of concretes with or without fly ash resulted in somewhat better resistance to deicer chemicals. However, concretes with

fly ash that were membrane cured showed essentially no difference in resistance to deicer chemicals for the two temperatures.

A statistical analysis of the data summarized in Table 2.1 was conducted in order to account for random experimental errors in the analysis of the observed trends. The results of statistical analysis (multiple comparison[14]) indicated that random experimental errors are relatively large and, given the limited number of replications in scaling tests reported by Gebeler et al.(1989)[3], the stated conclusions can not be verified statistically. The results of the multiple comparison study performed on the scaling test results of Gebeler et al.(1989)[3] are summarized in Figure 2.1. This figure presents the mean values of the scaling test results as well as the range of the least significance difference for each condition. The least significant difference is the smallest difference for which significance can be declared (in this case with 5% level significance, that is with 5% chance of error in declaring a significance difference). An analysis of Figure 2.1 indicates that, considering the random experimental errors for the given test data at 5% level of significance, the addition of fly ash to concrete does not have significant adverse effects on scaling resistance under similar curing conditions. The only exception to this rule was for moist curing at 73°F (23°C), where fly ash (particularly Class F) caused negative effects on scaling resistance. Considering the trends observed, however, one may suggest that more replications of tests are needed in order to have a more powerful conclusions regarding fly ash effects on scaling resistance.

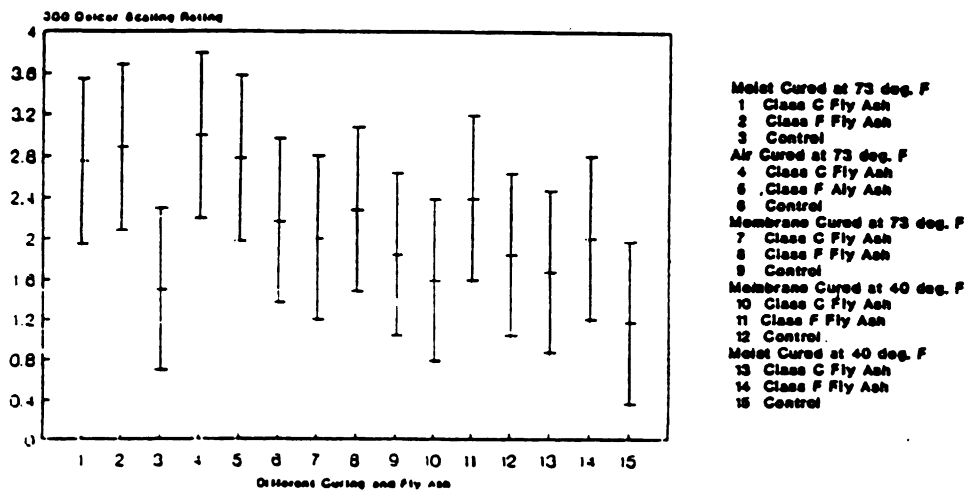


Figure 2.1 A Summary of the Multiple Comparison Analysis of Scaling Test Results.

Klieger et al. (1987)[9] have also reported the results of scaling resistance tests on fly ash and control concretes subjected to different curing conditions. The fly ash concrete used in this study contained 388 lb/cb.yd. (230 Kg/cu.m.) of cement and 129 lb/cu.yd. (77 Kg/cu.m.) of fly ash (a 25% cement replacement with fly ash). The control concretes had a cement content of 517 lb/cu.yd. (307 Kg/cu.m.), with no fly ash. Curing in this study was of five different types: moist curing at 73°F (23°C); air curing at 73°F (23°C); membrane curing at 73°F (23°C); membrane curing at 40°F (4.4°C); and moist curing at 40°F (4.4°C). The severity of scaling was determined visually.

The scaling test data reported by Klieger et al(1987)[9] indicated that :

- Air-entrained concretes with Class C fly ash cured at low temperature generally showed good performance when subjected to freezing and thawing in water or salt solution.
- The lack of moisture during curing had only a minor effect on the deicer scaling performance of air-entrained concretes with or without fly ash.
- Air-entrained concretes with either class of fly ash and moist-cured at 73°F (23°C) showed approximately equal performance when subjected to deicer chemicals during freezing and thawing.
- Air-entrained concrete with Class F fly ash cured at low temperature had slightly less resistance to deicer scaling than air-entrained concretes with Class C fly ash or without fly ash.
- Air-entrained concrete with Class C fly ash, membrane cured and stored at low temperature, showed essentially the same deicer scaling performance as air-entrained control concretes without fly ash.

Gebeler et al. (1989)[3] suggest that strength level is an important factor deciding the scaling resistance of concrete, and fly ash effects on deicer scaling performance can be partly illustrated by the fly ash effects on compressive strength. Figure 2.2 illustrates that, for concretes with or without fly ash cured at 40°F (4.4°C), deicer scaling resistance generally improves with increasing compressive strength. This finding is consistent with Kliger's[9] conclusion that "The development of a certain level of strength has merit as an index to the amount of curing required for air-entrained concrete prior to permitting the use of deicers."

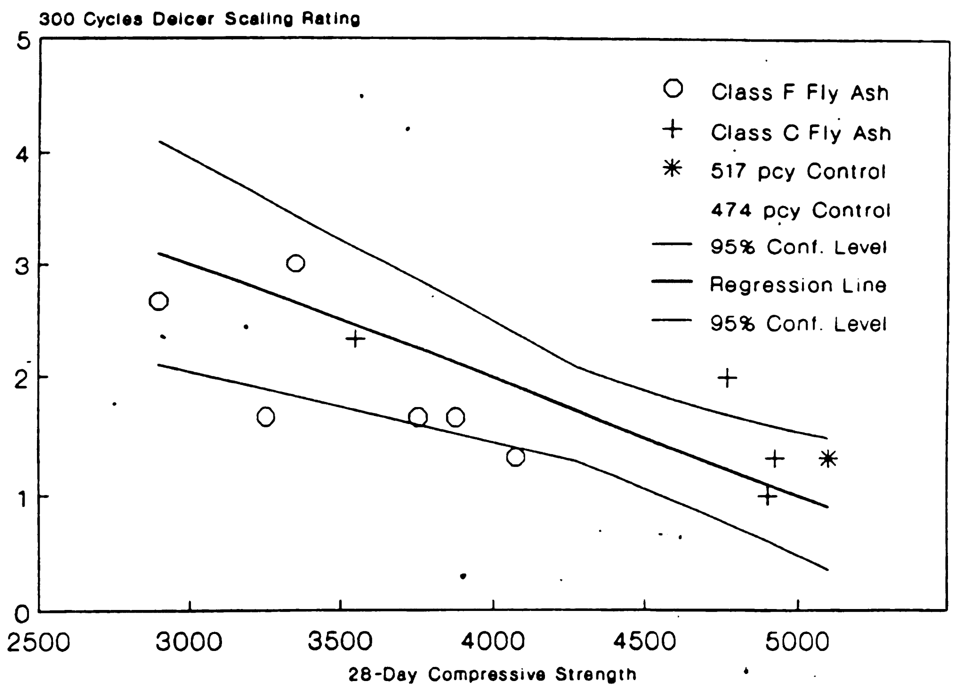


Figure 2.2 Deicer Scaling Performance Versus Compressive Strength of Low-Temperature-Cured Concretes With or Without Fly Ash.[3]

Johnston (1987)[10] suggests that a safe upper limit of water-to-cement plus fly ash ratio in fly ash concrete with respect to scaling is between 0.40 and 0.53, which is comparable to the limit of 0.45 on water-to-cement ratio recommended for normal concrete exposed to deicing agents. The laboratory and field test data analyzed by Johnston (1987)[10] indicate that fly ash concrete with 550 lb/cu.yd. (326 Kg/cu.m.) of cement and 275 lb/cu.yd. (163 Kg/cu.m.) of fly ash, can be satisfactorily used for applications involving deicer scaling exposures, provided that the water-to-cement plus fly ash ratio is about 0.4.

Malharta et al. (1987)[11] report test results on concretes with (Class F) fly ash content of 158 lb/cu.yd. (94 Kg/cu.m.) and cement content of 473 lb/cu.yd. (281 Kg/cu.m.), with 25% of cement substituted by fly ash, indicating that increased water-to-cement plus fly ash ratio has negative effects on surface scaling. At water-to-cement plus fly ash ratios of 0.6 and 0.4, slight scaling could be observed after 300 and 500 cycles of freezing and thawing, respectively.

Tyson (1987)[12] and Johnston (1987)[10] suggest that there are upper limits on cement replacement with fly ash beyond which scaling can become a problem. Test results presented by Johnston (1987)[10] on air-entrained concretes with cement plus fly ash contents of 503 lb/cu.yd. (299 Kg/cu.m.) and 488 lb/cu.yd. (290 Kg/cu.m.), at water-to-cement plus fly ash ratio of 0.53 indicate that scaling for the concrete without fly ash is negligible; it is slight for the concrete with 16% fly ash, and severe for the concrete with more than 27% fly ash. Tyson[12,13] suggests that scaling test results performed on concretes with 423, 517 and 564 lb/cu.yd. (250, 305 and 335 Kg/cu.m.) of cement plus fly ash at fly ash replacement levels of 25 and 50% indicate that optimum levels (for the specific fly ash types used in this investigation) appear to be closer to 25 percent than 50 percent.

2.4 CONCLUSIONS

Relatively large variations (random experimental errors) are observed in the limited test data reported on the scaling resistance of fly ash concrete. Statistically sound conclusions regarding fly ash effects on the scaling resistance of concrete can not be derived from the available experimental results. The following general trends may, however, be distinguished in the reported data:

(a) Fly ash effects on scaling resistance seem to be dependent on the curing conditions. For membrane-cured concretes, the scaling resistance of fly ash concrete (at 25% cement replacement level, with either Class C or Class F fly ash) was similar to that of conventional concrete.

(b) The scaling resistance of fly ash concrete seems to be dependent on the fly ash type. While under same curing conditions Class C and Class F fly ashes produced similar results, under other curing conditions Class C had a tendency to produce better scaling resistance than Class F fly ash.

(c) Scaling resistance of concrete, with or without fly ash, seems to improve with increasing compressive strength of concrete. The relationships between scaling resistance and strength have been observed to be similar in conventional and fly ash concretes (with 25% cement substitution with fly ash).

(d) There seem to exist limits on cement substitution with fly ash and also on water-binder ratio, beyond which fly ash concrete may exhibit pronounced deicer scaling.

CHAPTER 3

FACTORS EFFECT THE AIR VOID SYSTEM ON THE POZZOLANIC MATERIALS:A LITERATURE REVIEW

3.1 INTRODUCTION

The use of internal vibration to consolidate fresh concrete has been one of the most beneficial technological advances in concrete industry. It has greatly facilitated placement and consolidation of concrete of relatively stiff consistency and as a results, has permitted use of stronger and less massive reinforced concrete members. In virtually all applications, internal vibration has permitted wider use of denser, higher quality concretes.

Although considerable research has been undertaken to evaluate the effectiveness of vibration for consideration of concrete, its effects on the entrained air-void system and freeze-thaw durability of concrete are less well defined.[1]

Past research[5,6] has shown that fly ash can adversely affect the production of an adequate air content, but explanation of this effect has not been thoroughly establish. Other researchers[7,8,9] have found higher air-entraining admixture requirements for concretes containing fly ash than for concrete not containing fly ash. Larson[10] concluded that the higher air entraining admixture cement was due to the carbon content of the fly ash.

However, the air-entraining admixture requirement reported for concrete containing these fly ashes is still higher than for concrete without fly ash. Therefore, another main task is to obtain a better understanding of factors that influence the air entraining admixture requirement.[4] Nowadays, adding water to a plastic mix to increase slump is an extremely common practice, even though it is not recommended because it increases the porosity of concrete. Concrete often arrives on site more than half an hour after initial mixing. Placement operations can take anywhere from 10 to 60 min., depending on the field conditions and the size of load. When the slump decreases to an unacceptable level during the operations, water is added to the mix and, very often, experienced field inspectors will tolerate what can be termed "reasonable" retempering, i.e., enough to increase slump by 50 or 60 mm. If the air content of the fresh concrete is below the required minimum percentage when it arrives on site, it is also common to add an amount of air-entraining agent. Usually, just enough is added to reach the minimum acceptable value of air content because of the strength reduction due to the air-content increase.

Does retempering by adding water 30 or 60 min. after initial mixing have an effect on the air-void system, and particularly on the value of spacing factor? How much air-entraining agent must be used at about the same amount, not only increase air content but also decrease the spacing factor below the usual 200 um limit? These are very important questions concerning freeze-thaw durability and there are few data on the subject in the technical literature. Langan and Ward[17] have reported that using 2 to 5 percent of the original dosage of air-entraining agent is sufficient to increase the air content to the original level and will have little effect on the spacing factor. Results of field test by Burg[16] have shown that adding water to increase slump by an average of 25 mm had little influence on the spacing factor (L).

3.2 BACKGROUND

Thermodynamically, air void in fresh concrete is intrinsically unstable. Because of air pressure differentials within entrained air voids of different sizes, and at least temporary under saturation of air in mix water in fresh concrete, there is a natural tendency for air in smaller than average voids to dissolve into solution, and for air to be transferred to larger than average voids. The net result of these tendencies is an overall decrease in the fineness of the air-void system, growth of larger than average voids, and an increase in air content. There also is a tendency for air voids at exposed surfaces in to burst because of higher pressures in the air voids compared with ambient atmospheric pressure. Both tendencies are facilitated by high water-cement ratios. It is possible, however, that most spontaneous changes in air void systems are prevented from occurring while concrete is in the mechanically undisturbed state because of the cohesive strength of the concrete and the comparatively long diffusion paths between bubbles.

Work by Backstrom, Burrows, Mielenz, and Wolkodoff showed that compacction, including internal vibration, resulted in decreased air contents and smaller average size of air voids. Their work also indicated that vibration had little effect on void spacing factor (L). These authors also showed that longer periods of internal vibration resulted in greater loosed of air and further reduction in average size of air voids, where L remained virtually unaffected.[2] Work by Crawley[3] Produced results similar to those summarized above and further showed that frequency of vibration affected the stability of entrained air void system. Using frequencies of 6800 and 13,000 vibrations per minute (vpm), air losses were found to be greater with the higher frequency and to increased slump of fresh concrete. Both frequencies were found to remove nearly all entrained air when duration of vibration was exceed 1.5 and 4.5 minutes for concrete with initial contents up to 9%. These periods are considerably longer than commonly encountered in practice. Both frequencies also were found, after vibration for 90 second, to cause pronounced segregation of coarse aggregate and uneven distribution of entrained air voids. It is thus evident that internal vibration significantly alters the character of the entrained air-void system. Most significantly, it can be expected to reduced air contents.

The newly developed Dodson[11] "Foam Index" test was investigated. He suggested that this test could be used to estimate the air-entraining admixture requirement of Portland-cement concrete mixtures containing fly ash.[4]

3.3 LITERATURE TEST PROCEDURE AND RESULTS

David C. Stark[1] in his test, four parameters were used to determine the characteristics and performance of the concrete prisms. Air void characteristics of the hardened concrete were determined by linear traverse methods described in ASTM Designation: C457-82 Standard Practice for Microscopical Determination of Air Void Content and Parameters of the Air Void System in Hardened Concrete This was done on one of the four prisms for each variable combination. Numbers of /voids measured with chord intercepts in successive 12 micron intervals, up to 240 microns, also were recorded. Performance during freezing and thawing was evaluated by changing in weight and fundamental transverse frequency of vibration. Weights were measured on a balance sensitive to 0.5 g. All prisms were weight at 73 ± 1^{o}F in the saturated surface-dry condition. Fundamental transverse frequency of vibration was determined in accordance with ASTM Designation: C215-60 (Reapproved 1976) Standard Test Method for fundamental Transverse, Longitudinal, and Torsional Frequencies of Concrete Specimens. Relative dynamic modulus of elasticity, P, expressed in percent, was calculated from the following equation:

$$P = (N1/N)2 \times W \times 100 \qquad (1)$$

Where:

N = fundamental transverse frequency at zero cycles

N1 = fundamental transverse frequency at indicated number of cycles

W = ratio of weight of concrete prism at indicated number of cycles to weight at zero cycles.

As stated in ASTM C666-80, relative dynamic modulus of elasticity can be calculated from Equation 1, disregarding weights are relatively constant. However, significant weight losses developed for most of the concrete prisms; thus the weight change parameter, W, was included in the calculation of P. In this study, concretes were made with normal water-cement ratios of 0.4, 0.5, 0.6, and 0.7 and were subjected to internal vibration at frequencies of 0; 8000; 11,000; and 14,000 vpm prior to freeze-thaw testing in 4% NaCl solution. Air void characteristics of the various concretes were determined from linear traverse measurements while freeze-thaw durability were measurements of weight loss and changes in relative dynamic modulus of elasticity.

Test data revealed that, for all four water-cement ratio concretes, internal vibration, as carried out in this study, generally adversely affected the quality of the entrained air-void systems, compared with those in concretes that were not vibrated. Vibration led to reduced air contents and increased average void sizes and spacing factors. Change in air void parameters described above generally were reflected in the overall trends in relative freeze-thaw durability. Based on weight loss and change in relative dynamic modulus of elasticity, the greatest resistance to freeze-thaw deterioration occurred, in general, in the lowest water-cement ratio concretes subjected either to no vibration, or to vibration frequencies of 8000 vpm. Conversely, the lowest durability levels were found in the higher water-cement ratio vibrated at 14,000 vpm. None of the vibrated 0.40, 0.50, and 0.60 water-cement ratio concretes had durability levels as low as the 0.70 water-cement ratio concrete that was not vibrated. Results of this study thus support previous finding that internal vibration can significantly alter entrained air void system in concrete.[2] However, the manner in which vibration is carried out evidently determines whether it will adversely affect the final characters of air void systems and consequent durability of concrete in freeze-thaw exposures. In the present study, both were adversely affected by internal vibration. Since internal vibration has been used successfully in many applications for many years, the findings of this study illustrate the fact that it also can be used incorrectly with resultant adverse effects on the concrete durability. This possibility should bee kept in mind, particularly when high water-cement ratio concretes are being used.[1] Gebler et al.[4] in their investigation were to evaluate the effect of fly ash on the air void stability, and air entraining admixture requirement in concrete, and to investigate the applicability of "Foam Index" test. Fly ashes were selected to represent a wide range of chemical and physical compositions, as well as geographical location. Tests were performed on both freshly mixed and hardened concretes containing fly ash.

To evaluate the air void stability, air contents of plastic concrete were measured over a period of 90 min. After completion of initial mixing. A 1-min. remix, including retempering, was used at 30 min. intervals after the initial mixing. Concrete specimens were cast at 30 min. intervals for subsequent linear traverse measurements.

The "Foam Index" test for estimating the air entraining admixtures requirement was evaluated. Results of this test were compared to air entraining admixture requirement for concrete. This investigation was also directed toward obtaining a better understanding admixture requirements of concrete. The test concrete were proportion for a nominal cementitious material content of 517 pounds per cubic yard (307 Kg/m^3) with 75% Type I Portland cement and 25% fly ash by weight of Cementitious material.

Two control concrete mixtures without fly ash were also prepared. One control concrete had a nominal cement content of 517 pcy (307 Kg/m^3); the other control concrete had a nominal cement content of 474 pcy (281 Kg/m^3). The latter was used to provided early age strength development more nearly equal to concrete containing fly ash as well as for other durability studies.

The fly ash concretes used in this study contain 388 pcy (230 Kg/m^3) cement and 129 pcy (77 Kg/m^3) of fly ash. Relative to the control mixes, this fly ash concrete can be considered as a 25% cement replacement concrete to be compared with the 517 pcy (307 Kg/m^3) control and as a partial replacement plus admixture for comparison with the 474 pcy (281 Kg/m^3) control. In the latter case, 86 pcy (51 Kg/m^3) of cement (17%) is replaced by fly ash and 43 pcy (26 Kg/m^3) of fly ash (8%) is used as an admixture.

All concrete mixtures were proportioned to have a slump of 3 in. ± 1 in. (75 + 25 mm), with sufficient neutralized Vinsol resin to obtain a nominal air content of 6 ± 1 % in the plastic concrete.[4] The following findings and conclusions are based in large part on an arbitrary separation of the fly ashes used in this study into ASTM C 618 Class C and F designations based on 10% CaO content as a dividing line. Therefore, there may be exceptions to these general classifications. The findings and conclusion are presented below:

1. Generally, concretes containing Class C fly ash require less air entraining admixture than those concrete with Class F fly ash. All concretes with fly ash required more air entraining admixture than the Portland-cement concrete without fly ash.
2. Plastic concrete containing Class C fly ash tend to lose less air than concretes with Class F fly ash.
3. Spacing factors (L) on specimens cast over a period of 90 min. were essentially constant for the majority of concretes containing fly ash. In addition, the initial spread of results of specific surface and voids per inch (n) was essentially similar for concretes containing Class F or Class C fly ash. However, when measured on specimens cast at 90 min., concretes with Class F fly ash exhibited greater variability of results for these air void parameters than concretes with Class C fly ash.
4. As the air entraining admixture requirement increases for a concrete containing fly ash, the air loss increases.
5. Air contents in plastic concrete containing Class F fly ash at 90 minutes after completion of mixing were reduced as much as 59%. Similar results were obtained

on hardened concrete specimens cast at various time intervals after mixing.

6. The "Foam Index" test appears to be a good rapid test to predict relative air entraining admixture dosage requirements for concrete.
7. As the organic matter content, carbon content, and loss on ignition of fly ash increase, the air entraining admixture requirement increases, as does the loss of air in plastic concrete.
8. Generally, as total alkalis in fly ash increase, the air entraining admixture requirement decrease.
9. As the specific gravity of a fly ash increase, the retention of air in concrete increases. Concrete containing a fly ash that has a high lime content (Class C fly ash) and less organic matter tends to be less vulnerable to loss of air.
10. Generally as the SO_3 content of fly ash increases, the retained air in concrete increase.

3.3.1 Effect of Water/Cement Ratio

Water/cement ratio influences the size distribution of air voids because the cement paste air content and water phase viscosity are greatly altered as water/cement ratio changes.[12] As the water/cement ratio decreases, the viscosity of the water phase increases and the air content of cement paste decreases.

The effects of varying water/cement ratio on several air void system parameters were summarized in the following.

1. Increasing w/c while holding the ratio of air-entraining admixture to concrete volume constant greatly increases the total air content of the paste and produces larger air bubbles, thereby decreasing the specific surface of the voids. Note that spacing factor and freeze-thaw expansion decrease initially before developing an overall trend of increase. This indicates that the inclusion of some larger air bubbles may produce a better size distribution of air voids for freeze-thaw durability.
2. Increasing w/c while maintaining approximately constant air content results in the use of less air-entraining admixture at higher w/c ratios. Thus larger bubbles are again produced, specific surface decreases, spacing factor increases, and freeze-thaw resistance decreases accordingly.

3.3.2 Air-Entraining Admixtures

Air-entraining admixture are usually water-insoluble materials such as natural wood resins, fats, and oils that are processed and combined with the concrete mix water to produce microscopic voids in the cement paste. These entrained voids combine with voids produced by excess mix water and entrapped air to provide an air void size distribution that enhances freeze-thaw durability.

Air-entraining admixture can significantly alter the properties of both fresh and harden concrete[13]. Fresh air-entrained concrete is considerably more plastic and workable than nonair-entrained concrete. It can be placed and hardened with less segregation and has a lower tendency toward bleeding. Hardened air-entrained concrete.[13,14,15] This improved durability can be traced to improved mix uniformity, permeability, and absorption characteristics that are brought about by the increased number of small, closely-spaced voids in the paste.

Commonly-accepted critical values for air void spacing factor range from 0.006 to 0.01 in. (0.15 to 0.25 mm).[16] Analysis of hardened concrete air void systems reveals that the spacing factor for nonair-entrained concrete is generally higher than critical, while properly air-entrained concretes are generally lower than critical[15] and suggest that lack of adequate air-entrainment can seriously damage concrete subject to moderate or severe exposure.

While the use of entrained air improve the durability characteristics of Portland cement concrete, it is also known that reducing the w/c ratio can produce similar results (as described previously). However, tests by the U.S. Bureau of Reclamation found that air-entrained pastes with high w/c ratios were more durable than nonair-entrained pastes with low w/c ratios.[13] These findings lead to the conclusions that the relative improvement of durability due to air-entrainment is greater than increased durability that results when w/c is decreased.

The importance of air-entrainment in producing durable concrete is widely accepted. However, most known air-entraining admixtures (especially wood resin-based admixtures) have not been entirely satisfactory with respect to the stability of the number and/or volume of voids they have produced.[14] They have shown tendencies toward increased or decreased air content as mixing time is extended.

Another disadvantage of air-entrainment is the reduction of concrete compressive strength. Losses of up to 10% per 1% increase in entrained air have been reported. These are believed due in part to irregular void size and the coalescence of small voids during mixing or consolidation to produce much larger voids. These tendencies vary widely with the type of air-entraining admixture. For example, microscopic examination of a concrete produced using a methyl ester-derived cocamide diethanolamine (also known as cocamide DEA) found bubbles that are spherical in shape and have thick walls that resist coalescence. The wood resin-based admixtures produced bubbles with relatively thin walls that tend to be less spherical and prone to coalescence.[14] These difference were believed to account for differences in air content stability in the mixed and hardened concrete, with the cocamide DEA admixture performing more favorably. These more favorable air void sizes and distribution were found to result in increases in freeze-thaw durability of 400% and compressive strength increases of 25% at early ages and 10% at later ages.

From the above, it is clear that air-entrained concretes can produce air void systems that substantially improve concrete workability and freeze-thaw durability with minimal losses of compressive strength. However, there are substantial differences in the effectiveness and deleterious effects of various air-entraining admixtures.

Pigeon et al.[16] in their research was to studying the influence of retempering on the characteristics of the air-void system. It consists of preparing a mix with predetermined parameters and taking four sets of samples to determined the air-void characteristics of the harden concrete: at 10, 25, 55,and 85 min. after the initial water-cement contact. Periods of mixing followed by rest periods are used in laboratory to simulate agitation in mixer trucks.

Water retempering was investigated by adding enough water to the mix at 45 min., between the second and third sample preparation, to increase the slump from about 50 to 100 mm. This represents approximately 10 Kg of water per m^3 of concrete and, thus , a water-cement ratio increase of the order of 0.03 (0.45 to 0.48). Taking into account usual field practice and the effect on strength and freeze-thaw durability of the water-cement ratio, this amount of water was considered to be the upper limit of reasonable retempering. Four laboratory mixes were prepared using two different air entraining agents, each at two different dosages: one normal and one low. This was done to study the effect or retempering on two mixes with a normally stable air-void system, as well as on two with a probably unstable one. The two mixes with a normal amount of air-entraining agent were prepared a second time under field conditions.

Four laboratory and six field mixes were made, again systematically using two admixtures, to see if air-entraining admixtures can produce a correct air-void system, or significantly alter the existing one, when they are incorporated into the fresh concrete much later than the initial mixing period.

In the four laboratory concretes and in the first four field mixes, two different procedures were tested: two mixes were prepared with no air-entraining agent with the full dosage added at 45 min., two mixes were made with a low dosage of the admixture added in large quantity at 45 min. To serve as a reference point, two additional field mixes with a low air-entraining agent dosage were fabricated and not retempered. Water was always added with the admixture when the mixes were retempered to insure proper dispersion. Standard concretes with normal dosage of air-entraining agent (and no retempering) were fabricated for the first series of tests on air-void stability and, thus, were not repeated.

Water and air-entraining agent retempering was always carried out at 45 min. This allows air-void stability to be analyzed with two sets of samples before and after retempering, and also very approximately represents the time at which usual field mixes are retempered.[17]

The test results described indicate clearly that the air void spacing factor does not vary significantly when a mix is retempered by adding a sufficient quantity of water to increase the slump from approximately 50 to just about 100 mm. This is illustrated in Fig. 3.1 and 3.2, which show, respectively, the variation of the slump and variation of the spacing factor with time for five of the six mixes retempered with water only.

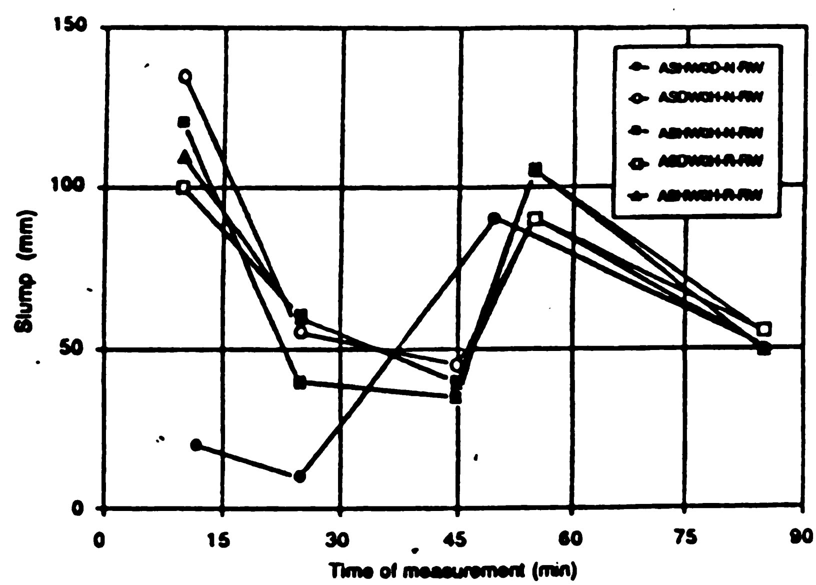


Figure 3.1 Variation of the Slump with Time for the Mixes Retempered with Water only at 45 Min.

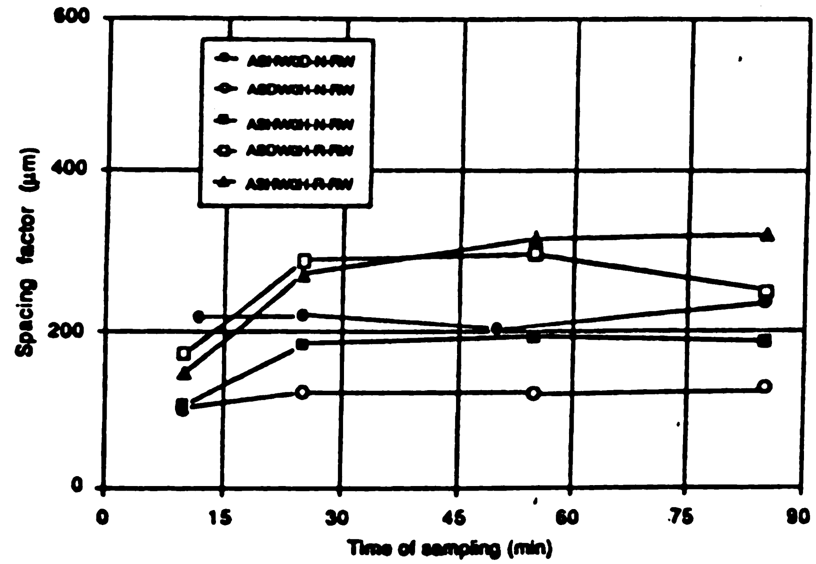


Figure 3.2 Variation of the Spacing Factor with Time for the Mixes Retempered with Water only at 45 Min.

The results shown in Fig. 3.1 and 3.2, although contrary to popular belief, are nevertheless extremely clear: when the slump increases sharply, the values of spacing factor stay constant. This is true for the three field and laboratory mixes with reduced dosages of the admixture and thus higher values of the spacing factor.

In some cases, retempering seems to cause a small increase in air content with a corresponding decrease of the specific surface, although the spacing factor stays relatively constant. Probably because less energy is required to entrain air in a less viscous paste, remixing a more fluid mix, as already pointed out, tends to cause the entrainment of additional air voids. These are large air voids, which have little effect on the spacing factor but increase the specific surface. As the results for air content and specific surface indicate, these air voids are not stable and tend to disappear with time.

The variation of the spacing factor with time for the mixes retempered with water and air-entraining agent at 45 min. is shown in Fig. 3.3 and 3.4. For the field and laboratory mixes that were nonair-entrained at the start (Figure 3.3), the spacing factor after addition of the air entraining agent is below 200 μm and stable in every case. For the mixes made with a reduced dosage the admixture (Figure 3.4), the value of the spacing factor immediately after retempering is correct, but it tends to increase with time for concretes containing the SH admixture. It is thus possible to entrain a correct air void system 45 min. after the initial water-cement contact, which means that the entraining and stabilizing effects of the air-entraining admixtures are still effective when various chemical reactions of hydration have been going on for that period of time. It is also possible to correct an unsatisfactory air-void system by adding more air-entraining agent after 45 min. The amount added, however, must be substantial, i.e. of this case, and the air-void spacing factor does not seem to become perfectly stable.

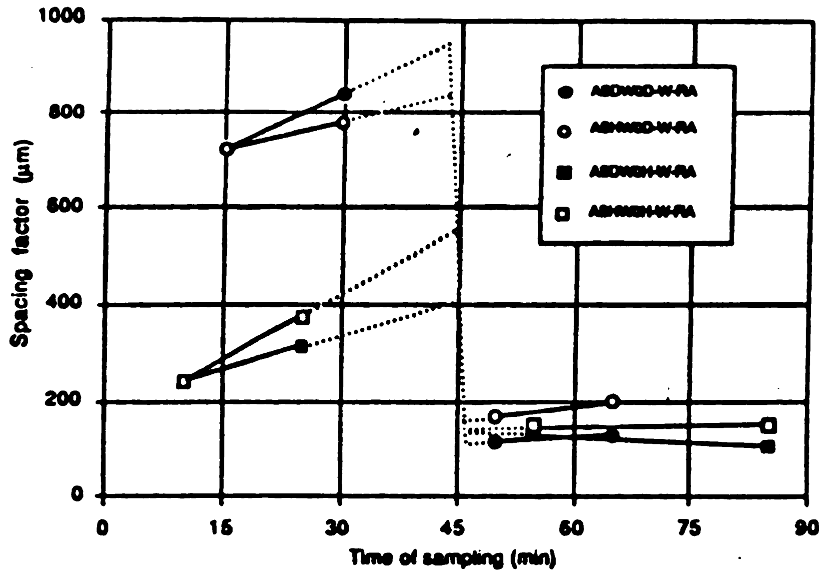


Figure 3.3 Variation of the Spacing Factor with Time for the Nonair-entrained mixes Retempered with Water and a Normal Dosage of Air-entraining Agent at 45 minute.

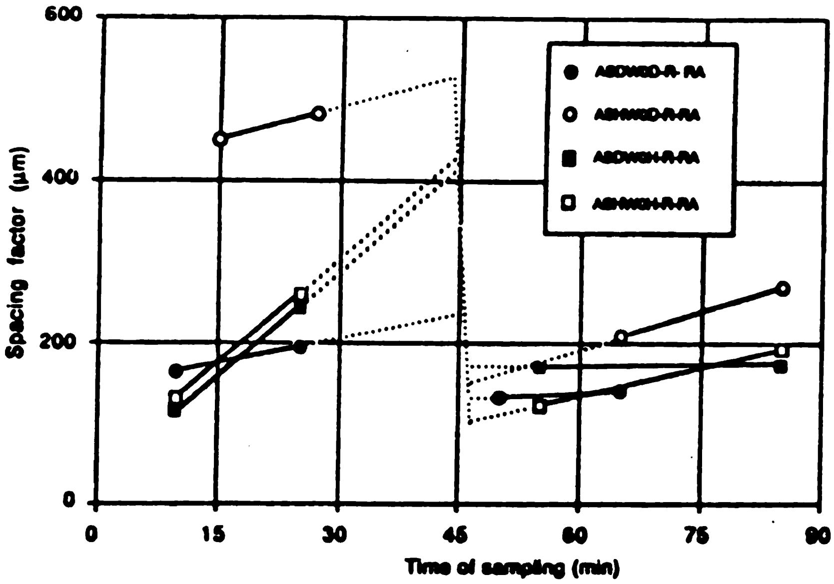


Figure 3.4 Variation of the Spacing Factor with Time for the air-entrained mixes Retempered with Water and a Normal Dosage of Air-entraining Agent at 45 minute.

It is also evident from the test results described that small air-content variations (less than about 2 percent) cannot be used to predict spacing factor variations. The spacing factor can increase significantly even if the air content stay relatively stable from 10 to 25 min., and the spacing factor can be stable while the air content decreases very substantially from 10 to 25 min. Of course, air losses can also correspond to spacing factor increases. These last examples illustrate another very important aspect of the problem of air entrainment: the difference between air-void production and stability. The air-void characteristics in samples prepared after 25 min. can be quite different from those in samples prepared after 10 min., even in mixes with normal initial air contents or in mixes with normal dosages of the air-entraining agent. The spacing factor can often be inadequate after 25 min. even if the value after 10 min. was lower than 200 um (Figure 3.2 to 3.4). This phenomenon seems to be more common in laboratory mixes, probably in part due to the high energy developed by the mixer.[17]

3.3.3 Summary

1. Retempering by adding enough water to increase the slump from approximately 50 to about 100 mm has no significant influence on the value of the air-void spacing factor, although it often causes a small increase in air content.
2. In a previously nonair-entrained mix, it is possible to entrained an adequate air-void system with a spacing factor of less than 200 μm if a normal dosage of air-entraining agent, with a little water, is incorporated into the mix 45 min. after the initial water-cement contact.
3. It is possible to correct an unsatisfactory air-void system by adding more of the air-entraining agent after 45 min., but to lower significantly the value of the spacing factor, the quantity of admixture that is added must be significant (more than about 30 to 50 percent of the normal dosage) to cause a marked increase of the air content.
4. Air-content variations of the order of 1 or 2 percent should not be used to predict spacing factor variations.

5. The characteristics of the air-void system tend to be more stable in field mixes than in laboratory mixes.
6. The air-entraining agents used in the series of tests can be both give satisfactory results, but at low dosages only the synthetic detergent admixture can produce an adequate and stable spacing factor.

CHAPTER 4

CLEAN COAL TECHNOLOGY BY-PRODUCTS:

A LITERATURE REVIEW

4.1 INTRODUCTION

The abundance of coal makes it one of the nation's most important strategic resources in building a more secure energy future. Coal can be one of the most useful energy sources of the country well into the 21st century and beyond. With current prices and technology, U.S. recoverable resources of coal could supply the nation's coal consumption at current rates for nearly 300 years (U.S. Department of Energy, 1989).[1] However, if coal is to reach its full potential and be both environmentally acceptable and economically competitive, an expanded slate of advanced clean coal technologies must be fully developed and implemented to provide substantially improved options that are superior to today's choices.

Almost 50% of the current inventory of electrical generating capacity in the United States will be over 30 years old by 1997 (U.S. Department of Energy, 1989).[1] The need to replace or refurbish this capacity, plus adding new capacity to keep pace with the rising demand for electricity, means that a major investment in electrical generation capacity should begin by the mid 1990's. Better technologies must be available for use on a commercial basis prior to the year 2,000 to avoid the economic and environmental penalties associated with continued investments in only the currently available state-of-the-art commercial technologies.

Through the 1980's concerns over acid rain and related air pollution issues have had the strongest impact on coal use. Many countries have taken steps to reduce sulfur dioxide (SO_2) and nitrogen oxides (NO_x), precursors of acid rain. In the U.S., the House and Senate bills amending the Clean Air Act include the provisions aimed at controlling acid rain through retrofit to existing plants. About 40% of the U.S. electricity generating units, representing 60% of capacity, could exceed the proposed criteria.

Recent concerns about global warming have also led to growing pressure for national and international action to curb emissions of "greenhouse gases," mainly carbon dioxide. Although scientists continue to debate the potential severity and even the existence of global warming, it makes sense to find ways to minimize coal's contribution to CO_2 emissions. Coal-fired generation and the industrial use of coal account for approximately one-third of CO_2 emissions in the United States.

4.2 CLEAN COAL TECHNOLOGIES

In 1983 a coalition of coal producers, utilities and equipment manufacturers proposed that the federal government join in a collaborative effort to accelerate the development of clean coal technologies designed to provide for effective and economical control of polluting emissions. This led to the Clean Coal Demonstration Program in 1986, administrated by the Department of Energy.

Recent work on clean coal has focused on reducing emissions of SO_2 and NO_x, which contribute to acid rain, through intervention before, during and after combustion. Technologies include:

1. Coal Cleaning and Upgrading
2. SO_2 Control
   -Lime/Limestone Flue Gas Desulfurization (FGD)
   -Furnace Sorbent Injection (FSI)
   -Duct Sorbent Injection
3. NO_x Control
4. Fludized-Bed Combustion
5. Integrated Gasification/Combined Cycle (IGCC)

4.2.1 Atmospheric Fluidized Bed Combustion

In fluidized-bed combustion, a granulated bed material (limestone or dolomite) encompasses the pulverized burning coal. This mixture of crushed coal and limestone is held in suspension by an upflow of combustion air. The coal burns in the bed and in the freeboard above the bed while the limestone is calcined to form lime which absorbs sulfur oxides, reducing their emission into the environment. This process generates large quantities of spent dolomite or limestone materials, magnesium or calcium sulfate, ash, and some unburned coal. During combustion, a portion of this material is continuously withdrawn to maintain optimum bed conditions and is carried by the combustion gases through the furnace to cyclones where a substantial fraction of the particulate matter is collected and recycled to the bed. The remaining particulate matter is carried by the flue gas to a fabric filter or electrostatic precipitator, where it is collected for disposal or use. Figure 4.1 presents a flow diagram of AFBC process located at Michigan State University, East Lansing, Michigan.

The fluidized-bed process generates by weight about three times as much spent bed residue as fly ash, and the total quantity of fluidized bed residues represents the total of the original dolomite or limestone sorbent plus the solid ashes from the burned coal and the chemical combination of sulfur and other reactive materials.[2]

The start-up of an atmospheric fluidized-bed boiler requires heating a portion of the bed to 315° C (600° F) to ignite the injected coal. After ignition, the temperature of the bed rises until the energy released in the bed equals the energy absorbed by the boiler tubes plus that in the hot gases leaving the bed, and the system achieves normal equilibrium. Excellent heat transfer and high heat capacity is maintained in a fluidized-bed boiler at a uniform temperature, typically in the range of 800 to 900° C (1472 to 1652 °F).[2]

High heat-transfer coefficients between the fluidized-bed and immersed steam generation surfaces reduce the steam tubing requirements and also permit operation at lower and more uniform bed temperatures. The lower temperatures reduce NO_X emissions and slag, decrease equipment corrosion, and produce ashes with chemical and physical properties which differ somewhat from those of conventional ash.

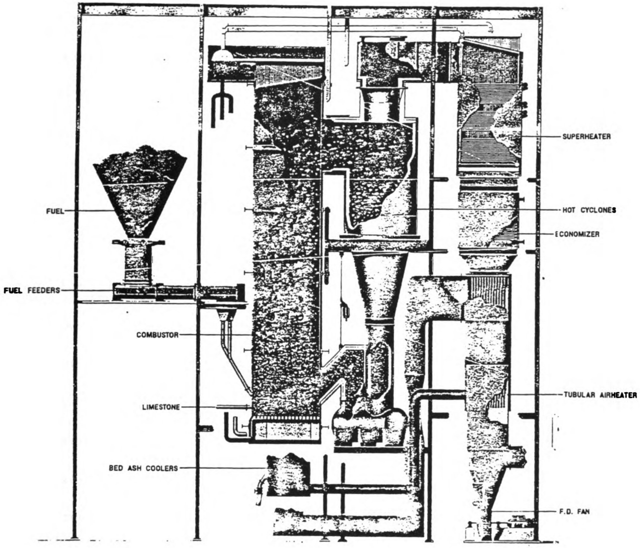


Figure 4.1 AFBC Process Located at Michigan State University.

4.2.2 Calcium Spray Drying

Spray drying is a process in which a slurry or solution is atomized into a hot gas stream to evaporate essentially all of the moisture. A dry product can then be separated from the gas. The spray dry FGD process consists of hot flue gas leaving the boiler and entering the spray dry chamber. Figure 4.2 is a schematic diagram of this process. In this reaction vessel, the gas is contacted with an atomized alkali solution, such as a lime slurry. Atomization can be achieved with either a rotary or nozzle-type atomizer and is necessary to maximize the SO_2/reagent contact. The water in the slurry is evaporated by the flue gas as the sulfur dioxide in the flue gas reacts with the alkali, forming dry sulfite and sulfate particles.[3] A variety of calcium-based and sodium-based alkalis have been evaluated, but slaked lime has the greatest commercial potential.

Some spray dryers act as a cyclone and collect some of the dry material in hoppers at the bottom of the contact chamber, while others rely on fabric filters or electrostatic precipitators to remove all the dry waste products from the gas stream. A flow diagram for such a system is shown in Figure 4.3. Although both systems work well, baghouses have an advantage over ESPs because some SO_2 removal is achieved on the bags. In either case, the flue gas exiting the spray dryer is directed to the particulate control equipment. The flue gas exiting the spray dryer is never allowed to reach its saturation temperature and is normally maintained at a temperature at least 11°C (20°F) above the saturation temperature. Normal approach to saturation temperatures may range from -6 to 10°C (20 to 50°F)[3,4].

In some installations, it is desirable to reheat the flue gas before it enters the particulate control equipment. Reheating prevents condensation in downstream equipment when a very low approach to saturation temperature is used. The need for reheat and the type of reheat is dependent on specific site conditions.

In a lime-based system, dry waste material is sometimes recycled to improve the system's lime utilization. The waste material recycled contains fly ash, unreacted lime, and waste reaction products. This also is the material collected by the particulate control equipment for later disposal or utilization. The solid waste is a dry flowable material with handling characteristics similar to fly ash. Normally the mixture is pneumatically conveyed to an ash silo for storage prior to disposal.

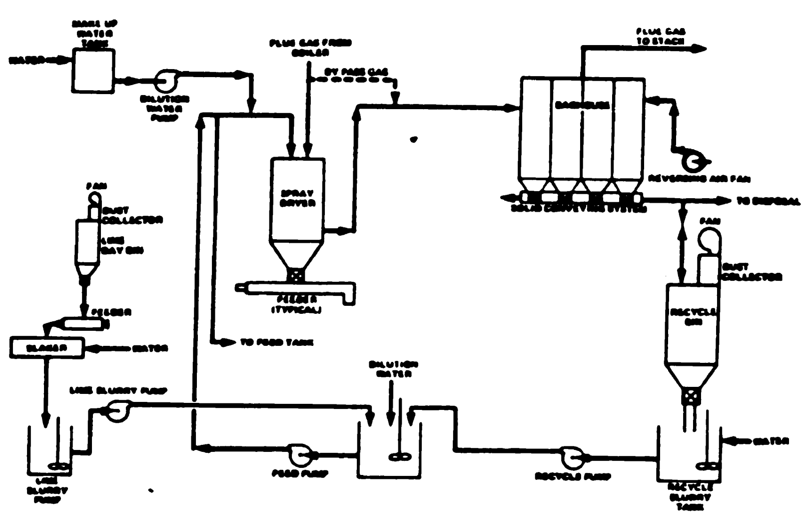


Figure 4.2 Spray Dry FGD System Schematic

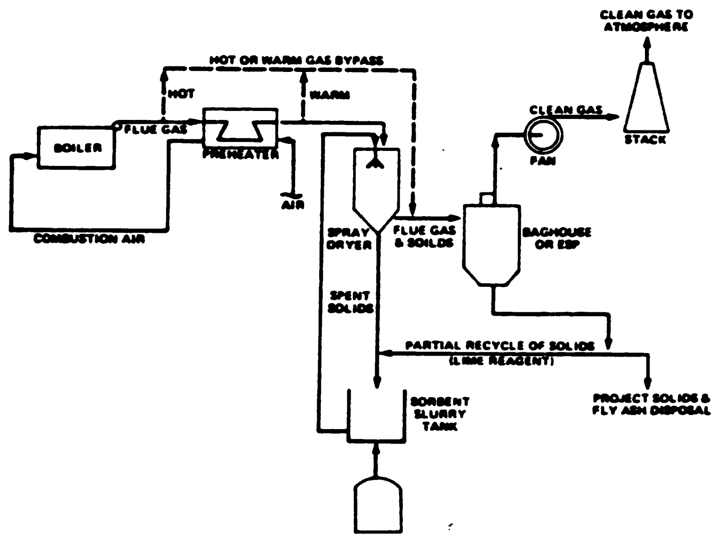


Figure 4.3 Typical Spray Dryer/Particulate Collection Flow Diagram.

4.2.3 Limestone Furnace Injection

Combustion-zone injection involves the addition of sorbent or reagent directly to the boiler along with pulverized coal. By injecting the sorbent directly into the combustion zone, the effective residence time is prolonged, resulting in greater SO_2 conversion.[5] Studies performed to date indicate that limestone injection is capable of removing from 50 to 80% SO_2, but that greater removal (up to 90%) can be achieved using nahcolite as the sorbent.[6] Furnace addition of bicarbonate also yielded good results; however, sorbent injection into the combustion zone caused several problems related to slagging, fouling, and corrosion.[5] The amount of SO_2 that can be captured is dependent on the type and amount of sorbent, its mixing with combustion gases and fly ash in the furnace, and its thermal history.[6] The highly reactive limestone and dolomite, when used as the injected sorbents, can create chemical scaling problems in certain absorber designs under particular operating conditions. In addition, it is desirable to avoid contact between the ash collected from a limestone injected boiler and water until the material is conveyed to its ultimate disposal. This is good practice because the dry/wet interfaces in the removal system may be a source of plugging or deposit buildup, which would reduce the capacity of the conveying system.[7]

A promising SO_2 removal technology utilizes a combined system of furnace limestone injection with dry scrubbing. In addition to greater possible reduction of SO_2 than can be achieved by either system alone, the combined technologies can represent significant savings in reagent costs by using limestone rather than lime. The low-cost limestone is injected into a furnace and is calcined into lime, which undergoes reaction with sulfur species in the flue gases. The collected lime and ash materials are then recycled and used as the principal reagent in the dry scrubbing technology for high-sulfur coals, as well as for low-sulfur coals.

4.2.4 Sodium Sorbent Injection

This "dry scrubbing" process removes SO_2 by injecting a dry sodium-based sorbent into the flue gas stream ahead of particulate control devices to produce a dry end product. This dry FGD technology offers unique advantages in terms of low cost and compactness of required process equipment.

In this process, the flue gas exits the combustor, flows through a duct, then through a heat exchanger, and finally through a fabric filter or electrostatic precipitator. Use of a baghouse generally produces better results because unreacted alkali on the bag surface continues to react with the SO_2. The sorbent injection point has been varied from the furnace burners to injection directly into the particulate collector,[8] with the majority of studies concentrating on injection into the heat exchanger section or just ahead of the baghouse, since the bulk of SO_2 removal occurs as the gas passes through the sorbent cake which has built up on the bags.[9]

Initial investigations used nahcolite, a naturally occurring sodium bicarbonate, as the alkali sorbent, but the lack of large supplies of this material prompted studies using other alkalis. Only sodium carbonate and sodium bicarbonate were found to be consistently effective,[10] with bicarbonate being the more reactive.[8] When dry powdered sodium carbonates and bicarbonates are pneumatically injected into the inlet duct of a fabric filter, a considerable degree of reaction occurs between the sulfur oxides in the gas and the finely divided sodium compounds. The dry particulate product is then collected with the fly ash in the baghouse.

Figure 4.4 presents a schematic of a typical dry injection system. Regardless of whether the sorbents used in commercial applications will be man-made sodium carbonate or bicarbonates, or their naturally occurring forms, refined trona and nahcolite, waste products from the dry injection process will be a mixture of fly ash, reaction products, and unreacted sodium compounds.

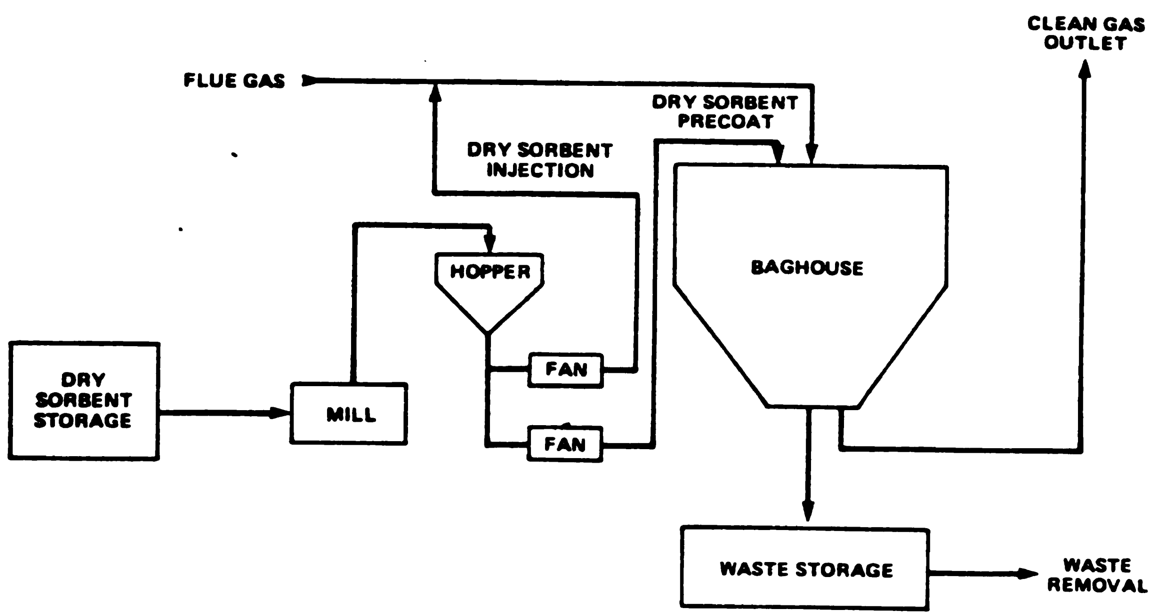


Figure 4.4 Typical Dry Sodium Injection System Schematic.

The waste products from this process will be generated in very large quantities and will require a significant area for land disposal. The waste will contain high levels of soluble sodium salts and could require pretreatment prior to disposal. Pelletizing and/or chemical-physical stabilization may be necessary, although regeneration of sodium compounds from the dry waste using technology from other fields is being tested.[8]

The above clean coal technologies, besides controlling the SO_2 and NO_x emissions, also influence the emission of the greenhouse gases. With respect to SO_2, some of the clean coal technologies improve the efficiency of the conversion of coal to useful energy. Technologies such as fluidized-bed combustion and integrated gasification/ combined cycle will consume less coal per unit of useful energy produced and thus lower the amount of CO_2 emitted per unit of useful energy produced. Other clean coal technologies, however, result in lower net amount of thermal conversion efficiency and hence, slightly increase the rates of CO_2 emission.

Many clean coal technologies trade off the reduction in polluting emissions with an increase in the production of solid wastes, particularly fly ash. According to the U.S. Department of Energy (1989),[1] the use of clean coal technologies may lead to more than 100% increase in the solid waste generation of power plants by the year 2010 (to approximately 220 million tons per year). Solid waste disposal will thus continue to be a growing problem for many utilities. Large land areas will be needed for disposal of the increasingly large amount of fly ash produced by the power plants adopting clean coal technologies.

Stricter regulations on landfill design and monitoring add to overall waste disposal costs. The development of solid waste utilization programs can help many utilities to decrease their overall waste disposal costs while adopting the emerging clean coal technologies. Many conventional power plant "wastes" have proven to be marketable by-products. Today, conventional pulverized coal combustion fly ash is considered an essential raw material in ordinary concrete, controlled low-strength cementitious materials (e.g., flowable fill), and roller compacted concrete. Similarity of the clean coal technology by-products (fly ashes) to conventional coal combustion fly ash is indicative of the strong potentials for beneficial use of the clean coal technology by-products in construction.

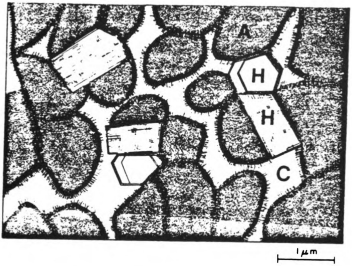
4.3 CLEAN COAL TECHNOLOGY BY-PRODUCTS

Many of the advanced clean coal technologies produce a "waste" that is comparable to conventional coal combustion fly ash. The sorbent, which is generally added to control polluting emissions, is intimately associated with the clean coal technology fly ashes (Radian Corporation, 1988).[11] This "modified fly ash" includes conventional fly ash particles that are coated with sorbent and sorbent reaction products, as well as smaller (non-fly ash) particles consisting of reacted and/or unreacted sorbent. Depending upon the particular clean coal combustion system, the volume of "modified fly ash" is approximately twice that of conventional coal fly ash due to the addition of sorbent material. As the advanced clean coal technologies are employed by full scale commercial systems, they will result in larger volumes of waste which will have to be managed by the electric utilities involved. Given the current marketability of conventional coal combustion fly ash for various applications and similarity of the so-called "modified fly ashes" to conventional fly ash, the utilization potentials of these new by-products warrant investigation.

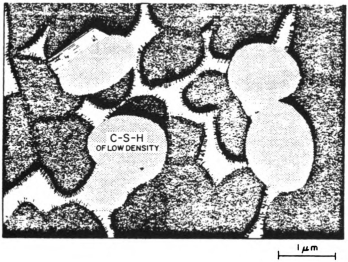
Conventional coal fly ash is a by-product of the combustion of pulverized coal in thermal power plants. It is removed by the dust collection system as a fine particulate residue from the combustion gases before they are discharged into the atmosphere. Conventional coal fly ash is a siliceous and aluminous material which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.

Fly ash contains alumina-silicates that react with the calcium ions released by Portland cement in the presence of moisture to form Calcium Silicate Hydrates. Figure 4.5a schematically shows the structure of hydrated cement paste (no fly ash used). The structure (see Figure 4.5a) consists of "A" which represents aggregations of Calcium Silicate Hydrate particles (a stable cement hydration product with desirable strength development and durability characteristics); "H" representing Calcium Hydroxide in the form of large crystals which are unstable in the presence of water especially when some aggressive chemicals are also present; and "C" representing capillary void system which is the route for entry of water and aggressive chemicals responsible for the aging of concrete.

The structure of fly ash-cement paste is presented in Figure 4.5b. The major change is that the Calcium Hydroxide ("H") crystal products, as a result of pozzolanic reaction, change to Calcium Silicate Hydrate ("A") particles of low density which fill the large capillary voids and reduce the continuity of the capillary void system. This blocking of capillary voids reduces the permeability of concrete. Reduced permeability and substitution of Calcium Hydroxide with Calcium Silicate Hydrate in the presence of fly ash, which is used in concrete as a partial substitute for Portland cement, provide improvements in resistance against sulfate attack, alkali-aggregate reaction, and diffusion of chloride ions which are responsible for the corrosion of embedded steel reinforcement. Fly ash is also capable of enhancing the workability of fresh concrete mixtures and reducing the heat of hydration of concrete. There are, however, concerns regarding the adverse effects of fly ash on the deicer salt scaling resistance and air entrainment for freeze-thaw durability of concrete.



(a) Cement Paste



(b) Fly Ash-Cement Paste

Figure 4.5 Structure of Cement Paste Versus Fly Ash-Cement Paste.

4.4 POTENTIAL APPLICATIONS

Technical and economical advantages of utilizing conventional coal fly ash in concrete have led to the development of a large-volume market for fly ash accounting for half of all the fly ash utilized in the United States (approximately 10 million tons per year). In the recent years, with the increased production of fly ashes failing to satisfy specific (e.g., Loss On Ignition) ASTM requirements for pozzolanic concrete admixtures, many new techniques have evolved to utilize conventional coal fly ashes in cementitious materials.

By-products of three major clean coal technologies (Calcium Injection, Furnace Injection, and Spray Dryer) possess chemical and physical characteristics which closely simulate those of conventional coal fly ashes. Tables 4.1 and 4.2 compare the chemical and physical characteristics, respectively, of these clean coal technology by-products with those of conventional coal ash. These tables are indicative of the potentials of clean coal technology by-products to repeat the success of conventional coal fly ash in finding high-value and large-volume markets in concrete. The relatively high CaO content of the clean coal technology by-products, when compared with conventional coal fly ash, suggests that these by-products present not only pozzolanic qualities but also cementitious potentials in the sense that, in the presence of moisture, they themselves may be capable of releasing sufficient calcium ions for strength development through pozzolanic reaction. This phenomenon can reduce the need for Portland cement as a source of calcium ions in concrete.

Table 4.1 Chemical Characteristics (%) of Clean Coal Technology By-Products and Conventional Coal Fly Ash (ICF Northwest, 1988 & Malhorta).

By-Product	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	SiO_2	Na_2O	SO_3
Calcium Inj	31.4	15.4	8.9	1.1	3.4	30.0	1.2	NA
Furnace Inj	30.0	16.8	16.9	0.7	2.1	27.9	1.0	3.5
Spray Dryer	24.9	20.0	6.5	2.6	0.8	21.3	1.8	10.25
Coal Ash	12-23	1-13	3-26	1-3	1-3	35-60	.1-5	.2-4

NA - Not Available

Table 4.2 Physical Characteristic of Clean Coal Technology By-Products and Conventional Coal Fly Ash (ICF Northwest, 1988).

By-Product	% Retained on No. 325 Sieve
Calcium Injection	6
Furnace Injection	20
Spray Dryer	3
Conventional Coal Ash	14-35

4.5 UTILIZATION IN CONCRETE

4.5.1 Chemical and Physical Requirements

Six advanced SO_2 control by-products samples were used in a laboratory testing program reported by Perri et al. (1987):[12] an AFBC baghouse ash, an AFBC spent bed material, two calcium spray dryer ashes, a limestone furnace injection ash, and a dry sodium injection ash. Table 4.3 gives the by-product sample numbers (which are referred to in the subsequent table) and shows where the by-product samples were obtained from. The chemical and physical analyses of the by-products are presented in Tables 4.4 and 4.5 respectively.

Table 4.3 By-Product Samples.

Sample No.	Plant	Utility	Location
AFBC:			
TV03 (bed)	Shawnee[a]	Tennessee Valley	Paducah, KT
TV05 (ash)	Shawnee[a]	Tennessee Valley	Paducah, KT
Spray Dryer:			
LR07	Laramie River	Basin Electric Power	Wheatland, WV
HS05	Holcomb	Sunflower Electric	Holcomb, KS
Limestone Injection:			
OL03	Lakeview TGS	Ontario Hydro	Mississauga, Ontario
Sodium Injection:			
NX04	R.D. Nixon	City of Colorado Spring	Colorado Springs, CO

Table 4.4 Chemical Characteristic.

Sample No.	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	SiO_2	Na_2O	SO_3
AFBC:								
TV03	2.72	45.1	4.77	0.62	0.31	3.17	0.27	6.50
TV05	15.0	22.6	18.9	0.51	1.93	15.3	0.34	17.3
Spray Dryer:								
LR07	21.1	26.9	6.11	2.33	0.74	17.7	2.08	12.3
HS05	24.9	30.0	6.51	2.62	0.75	21.3	1.81	10.3
Limestone Injection: OL03	17.8	36.1	13.2	0.63	1.11	15.8	0.48	6.25
Sodium Injection: NX04	28.9	4.54	2.50	1.16	0.77	25.2	24.8	12.0

As shown on Table 4.4 all the by-products, except for sodium injection ash NX04, primarily consist of calcium, silica, alumina, sulfur, and iron oxides. Calcium oxide concentrations ranged from 20-45% by weight for the calcium-based advanced SO_2 control by-products. The sodium-based process by-product had 25% by weight concentration of sodium oxide and a relatively low CaO content of 4.5%. The by-product silicon oxide concentrations (3-25% by weight) were much lower than would be encountered in conventional pulverized coal (PC) fly ash which tends to have an SiO_2 content in the 30-60% range.[13] The sulfur trioxide concentration of the by-product samples ranged from 6-17%; these concentrations are much higher than normally found in conventional pulverized coal fly ash which are generally under 3%.[13] All other parameters (Al_2O_3, Fe_2O_3, MgO, and K_2O) are present in concentrations which are similar to those found in conventional pulverized coal fly ash.

Table 4.5 provides the by-product physical analyses test results. All of the by-products, except for the AFBC spent bed material, were fine ashes with the majority of particles in the silt size range (2-75 μm). The majority of AFBC spent bed material particles fell in the coarse sand size range (425 μm-2 um). The physical property with the most variability among the six by-product samples analyzed was permeability; the by-product permeability values varied from 3.4×10^{-4} cm/sec (1.34×10^{-4} in/sec) for the AFBC spent bed to 7.7×10^{-9} cm/sec (3×10^{-9} in/sec) for the AFBC baghouse ash.

Table 4.5 Physical Characteristic.

BY-PRODUCT PHYSICAL CHARACTERISTICS

Sample No.	Particle Size Distribution ª (%)				Denstiy (lbs/ft³)		Optimum Moisture %	Liquid Limit %	Plastic Limit %	Permeability (cm/sec)
	gravel	coarse sand	fine sand	silt	Packed Bulk	Maximum Dry				
AFLC										
TV03 (bed)	10	72	18	0	100 46	94 28	32	NL	NP	3 4x10-4
TV05 (ash)	0	0	0	100	52 67	70 07	50	39	5	7 7x10-9
Spray Dryer:										
LR07	NA	2	1	97	62 52	82 81	28	38	17	6 8x10-7
HS05	0	1	0	99	73 01	95 55	24	24	5	1 6x10-7
Furnace Injection:										
OL03	0	1	9	90	56 78	68 80	42	38	NP	2 8x10-5
Sodium Injection:										
NX04	0	0	0	100	52 29	91 73	20	21	1	9 4x10-6

Notes:

NL - No liquid limit because of non-plastic behavior
NP - Non-plastic behavior
NA - Not Analyzed
ª Gradation as specified in ASTM D3282:
- gravel - particles that will be retained on a No 10 (2 mm) sieve.
- coarse sand - particles that will pass a No 10 sieve and be retained on a No 200 (75 μm) sieve
- fine sand - particles that will pass a No 40 sieve and be retained on a No 200 (75 μm) sieve
- silt-clay - particles that will pass a No 200 (75 μm) sieve

The technical criteria for the utilization of conventional coal fly ash in cementitious materials are provided in ASTM C 618. These criteria cover: (1) Silica, Alumina, and Iron Oxides (SiO_2+Al_2O_3+Fe_2O_3); (2) SO_3 content; and (3) Particles passing No. 325 sieve. The clean coal technology by-products are observed in Table 4.6 to satisfy these specific criteria. There is, however, a need to fully evaluate these by-products against all the criteria specified in ASTM C618; some specific concerns relate to: (1) potentially high sulfate content of some clean coal technology by-products in the form of the reaction products of sorbent with the SO_3 in flue gas; and (2) potential increase in the Loss On Ignition (LOI) of clean coal technology by-products due to insufficient ignition of the sorbent and its reaction products. Any potential problem in these areas will encourage the adoption of a performance-based approach to the use of clean coal technology by-products in concrete, and will increase the emphasis on lower-grade (e.g. flowable fill) applications of the by-product where the ASTM standards for pozzolanic concrete admixtures should not be necessarily satisfied.

ASTM C618 provides specifications for use of fly ash as a mineral admixture in Portland cement concrete. Table 4.6 presents by-product physical and chemical analyses along with the corresponding ASTM C618 physical and chemical requirements reported by Perri et al. (1987).[12] None of the by-products meets the ASTM C618 requirements for combined SiO_2 + Al_2O_3 + Fe_2O_3 or for SO_3 concentration. Only the spray dryer ash

HS05 had an LOI concentration below 6.0%. All by-products, except the AFBC spent bed material, meet the limits of percent retained on a No. 325 Sieve and for autoclave expansion. Furnace injection ash OL03, AFBC baghouse ash TV05, and spray dryer ash HS05 achieved pozzolanic activity indexes above the required 75%.

Table 4.7 provides the results of the cement replacement testing for three of the by-product samples. The concrete mixes were prepared with 30% by weight replacement of the Portland cement with advanced SO_2 control ash. Even though these ashes did not meet the ASTM C618 chemical requirements, they did produce acceptable quality concretes when compared with both the no fly ash and conventional fly ash control mixes. Although the spray dryer ash mixes had exceptionally long setting times (17-21 hours to final set), their compressive strength (even at early ages) and durability exceeded the 100 percent cement control. These mixes also performed very well in freeze/thaw testing; the spray dryer ash concrete mixes showed no surface deterioration after 300 freeze/thaw cycles.

Table 4.6 Properties of Clean Coal Technology By-Products Vs. ASTM C 618 Requirements.

Sample No.	SiO_2 + Al_2O_3 + Fe_2O_3	SO_3	LOI	Retained on No.325 Sieve	Pozzolanic Activity Index	Autoclave Expansion
Reference Specification:						
ASTM C618	50-70(min)	5.0 (max)	6.0 (max)	34 (max)	75 (min)	0.8 (max)
ASTM 595*				20 (max)	75 (min)	
AFBC:						
TV03 (bed)	10.66	6.50	NA	100	NA	NA
TV05 (ash)	49.18	17.25	12.64	0	88	NA
Spray Dryer:						
LR07	45.03	12.25	6.2	10	69	+0.05
HS05	52.71	10.25	1.9	3	107	+0.03
Furnace Injection: OL03	46.72	6.25	10.97	20	108	+0.08
Sodium Injection: NX04	56.58	12.00	NA	0	NA	NA

Key: NA - Not Analyzed

* ASTM C595 requirements for pozzolan for use in blended cements.

By-Product	SiO_2+Al_2O_3+Fe_2O_3 %	SO_3 %	% > #325
Calcium Injection	70	NA	6
Furnace Injection	75	3.5	20
Spray Dryer	53	NA	3
ASTM C 618	Min. 50	Max. 5	Max. 34

Table 4.7 Cement Replacement Testing Result

	Spray Dryer LR07	Spray Dryer HS05	Furnace Injection OL03	Control #1 (no ash)	Control #2 (conv.ash)[a]
Mixture Proportions (1 yd^3)					
Cementitious Material					
1. Cement (lbs)[b]	410	410	410	590	410
2. Ash (lbs)	180	180	180	0	180
Fine Aggregate (lbs)	1380	1380	1380	1380	1380
Coarse Aggregate (lbs)	1875	1875	1875	1875	1875
Admixtures					
1. Air Entrainment (ozs)[c]	7.73	7.73	25.1	7.92	4.42
2. Water Reducer (ozs)[d]	12.3	12.3	12.3	17.2	12.3
Water (lbs)	265.5	265.5	165.5	247.5	211.5
General Data					
Slump (inches)	4.0	4.0	3.5	4.5	4.5
Air Content (%)	5.8	5.6	4.5	5.6	6.0
Unit Weight (lb/ft^3)	147.1	146.3	138.3	145.7	147.1
Concrete Temperature (^oF)	83	79	84	NA	NA
Time of Set (hr:min)					
Initial (500 psi)	13:55	18:30	3:50	6:00	6:15
Final (4000 psi)	17:00	21:15	5:35	8:00	8:00
Compressive Strength[e]					
3-day (psi)	3523	3607	2063	3280	3140
7-day (psi)	4557	4645	2581	4280	4100
28-day (psi)	5682	5093	3784	4940	5310
90-day (psi)	6331	6343	6083	5626	6740
Modulus of Rupture (psi)[f] (at 28 days)	597	630	543	763	702
Freeze/Thaw Durability[g]					
Durability Factor	99.3[h]	94.2[h]	89.6[i]	92.5	98.25
Length Change (%)	0.04	0.04	0.07	-0.02	-0.11

Notes:

a Conventional fly ash from a pulverized coal-fired boiler collected by ESP from the United Power Association's Coal Creek Station in Underwood, North Dakota. A lignite ash with approximately 40% SiO_2, 12% Al_2O_3, 7% Fe_2O_3 and 24% CaO.

b ASTM C150 Type I cement.

c Air entrainment agent - Master Builders MB-VR.

d Water reducing agent - Gillford Hill PSI

e ASTM C39, average of three samples.

f ASTM C78, average of three samples.

g ASTM C666, procedure A @ 28 days, average of three samples.

h No surface deterioration after 300 freeze/thaw cycles.

i Slight surface deterioration after 300 freeze/thaw cycles.

CHAPTER 5

CONCRETE MICROSTRUCTURE:

A LITERATURE REVIEW

5.1 INTRODUCTION

Concrete is a porous structure, usually containing 20 to 40 percent by volume of void space. This void space strongly influences the concrete performance, characteristics. Different pore sizes affect different characteristic like strength, shrinkage, permeability, creep, freeze-thaw durability, etc. This chapter reviews the past research studies concerning concrete pore system.

5.2 PORE STRUCTURE

In general, concrete microstructure can be categorized into entrapped air void system, entrained air void system, capillary pores, and gel. The entrapped air void system has irregular voids which are greater than 1 mm in size. This system is the typical symptom of improper handling of fresh concrete, and may cause significant drop in the strength of hardened concrete. It is usually caused by a too stiff fresh concrete or an improper consolidation practice such as vibrating too short, using a vibrator head which is too

The entrained air void system is between few microns and 1 millimeter in void size. The entrained air void system is purposely put into the concrete structure. These void system has a spherical shape and a uniformly distributed void size. A well entrained air void system can help hardened concrete overcome the freezing and thawing problem, and can enhance the concrete durability. Past, researchers have intensively studied this area.

Capillary void system represents the unfilled space in the hydrated cement paste. They range in size from 0.01 micron to few micron. Concrete consists roughly one part by volume of cement with three parts of water. During hydration, cement reacts with water and produces hydration products. There exists a gel gap in between hydration products because they can not fully occupy the space previously occupied by cement and water. Excess of mixing water thus causes higher capillary porosity. The capillary pore system is somewhat continuous; this is partly caused by the evaporation of excess water through microchannels towards the surface. Continuity of the capillary pore system increases the permeability of concrete and damages its durability.

5.3 CAPILLARY PORE SYSTEM CHARACTERISTICS

The microstructure of Portland cement paste was first studied in details by Power et al. (1946)[6]. This study concluded that: (1) when a unit volume of cement hydrates, it produces 2.2 volumes of hydrated material; (2) the hydrated material, commonly called gel because of its colloidal nature, has an inherent porosity of about 26 percent; (3) because of the small size of the gel pores, they attract any water that is available, and when the water enters the pores, since much of it is adsorbed water rather than free water, it has a specific volume of 0.9.

Based on the above conclusions, a unit mass of Portland cement would react with a certain (~ 0.38) unit mass of water in the hydration process. When in a cement paste the water-to-cement ratio exceeds this level, after the completion of hydration there will still be unfilled space in the original cement and water filled space. As hydration process continues, this space would be subdivided into isolated pockets. Power calls these isolated pockets "capillary pores" in order to distinguish them from the gel pores. Under the condition of water to cement ratio less than 0.38, there would be insufficient water to hydrate the cement, and thus portion of cement remains unreacted. Unless the hydration process continues over time, there will exist unreacted particles in the cement paste.

Furthermore, Power observed that the water in the gel will not freeze at temperatures as low as -20°C when water in capillary pore did freeze. More recently, Kashi and Weyer

(1989)[14] confirmed these findings. The relationship between pore size and freezing temperature is presented in Table 5.1.

Table 5.1 Relationship Between Pore Size and Freezing Temperature (Philleo, et al.)[3]

Freezing Temperature	**Size of pore required for ice formation at selected temperature**
°C	**nm**
-2	20.8
-6	8.3
-10	5.9
-15	4.4
-20	3.5

5.3.1 Relationship between Strength and Porosity

The most popular property to evaluate concrete is compressive strength. Three types of semi-empirical models for predicting concrete strength in terms of its porosity have been widely used[12] :

Balshin model: $\sigma = \sigma_0 (1-P)^A$

Ryshkewitch model: $\sigma = \sigma_0 e^{-BP}$

Schiller model: $\sigma = C \ln (P_{CR} / P)$

In the Balshin and Ryshkewitch[7,16] models, σ_o represents the compressive strength at zero porosity and P is the porosity. In the Rayshkewitch's model, the P_{CR} is zero strength porosity. A, B and C are material constants. In general, the Ryshkewitch model is accurate at low porosity level, but the Schillier's model is good at high porosities.

Brownyard and Power present their model of compressive strength of Portland cement paste in terms of the gel to space ratio[6]:

$$\text{Strength} = \text{constant} \bullet x^3$$

$$\text{where } x = 2.06\, V_c\, \alpha \,/\, (V_c + W_0/c)$$

Where c is the weight of cement, V_c is the specific volume of cement, W_0 is the volume of mixing water, and α is the degree of hydration of cement. This equation is very sensitive to small changes when the gel to space ratio is above 0.2. Furthermore, in Power's later research, he simplified the relationship of porosity and strength. Power found that the 28-day compressive strength f_c was related to the gel/space ratio, or to the ratio between the solid hydration products in the system and the total space:

$$F_c = a\, x^3$$

where a is the intrinsic strength of the material at zero porosity (p) and (x) the solid/space ratio or the amount of solid fraction in the system, which is therefore equal to (1-p). Power's data are shown in Figure 5.1. The value of (a) was found to be 34,000 psi (234 MPa).

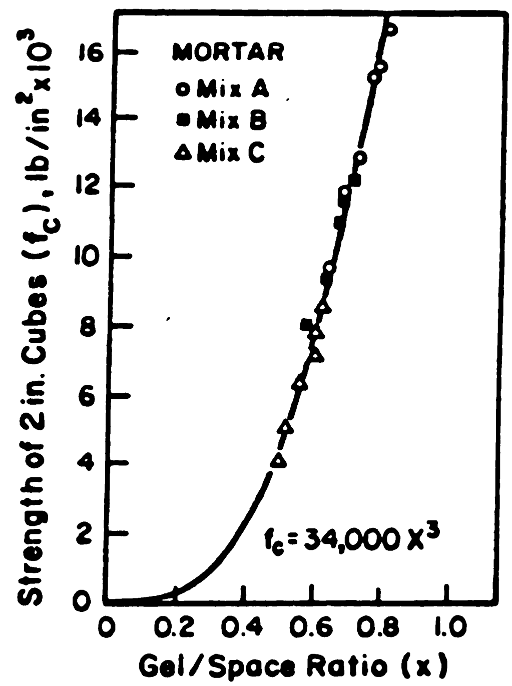


Figure 5.1 Relationship of Strength with Gel/Space Ratio (Powers, 1958).[1]

Jambor (1973)[9] did the study on the pore structure by measuring the pore size distribution, pore volume, and compressive strength. He concluded that the higher compressive strength, the smaller the average pore size at a given porosity. Furthermore, he expresses the low-porosity compressive strength as:

$$S = K\sqrt{P_0 - P}\ /\ (w/c + P)$$

where the P is the total porosity, w/c is the water to cement ratio, P_0 is the porosity at the onset of the hydration, and K is a coefficient dependent on the type of cement, curing conditions, and volume concentration of cement in the paste.

Odler (1972)[19] developed a relationship between strength and porosity where porosity was measured, using the mercury intrusion technique. The following relationship was derived under the conditions cement hydration at 25^0C and with the water-to-cement ratio ranging from 0.25 to 0.31:

$$S = S_0 - a\, P_{<10\ nm} - b\, P_{10\text{-}100\ nm} - c\, P_{>100\ nm}$$

where a, b and c are constants, P is porosity, and S_0 is the strength at zero porosity.

Beaudoin and Feldman(1994)[4] concluded in their research on and modulus of electricity that the relationship between elastic modulus and porosity can be given as:

$$E = E_0\, e^{-BP}.$$

5.3.2 Relationship between Permeability and Porosity

There are numerous ways to measure the permeability of hardened concrete and paste. All of the methods measure how the liquid or electron can pass through the capillary pores. This depends on how big the thread of the capillary pores is and how well they are connected. The fundamental relationship of permeability and porosity can be expressed from the Hagen-Poisevill law as follows[17]:

$$Q/A = K\, \Delta P/(\eta h)$$

Where Q/A is the volume flux passing through the specimen area A, ΔP is the pressure difference between the two sides of the specimen, η is the liquid viscosity, h is the thickness of the specimen, and K is the coefficient of permeability. K can be related to the average pore radius γ_t by the equation of:

$$K = w\, \varepsilon \gamma_t^{\,2}$$

where w is a form factor (for example 1/8 for cylindrical pores) and ε is the porosity.

A more exact expression which includes the pore size distribution is presented in the following:

$$K = C \int r^2 f(r)\, dR$$

where C is constant.

Setzer et al, (1973)[10] discussed the main factors correlating the permeability with the pore size distribution. They concluded that an average pore radius affects permeability, and derive a simplified equation based on the Hagen-Poiseville law[17], using an effective porosity of $\varepsilon/3$. The value r_m determined from mercury intrusion data was taken from the maximum of differential curve. The ratio r_m/r_t increased greatly with water-to-cement ratio, and r_t was always smaller than r_m.

Nyame et al.[13,20] conducted a similar research on the relationship between pore structure and permeability. They used the technique of mercury intrusion to obtain the pore size distribution, and concluded that a linear relationship exists between log (water permeability) and mean pore radius. In this study, they correlated the pore structure and permeability using the radius obtained from the differential mercury intrusion curve:

$$K = 1.684 r_m^3 \times 10^{-22}$$

The value of the correlation coefficient was 0.96, but for the values of r_m less than 100 nm the scatter of data was found to be large.

Bier et al,(1988)[20] measured permeability of water through oven-dried and non-oven-dried specimens. They found that oven drying creates visible cracks and increases permeability by about an order of magnitude. These high values, however, decreased during further exposure to water and reached the same values as observed for samples not dried in a short period. This result occurred despite the fact that the oven dried samples had coarser pore structures as determined by mercury intrusion after the experiment. It was concluded that the deposition of particles into the cracks rapidly reduces permeability. These results emphasize the difficult in making precise conclusions with regard to pore size distribution-permeability relationships.

5.3.3 Effects of Pozzolans on the Pore Structure of Hardened Concrete

Cebrera has concluded that fly ash additions to concrete leads to a more refined pore system. The pore structure in concrete is altered in at least to ways: (1) fly ash will reduce the amount of water needed to maintain good workability, thus producing a tighter matrix; and (2) fly ash will react with calcium hydroxide produced during hydration to form products which will have a tendency to fill empty spaces in the matrix, thus creating a more discontinuous pore system. Figure 5.2 shows the pore size distribution of an ordinary Portland cement mortar designed for a compressive strength of 40 MPa and a 50 mm slump. It can be seen that the total porosity decreases with time and that the volume of large pores (>.01 mm) decreases sharply with age. On the other hand, Figure 5.3 depicts the pore size distribution of a mortar obtained from a fly ash concrete containing 30 percent fly ash by weight of cementitious component. It was designed to meet the conditions stated above for the plain matrix, but the water required to maintain constant slump was reduced by 9 percent. Examination of Figure 5.3 shows that the total early porosity (at 3 days of age) was reduced, perhaps due to the lower water content. It is also evident from the figure that the volume of large pores (>0.01 mm) has been reduced in the fly ash mortar, particularly at later ages.

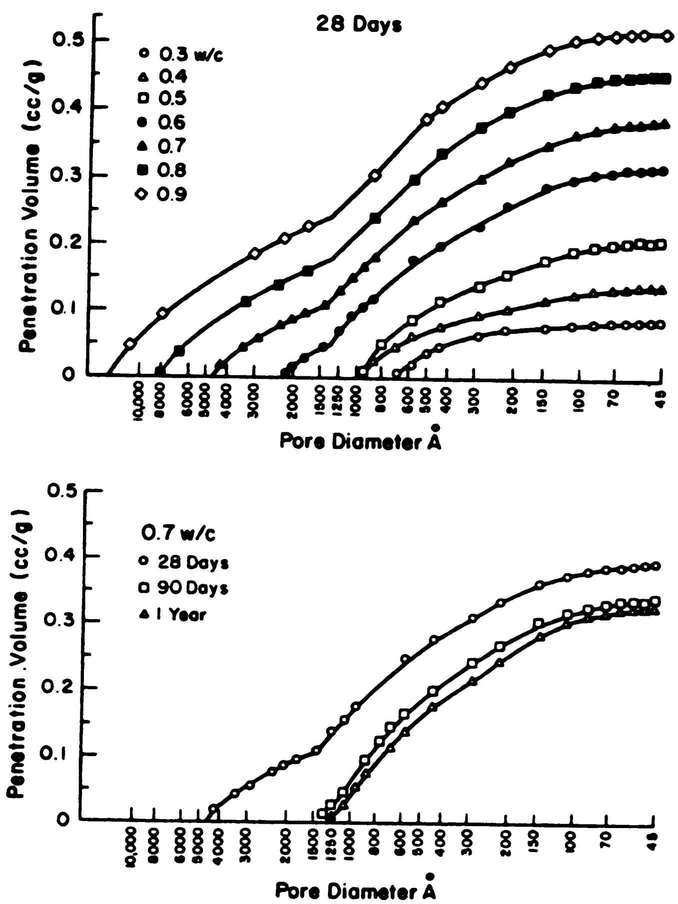


Figure 5.2 Pore Size Distribution Versus Age in Ordinary Portland Cement Mortar[1].

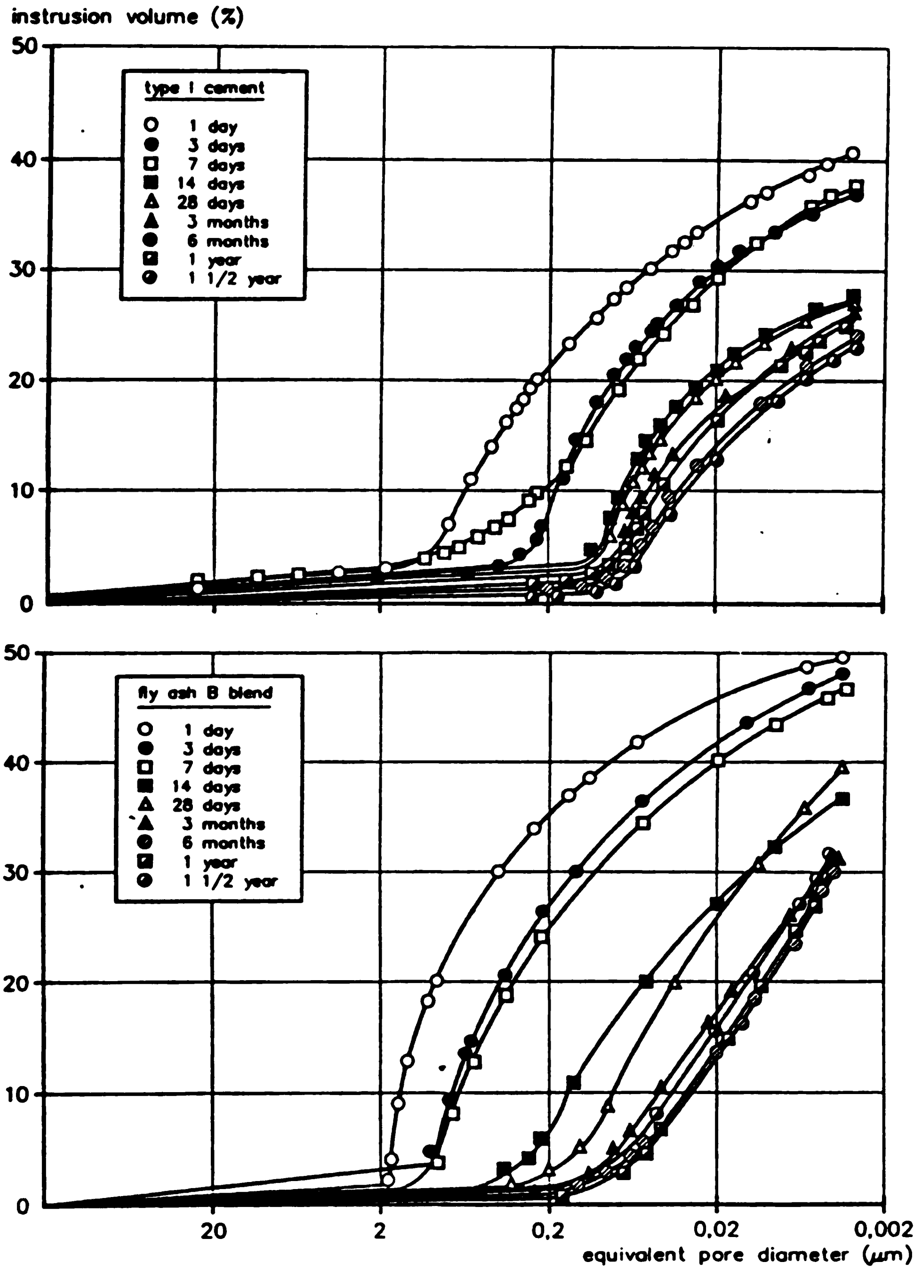


Figure 5.3 Pore Size Distribution Vs. Age in a Mortar Containing Fly Ash.

Mehta and Manmohan (1981)[20] have studied the effect of pozzolans on the pore size distribution of hardened cement paste. Class F fly ash was added at 10, 20 and 30 percent by weight of cementitious material, and type II Portland cement was used throughout the investigation. The pastes were prepared using distilled water at a water to solid ratio of 0.5. In order to reduce bleeding, the pastes were mixed for 30 minutes. Mercury porosimetry was used to evaluate the pore size distribution of the samples (the contact angle used was 130^{o}). The results obtained are shown in Figure 5.4 a and b, where it can be seen that the pozzolanic lime-silica and lime-alumina reactions were slow. For example, at 28 days of age, all fly ash pastes exhibited a coarser pore system than the corresponding control pastes. After 1 year of curing, all pastes exhibited finer porosities, but the fly ash pastes had more refined porosities than the controls. These results indicate that the pore refining effect of a pozzolan is a function of its pozzolanic reactivity. Moreover, it was concluded that type F fly ash was not effective in reducing the volume of larger pores at early ages.

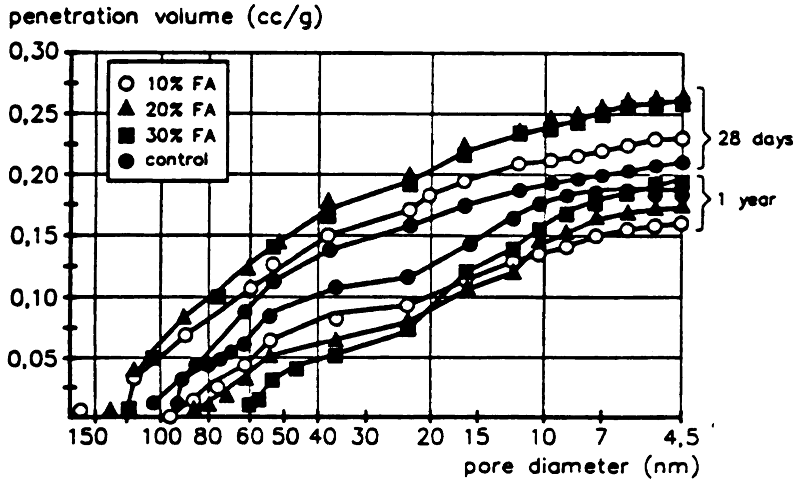


Figure 5.4 Fly Ash Effects on the Pore Size Distribution of Pastes[1].

Hooton studied the effcts of fly ash at 25 and 35 percent replacement levels on the pore size distribution of sulfate-resistant Portland cement (Type V). Two different water-to-cement ratios of 0.25 and 0.36 were used in this study. The pore size distributions were measured by mercury intrusion (a contact angle of 140° was used). The results showed that the pore structure of the pastes containing fly ash (water-to-solids ratio of 0.25) was not finer that of controls. However, this was found to be inconsistent with the strength and permeability data obtained for equivalent samples, which showed evidence of continued pozzolanic reaction with time. For pastes having a water-to-cementitious material ratio of 0.36, at 25 percent fly ash the results showed coarser porosities at 7 days at curing, but at 28 days the porosities of both control and fly ash pastes were found to be similar. At this same age for the 35 percent replacement level, the volume of pores larger than 0.025 mm was found to be smaller than that of controls. After 28 days, higher porosities were noticed for pores finer than 0.005 mm, indicating the presence of larger quantities of gel pores.

CHAPTER 6

EXPERIMENTAL PROGRAM

6.1 INTRODUCTION

The experimental program presented in this Chapter has been designed to provide comprehensive and statistically reliable information on the impacts of fly ash and calcium spray dryer fly ash (a clean coal technology by-product) on the freeze-thaw durability, deicer salt scaling resistance and relevant engineering and microstructural properties of concrete. The results can help distinguish between the effects of conventional fly ash and a specific clean coal fly ash on concrete properties, and also provide a basis to develop structure-property relationships and illustrate the mechanisms of action of conventional and clean coal fly ash in concrete materials; (this research emphasizes the freeze-thaw durability and deicer salt scaling resistance of concrete).

The effects of five variables on the structure and engineering properties of concrete were investigated in a 2^5 factorial design of experiments (see Table 6.1):

- fly ash type (conventional Class F and Calcium Spray Dryer)
- fly ash content (15% and 30% replacement by total weight of cement)
- water-cementitious material ratio (0.40 and 0.45 by weight)
- moist curing period (28 and 56 days)
- air content (2.5% and 7.5%)

Control concrete specimens (with 0% ash content) were also considered at all the levels of water-cementitious ratio, moist curing period and air content.

Table 6.1 2^5 Factorial Design of Experiments

w/c Ratio	0.40								0.45							
Ash Content	15%				30%				15%				30%			
Air Content	2.5%		7.5%		2.5%		7.5%		2.5%		7.5%		2.5%		7.5%	
Curing Period	28	56	28	56	28	56	28	56	28	56	28	56	28	56	28	56
Class F	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Calcium Spray	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Control	*	*	*	*					*	*	*	*				

The concrete specimens produced based on the above experimental design were subjected to the following tests:

- ASTM C 666, Resistance of Concrete to Rapid Freezing and Thawing
- ASTM C 672, Scaling Resistance of Concrete Surface Exposed to Deicing Chemical
- ASTM C 1202, Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration
- ASTM C 39, Compressive Strength of Cylindrical Concrete Specimen
- ASTM C 457, Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete
- Mercury Intrusion

6.2 MATERIALS AND MIX PROPORTIONS

The Materials used in this research are listed below:

- Cement: regular Type I Portland cement (Table 6.2)
- Coarse Aggregate: crushed limestone with a maximum aggregate size of 1/2 inch (12.5mm) (Figure 6.1)
- Fine Aggregate: regular concrete sand (Figure 6.2)
- Conventional Coal Combustion By-Product: Class F Fly Ash, from Lansing Board of Water and Light (Table 6.2)
- Clean Coal Technology By-Product: Calcium Spray Dryer Fly Ash, from American Power Association, North Dakota Plant (Table 6.2)
- Air Entraining Agent: Darair, a type of vinsol resin (AEA1), produced by W. R. Grace & Company

Table 6.2 Chemical and Physical Properties of Cement Conventional Coal Fly Ash, and Clean Coal Technology By-Product.

	Cement	Class F Fly Ash	Clean Coal Technology By-Product
Silicon Dioxide (SiO_2)	20.58	49.3	28.73
Aluminum Oxide (Al_2O_3)	5.35	26.7	16.09
Ferric Oxide (Fe_2O_3)	2.56	8.95	4.32
Calcium Oxide (CaO)	62.44	1.83	29.63
Magnesium Oxide (MgO)	3.46	1.5	5.24
Sulfur Oxide (SO_3)	3.46	0.52	4.48
Alkalies as (Na_2O)	0.77	3.8	2.5
Loss on Ignition	2.0	5.5	3.17
Fineness (% retained on #325 sieve)	10.7	19.6	24.03

The mix designs were developed based on the absolute volume method.[1] The total cementitious material content was kept constant, and the target amount of air content was achieved by adjusting the dosage of air-entraining agent. Many trial mixes were investigated in order to develop the final mix proportions.

The base mix considered in this project is presented in the Table 6.3.

Table 6.3 Mix Proportions.

	Gradation	Quantity	Source
Coarse Aggregate	6AA	1800 lb	crushed limestone
Fine Aggregate	2NS	1400 lb	concrete sand
Cement	Type I	560 lb	Portland cement
Water		224 lb	

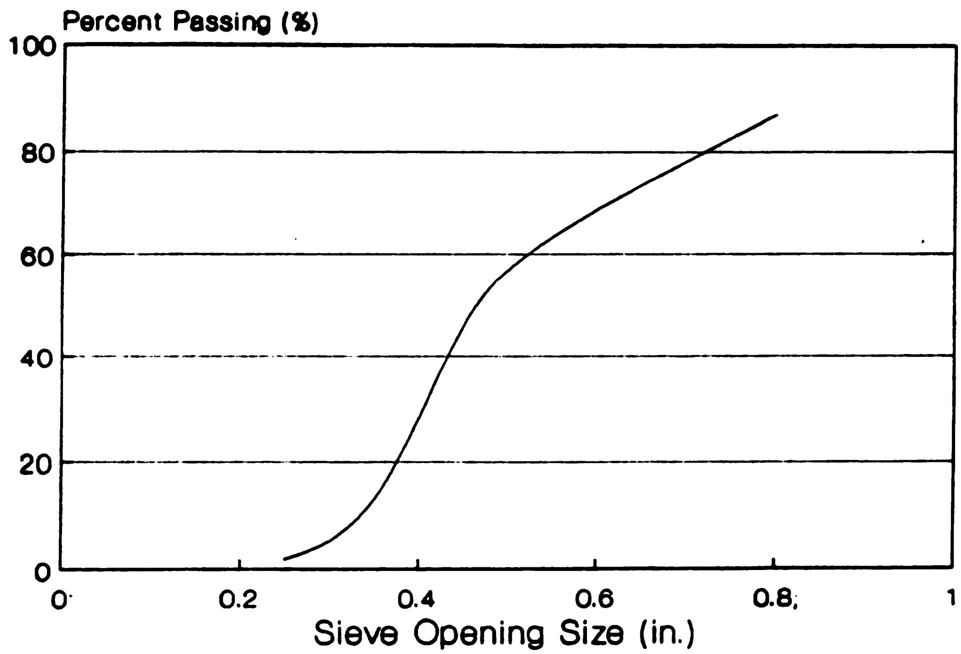


Figure 6.1 Gradation Curve of Coarse Aggregates.

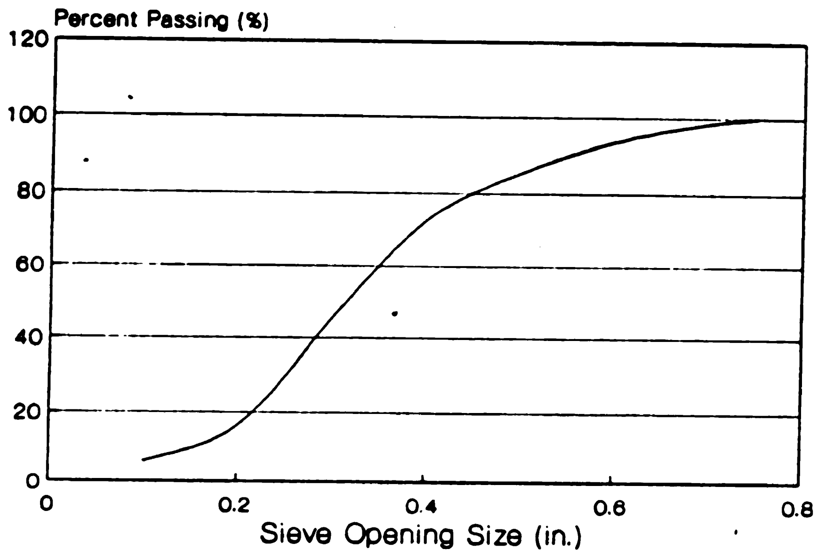


Figure 6.2 Gradation Curve of Fine Aggregate.

6.3 TEST PROCEDURES

Most test procedures conducted in this research project follow the ASTM guidelines. This section briefly reviews these test procedures.

6.3.1 Resistance of Concrete to Rapid Freezing and Thawing (ASTM C666)

This test determines the concrete's freezing and thawing resistance. The freeze-thaw test specimens are 3 inch x 4 inch x 16 inch (7.62 x 10.16 x 40.6 cm). Concrete is kept inside mold for 24 hours; after demolding, the specimens are stored in saturated lime water until the time to start the test. Right before starting the test, the specimens are temporarily stored inside a tempering tank in order to cool down the specimen temperature to prevent initial reading errors. The tempering tank has a temperature within the range of $\pm$ 2°F ($\pm$ 1.1°C) of the target thaw temperature for specimens in the actual freezing-and-thawing cycles. After starting the freeze-thaw cycles measurements were done on specimens, every 25 cycles in thaw condition.

The key measurements conducted here are:

1. Length Change (ASTM C 215), using a comparator capable of measuring to the nearest 0.0001 in (0.0025 mm).
2. Weight Change, measured using a scale accurate to 0.0022 lb (1 g).
3. Fundamental Transverse Frequency (ASTM C 490).

Based on these measurement, the dynamic modulus of elasticity can be calculated as follows:

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

where:

P_c = relative dynamic modulus of elasticity (percent), after c cycles of freezing and thawing,

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

n_1 = fundamental transverse frequency after c cycles of freezing and thawing

All the specimens are subjected to 300 cycles for freezing and thawing unless they fail earlier. Each cycle is approximately 6 hours.

6.3.2 Scaling Resistance of Concrete Surface Exposed to Deicing Chemicals (ASTM C 672)

This test determines the resistance to scaling of a horizontal concrete surface exposed to freezing-and-thawing cycles in the presence of deicing chemical. The surface resistance is evaluated qualitatively by visual examination. The specimen size used in this test was 8 inch x 10 inch x 3 inch (20.3 x 25.4 x 7.6 cm).

All specimens are stored in curing room until the testing age; they are then placed in a freezing environment for 16 hours. At the end of this time the specimens are removed from freezer and placed in laboratory air at 73°F (23°C) and a relative humidity of 45 to 55% for 8 hours. These cycles are repeated typically 50 times, flushing off the surface every 5 cycles. Visual observation of the surface is made after completion of all cycles.

Visual rating of the surface in accordance with the following scale:

Rating	Condition of Surface
0	no scaling
1	very slight scaling (max. 1/8 in., 3.2 mm, depth, 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)

6.3.3 Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete (ASTM C 457)

The test conducted here is ASTM procedure A, the linear-traverse method. This test method uses a microscopical device to determinate the air content of hardened concrete, and the specific surface, void frequency, spacing factor, and paste-air ratio of the air-void system in hardened concrete. The 1" x 3" x 4" (2.5 x 7.6 x 10.1 mm) specimens used in this test were obtained by saw cutting one of the freeze-thaw specimen. The rough surface of the saw cut specimen was subjected to a series of lapping procedures in order to obtain satisfactory visual microscopical observations. The lapping procedure involved the use of a commercially available lapping machine. All the specimens were subjected to the following sequence: (1) apply No. 1560 grit (with the maximum size of 75 μm) for 12 minutes; (2) wash the polishing surface; (3) apply No. 2320 grit (with the maximum size of 35 μm) for 12 minutes; (4) wash the polishing surface; (5) apply No. 2800 grit (with the maximum size of 14.5 μm) for 12 minutes; and (6) wash and dry the surface.

Because the maximum size of coarse aggregate is 3/4 inch (19 mm), the total traveling distance is 90 inches (2286 mm).

The microscope used here had a magnification of 75x. The testing procedure, under the microscopic, involved counting all the aggregates and voids passing through the reference point located in one of the eyepieces. The testing apparatus will automatically store all the observed data and calculate the desirable results.

6.3.4 Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration (ASTM C 1202)

This test monitors the amount of electric current passed through a 4 in. (10.1 mm) diameter cylinder with a thickness of 2 inches (50.8 mm) for a period of 6 hours. A potential difference of 60 V dc is maintained across the ends of the specimen. One end of the specimen is immersed in a sodium chloride solution, and the other in a sodium hydroxide solution. The total charge passed, in Coulombs, has been found to be related to the resistance of the specimen to chloride ion penetration.

All the casting specimens will be allowed to surface dried in air for at least 1 hour. A surface coating epoxy is then brushed onto the side surface of the specimen. After the epoxy coating cures, the specimen is placed into a vacuum chamber; the pressure is maintained at less than 0.04 in (1 mm) Hg for 3 hours. The vacuum chamber is then filled with tap water and vacuum is continued for another hour. The specimen is subsequently soaked without vacuum for 18 hours, after which the specimen is placed in the testing cell. One side of the cell is filled with 3% NaCl solution, and the other side with 0.3 N NaOH solution. The coulombs electricity passing through concrete cell are measured every 30 minutes for a total period of 6 hours. The final result will be compared with the following ASTM C 1202 table in order to assess the chloride permeability level.

Table 6.4 Chloride Ion Permeability Based on Charge Passed

Charge Passed (coulombs)	**Chloride Ion Penetrability**
> 4,000	High
2,000 - 4,000	Moderate
1,000 - 2,000	Low
100 - 1,000	Very low
< 100	Negligible

6.3.5 Compressive Strength of Cylindrical Concrete Specimen (ASTM C79)

All the specimens used in this test were 6 inches (152 mm) in diameter and 12 inches (305 mm) high. After completion of the moist curing period, the specimen are air dried for approximately one hour before capping. After capping, the specimens are placed in the hydraulic compressive machine and subjected to a compressive force at a rate around

35 psi/sec (0.24 MPa/sec). The maximum load divided by the area becomes the final result.

6.3.6 Bleeding of Concrete (ASTM C 232)

This test determines the relative quantity of mixing water that will bleed from a freshly mixed concrete sample. The bleeding test conducted here is the ASTM C 232 Method A - Sample Consolidated by Tamping. In this test a half cubic foot volume container is filled with freshly mixed concrete. The cover is kept in place through out the test, except when drawing the water. The water that has accumulated on the surface is drawn off with pipet at 10-minute intervals during the first 40 min. and at 30-minute intervals thereafter until cessation of bleeding. To facilitate the collection of bleeding water, the specimen is tilted carefully by placing a 2-in (50-mm) block under the container 2 minutes prior to each time the water is withdrawn. All the collected water is accumulated to a 100-ml gradual. The volume of bleeding water per unit area of surface, V, is then calculated as follows:

$$V = V_1/A$$

where:

V_1 = volumer of bleeding water measured during the selected time interval, ml, and

A = area of exposed concrete, cm^2

6.3.7 X-Ray Diffraction

The X-Ray diffraction is a commonly used method to determine the mineralogical composition of material. In this study, a powder sample (ground from the hardened concrete sample) was struck by an X-ray beam. The regular crystalline nature of many of the phases in the sample causes diffraction of the incoming X-rays at particular angles. The intensity and angles of these diffraction effects produce a pattern of peaks (the diffraction pattern or diffractogram) representing what phases are present in the residual. Each crystalline compound has its own peak positions and intensities, and these characteristics (X-ray powder patterns) can be used to assess the mineralogical characteristics of material.

6.3.8 Concrete Surface Finishing

In order to understand the effects of finishing techniques on the surface scaling of concrete, additional specimens were prepared and subjected to different finishing procedures. The finishing procedures consisted of: (1) placing the fresh mix into specimen mold; (2) screeding or striking off the top surface; (3) bullfloating or darbying to eliminate high and low spots and to embed large aggregate particles. After bleeding, the extra specimens were finished with a steel bullfloating. The purpose of the final finishing is to seal the surface and provide a smooth finish.

6.3.9 Mercury Intrusion

In the mercury intrusion porosimetry test technique, mercury is forced under pressure into dried concrete specimens. The pressure required to force mercury into the voids is related to the size of the entranceway of the pores. Using this relationship, by recording the pressure and the volume of mercury intruded, one may obtain an estimation of the pore size distribution. The tests conducted here used a contact angle of 117 degree, and the pressure could reach as high as 30,000 psi (206 MPa).

CHAPTER 7

EXPERIMENTAL RESULTS AND ANALYSES: ENGINEERING PROPERTIES

7.1. INTRODUCTION

The extensive nature of the experimental data produced in this research makes it necessary to analyze subgroups of test results in order to reach practical conclusions. The sequential analysis we have conducted concerns: (1) the performance of clean coal technology by-product versus conventional coal fly ash; (2) effects of the clean coal by-product; and (3) effects of conventional coal fly ash. This chapter focuses only on the engineering properties of concrete. Microstructural analyses and structure-property relationships will be discussed in the next chapter.

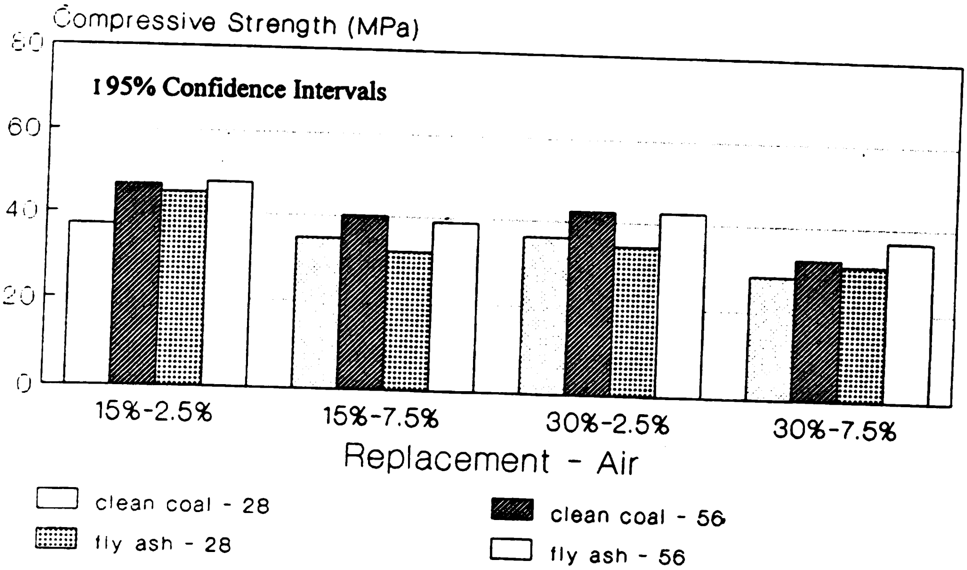
7.2. PERFORMANCE OF THE CLEAN COAL TECHNOLOGY BY-PRODUCT VERSUS CONVENTIONAL COAL FLY ASH

The subcomponent of experimental program analyzed here in order to compare the performance of the clean coal technology by-product and the conventional fly ash is shown in Table 7.1.

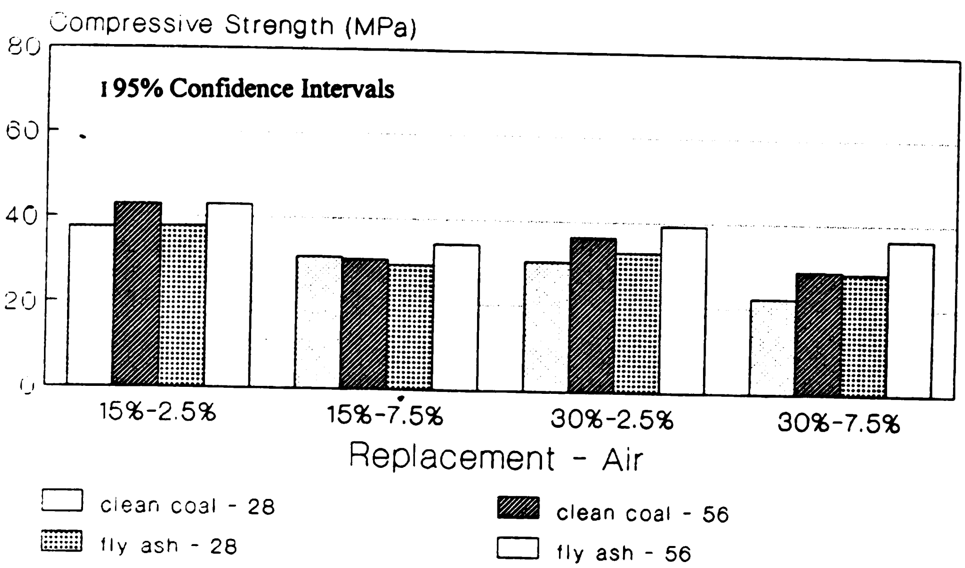
Table 7.1 Subcomponent of the Experimental Program.

Variables	Experimental Program															
W/C	0.4								0.45							
Ash Content	15%				30%				15%				30%			
Air Content	2.5%		7.5%		2.5%		7.5%		2.5%		7.5%		2.5%		7.5%	
Curing Period	28	56	28	56	28	56	28	56	28	56	28	56	28	56	28	56
Clean Coal	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Conventional	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*

The engineering properties considered here are compressive strength, rapid chloride permeability, deicing salt scaling resistance and freeze-thaw durability. Test results are presented in Figures 7.1, 7.2, 7.3 and 7.4.

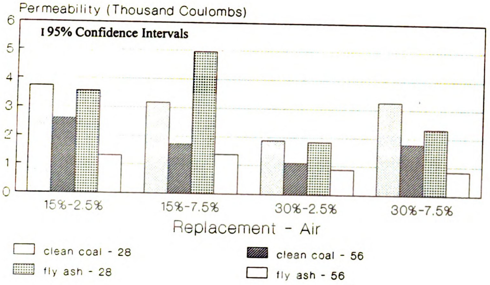


(a) Water-Cement Ratio = 0.4

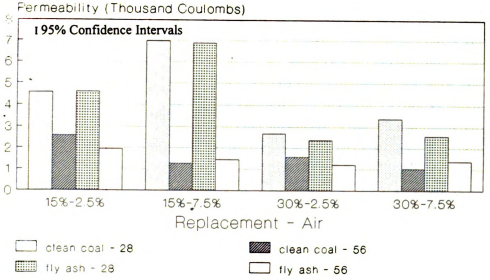


(b) Water-Cement Ratio = 0.45.

Figure 7.1 Compressive Strength Test Results (Means & 95% confidence Intervals).

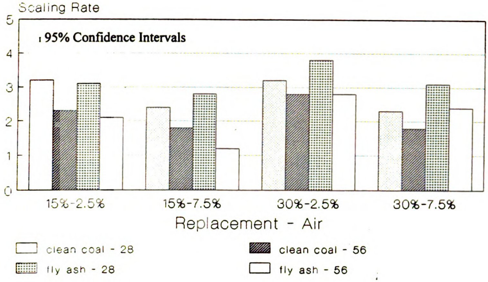


(a) Water-Cement Ratio = 0.4

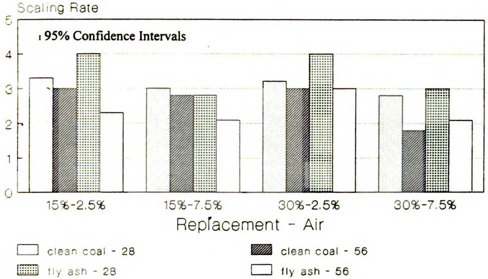


(b) Water-Cement Ratio = 0.45

Figure 7.2 Rapid Chloride Permeability Test Results (Means & 95% confidence Intervals).

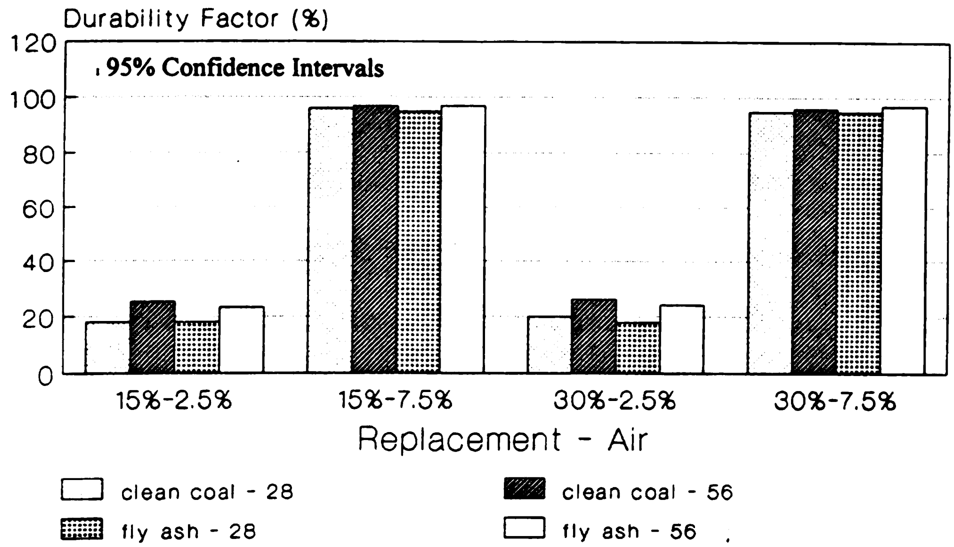


(a) Water-Cement Ratio = 0.4

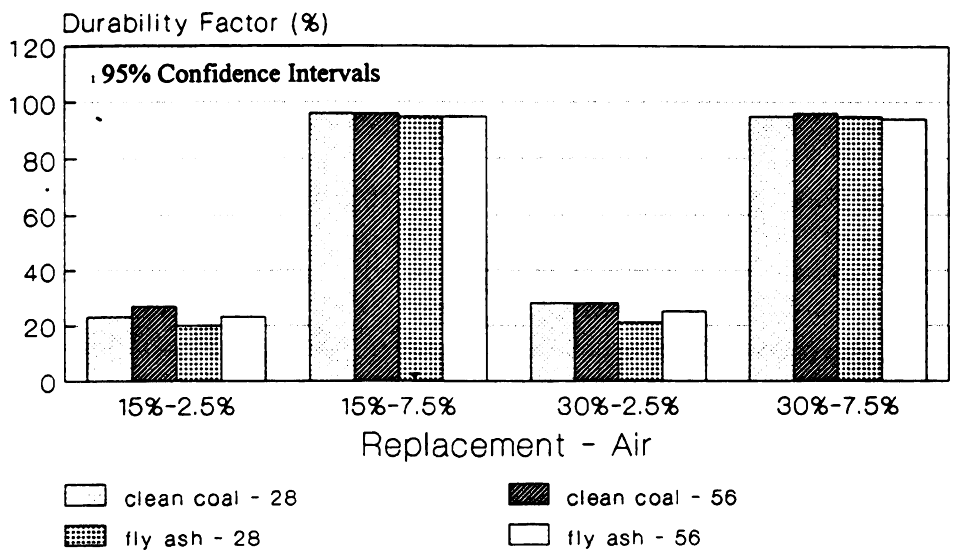


(b) Water-Cement Ratio = 0.45

Figure 7.3 Deicer Salt Scaling Resistance Test Results (Means & 95% confidence Intervals).



(a) Water-Cement Ratio = 0.4



(b) Water-Cement Ratio = 0.45

Figure 7.4 Freeze-Thaw Resistance Test Results (Means & 95% Confidence Intervals).

The results of factorial analysis of variance are summarized in Table 7.2.

Table 7.2 Results of the Factorial Analysis of Variance.

Variables	Compressive Strength	Permeability	Scaling Resistance	Freeze-Thaw Resistance
Ash Type	**	-	I	-
W/C	***	I	I	-
Ash Content	***	I	I	-
Air Content	***	I	***	***
Curing Period	***	I	I	-

I : Significant Interaction
* : Influential at 90% confidence level
** : Influential at 95% confidence level
*** : Influential at 99% confidence level

7.2.1 Compressive Strength

The factorial analysis of variance of the compressive strength test results indicates that there is a significant difference between the clean coal technology by-product and the conventional Class F fly ash at 95 percent confidence level. On the average, concrete mixtures with conventional coal fly ash provided 5% more compressive strength than mixtures with the clean coal by-product. This slight drop could partly result from the improved workability of fresh mix in the presence of coal fly ash. Increasing the fly ash level from 15% to 30% caused an average drop of 7% in compressive strength while the same increase in the content of the clean coal by-product led to a drop of 15% in compressive strength. Overall, the performance of clean coal by-product as a mineral additive in concrete was satisfactory from the strength point of view.

7.2.2 Rapid Chloride Permeability

On the average, specimens with the clean coal by-product showed a 9% more chloride permeability than those with conventional fly ash. This increase, however, was not statistically significant. In the case with lower (15%) ash contented high (7.5%) air content, chloride permeability actually dropped by 11% in mixtures with the clean coal by-product when compared those with conventional coal fly ash. Increasing the fly ash and clean coal by-product contents from 15% to 30% led to drops of 50% and 33% in permeability, respectively. Increasing the moist curing period from 28 to 56 days caused drops of 65% and 54% in the permeability of concrete mixtures with conventional coal ash and the clean coal by-product, respectively.

7.2.3 Scaling Resistance

The analysis of variance of scaling test results indicates that there are interactions between most variables; only air content was independent and had statistically significant effects on scaling resistance. Overall, the scaling rate of concrete with conventional fly ash was 5% worse than that with the clean coal by-product. Increased ash content actually improved the scaling resistance with the clean coal by-product while it had adverse effects with conventional Class F fly ash (Figure 7.5). Prolonged moist curing improved the scaling resistance of concrete specimens with both conventional fly ash and the clean coal by-product (Figure 7.6).

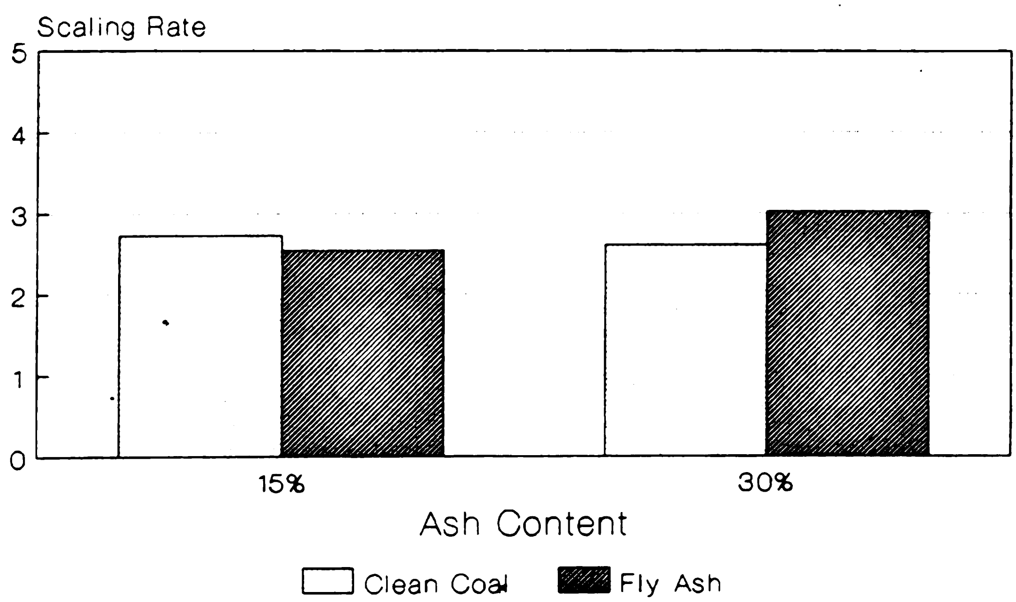


Figure 7.5 Ash Content Effects the Scaling Resistance.

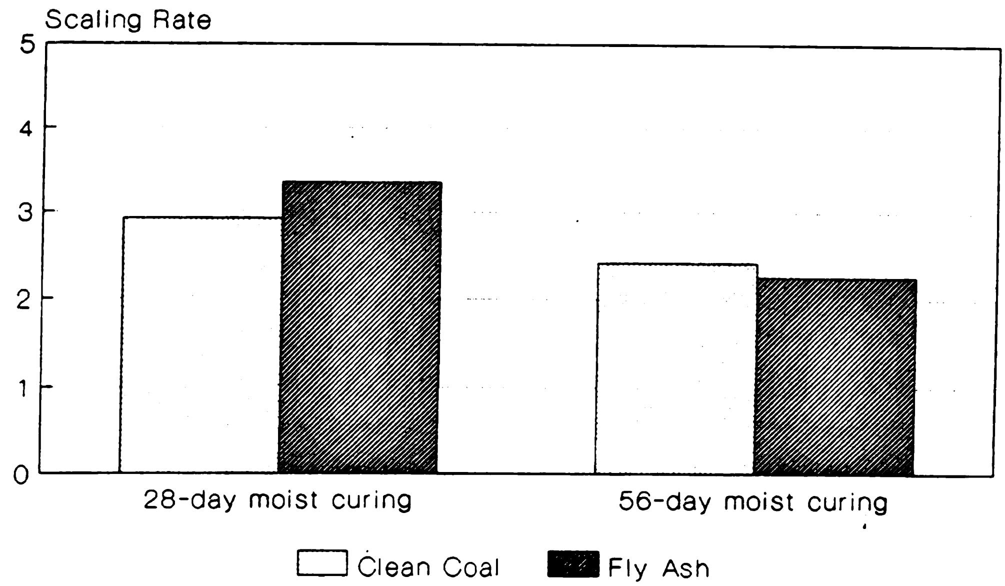


Figure 7.6 Prolonged Curing Effects on the Scaling Resistance.

7.2.4 Freeze-Thaw Resistance

The analysis of results show that the hardened concrete air content is the only factor effects the hardened concrete freeze-thaw resistance. Irrespective of different mix proportioning specifics, sufficient air content guaranteed that the concrete sustains repeated freezing and thawing.

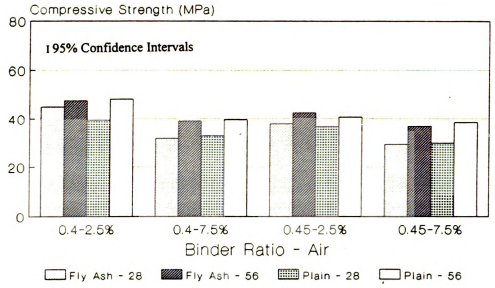
7.3 Effects of 15% Class F Fly Ash

The overall analysis in this section focuses on the performance of plain concrete vs. that with 15% replacement of cement with Class F fly ash. Figure 7.7 shows the relevant test results, and Table 7.3 presents the results of the analysis of variance of the test results.

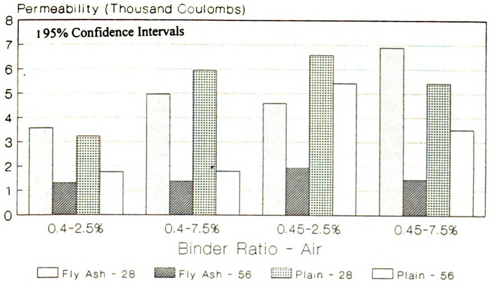
Table 7.3 Results of the Factorial Analysis of Variance.

Variables	Compressive Strength	Permeability	Scaling Resistance	Freeze-Thaw Resistance
W/C	**	**	**	-
Ash Content	-	-	-	-
Air Content	***	-	-	***
Curing Period	***	***	***	-

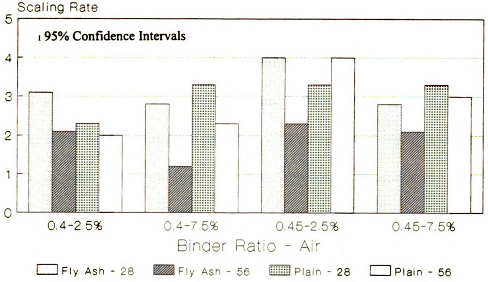
I : Significant Interaction
* : Influential at 90% confidence level
** : Influential at 95% confidence level
*** : Influential at 99% confidence level



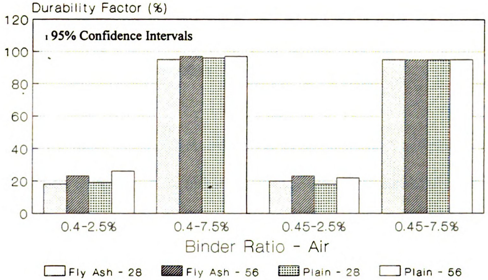
(a) Compressive Strength



(b) Rapid Chloride Permeability



(c) Deicer Salt Scaling Resistance



(d) Freeze-Thaw Resistance

Figure 7.7 Test Results (Mean & 95% confidence Interval).

7.3.1 Compressive Strength

The overall analysis shows there is no statistically significant difference between the class F fly ash concrete and plain concrete in compressive strength. Both plain and class F fly ash concrete have the same trends of dropping 12% compressive strength in response to the increase in water to cement ratio. With increased dosage of entrained air from 2.5% to 7.5%, plain concrete has a tendency towards a strength loss of about 15%. Under the same condition, the 15% class F fly ash concrete would drop 22% of the strength. This indicates that the class F fly ash is more sensitive to water content. Under the prolonged curing period, both class F fly ash and plain concrete show an increase in strength of 14% and 20%, respectively.

7.3.2 Rapid Chloride Permeability

Overall, there is a significant difference between the class F fly ash and plain concrete in the performance of rapid chloride permeability. The plain concrete shows an average of 24% higher permeability value than the class F fly ash concrete. Under the condition of increased water content, fly ash concrete has a 32% increase in permeability value and the plain concrete shows a 55% increase. Figure 7.8 presents the results of changing water to binder ratio effects on the permeability.

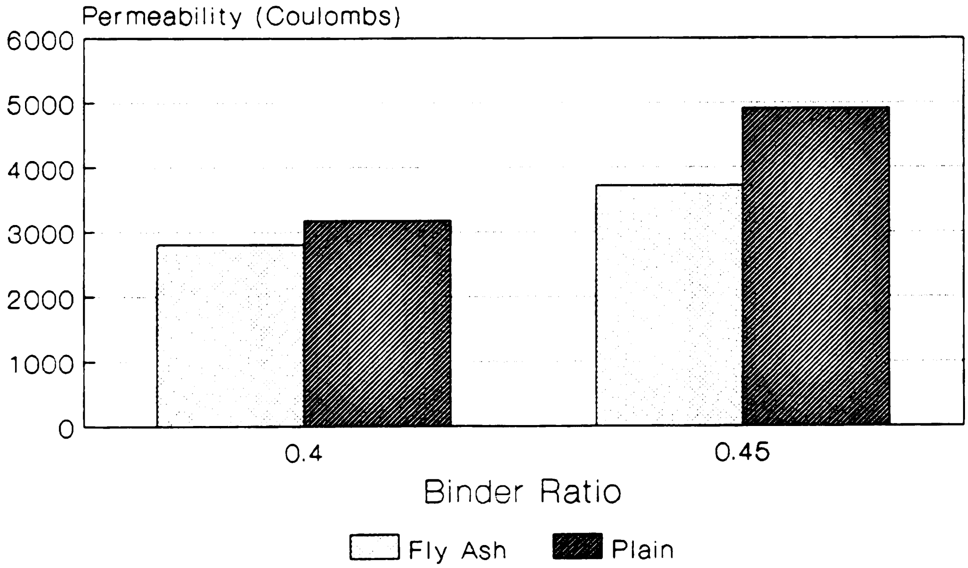


Figure 7.8 Water to Cement Ratio Effects on the Permeability.

Air content is another important factor which affects permeability. Overall, there is only 6% increase in plain concrete permeability when increasing the air content from 2.5% to 7.5%, but 28% increase in the case of fly ash concrete. Figure 7.9 presents the air content effects on permeability. It can be noted that the fly ash is very effective in reducing permeability. Irrespective of the mix proportions, fly ash significantly reduces the chloride permeability of concrete. Class F Fly ash, a round and fine particle, can fit well between all ingredients during the mixing and thus block the continuity of capillary pores structure. The pozzolanic action of fly ash further fills and block capillary pores with the pozzolanic reaction products.

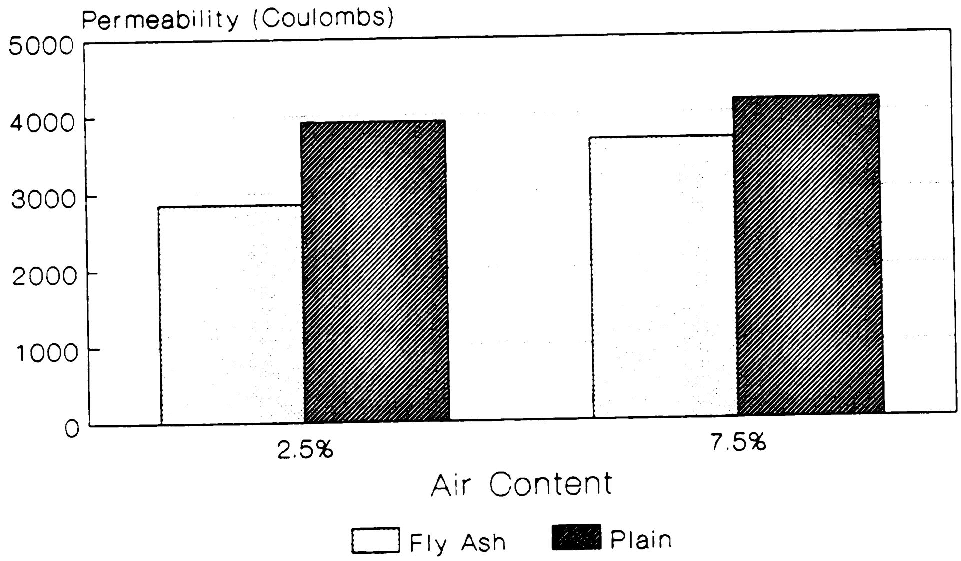


Figure 7.9 Air Content Effects on the Permeability.

One of the most important characteristics of fly ash concrete is the proper curing to ensure the pozzolanic reaction which densifies the microstructure of paste. Usually, this reaction takes place over time in the presence of moisture. In order to take advantage of this phenomenon, a prolonged moist curing period is essential. Of with Class F fly ash, permeability dropped by 70%, and by 487. For plain concrete when the curing period was increased from 28 days to 56 days.

7.3.3 Deicer Salt Scaling Resistance

The Class F fly ash concrete with 15% fly ash performed better than the plain concrete from the scaling resistance point of view. This result may be illustrated by reasons such as: (1) 15% replacement of cement by fly ash would not significantly affect the early age strength of the paste; (2) the use of Class F fly ash significantly reduces the permeability of hardened concrete; and (3) the pozzolanic reaction further densifies the microstructure and helps concrete relieve the adverse effects of deicer salt under repeated freezing and thawing.

Both fly ash and plain concrete were sensitive to changes in water to binder ratio. Increased air content did not change the scaling resistance of plain concrete, but improved that of fly ash content from 2.9 to 2.2. Under prolonged moist curing fly ash concrete showed a dramatic improvement in scaling resistance from 3.2 to 1.9, while plain concrete showed a smaller improvement from 3.1 to 2.8.

7.3.4 Freeze-Thaw Resistance

The analysis of results show that the hardened concrete air content is the only factor affecting freeze-thaw resistance. Irrespective of different mix proportions, sufficient air content will guarantee that the concrete sustains repeated freezing and thawing.

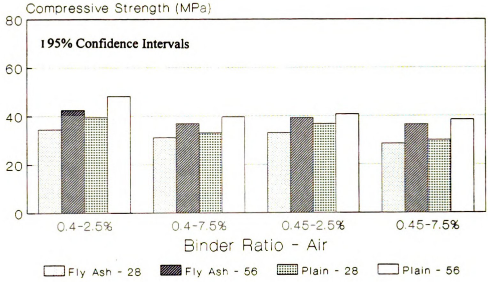
7.4 EFFECTS OF 30% CLASS F FLY ASH

The overall analysis in this section focuses on the performance of plain concrete versus that with 30% replacement of cement with Class F fly ash. Table 7.4 presents the results of the analysis of variance of the test results, and Figure 7.10 shows the relevant test results.

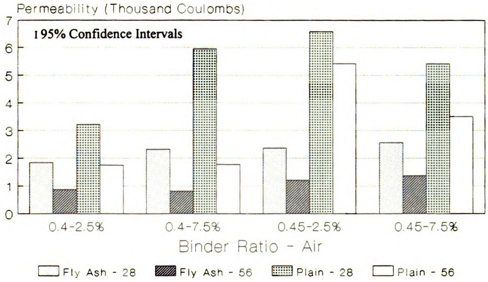
Table 7.4 Results of the Factorial Analysis of Variance.

Variables	Compressive Strength	Permeability	Scaling Resistance	Freeze-Thaw Resistance
W/C	*	**	*	-
Ash Content	***	***	I	-
Air Content	***	-	**	***
Curing Period	***	***	I	-

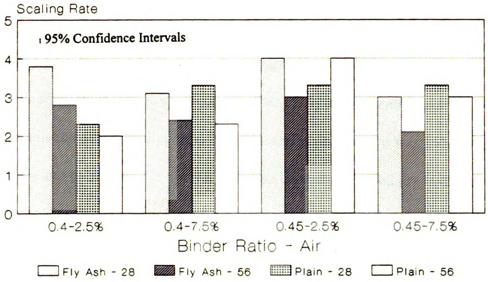
I : Significant Interaction
* : Influential at 90% confidence level
** : Influential at 95% confidence level
*** : Influential at 99% confidence level



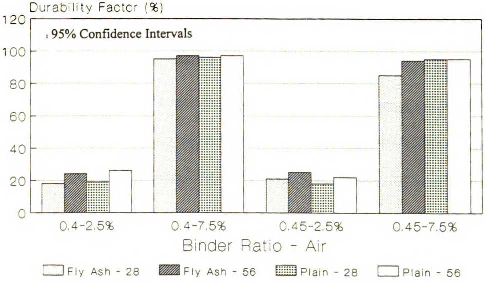
(a) Compressive Strength



(b) Rapid Chloride Permeability



(c) Deicing Salt Scaling Resistance



(d) Freeze-Thaw Resistance

Figure 7.10 Test Results (Mean & 95% confidence Intervals).

7.4.1 Compressive Strength

Overall, the plain concrete provide a higher compressive strength than class F fly ash. Under the condition of increased air content, Class F fly ash showed a decrease of 10% in strength while the corresponding drop in the case of plain concrete was 15%. With increasing water to binder ratio, fly ash and plain concretes showed drops of 5 and 10%, respectively. Prolonged curing significantly increased the fly ash and plain concrete strengths by about 20%.

7.4.2 Rapid Chloride Permeability

Overall, the analysis shows that there is a significant difference between the permeability of fly ash and plain concrete. Figure 7.11 compares the rapid chloride permeability of fly ash and plain concrete. It can be seen that the plain concrete possess permeability values as high as 140% more than the fly ash concrete. Under the condition of prolonged curing, both fly ash and plain concrete show a drop of about 50% in the initial permeability value.

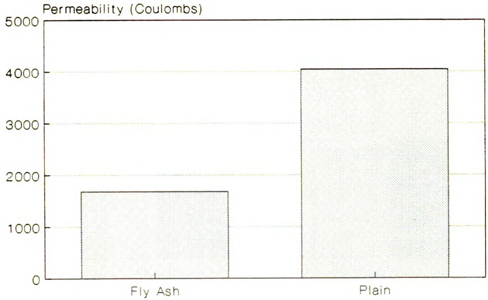


Figure 7.11 Fly Ash Effects on Concrete Permeability.

7.4.3 Deicer Salt Scaling Resistance

In general, there is a significant interaction between the use of fly ash and its curing period as far as the deicer salt scaling resistance of concrete is concerned. The test results are shown in Figure 7.12. Under prolonged curing, fly ash concrete tends to improve its scaling resistance by 26%, while plain concrete shows an improvement of only 7%. It should be noticed that without a proper curing period of 56 days, fly ash would perform 16% worse than the plain concrete from the scaling resistance point of view.

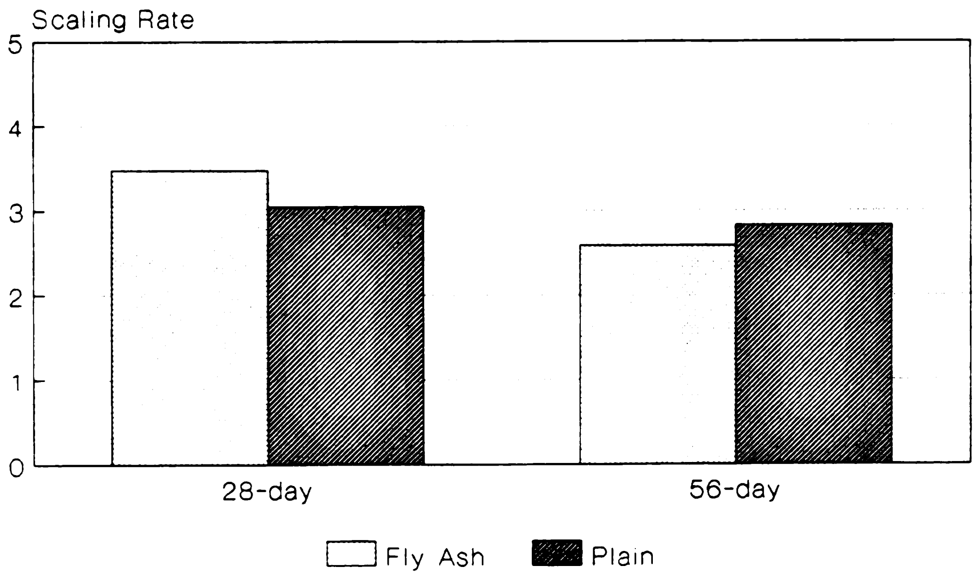


Figure 7.12 Fly Ash Interacts with Prolong Curing Period.

7.4.4 Freeze-Thaw Resistance

The analysis of results shows that the hardened concrete air content is the dominant factor in regard to freeze-thaw durability. Other factors, including fly ash content, are not critical in this regard as far as sufficient air content is entrained into concrete.

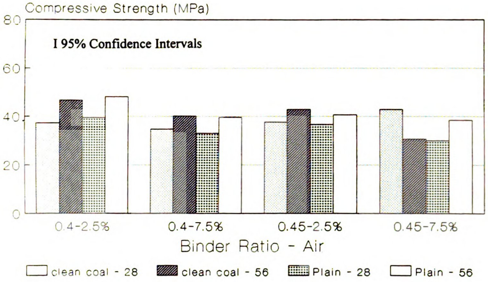
7.5 EFFECTS OF 15% CLEAN COAL TECHNOLOGY BY-PRODUCT

The overall analysis in this section focuses on the performance of plain concrete versus that with 30% replacement of cement with the clean coal technology by-product. Table 7.5 presents the results of the analysis of variance of the test data, and Figure 7.13 shows the relevant test results.

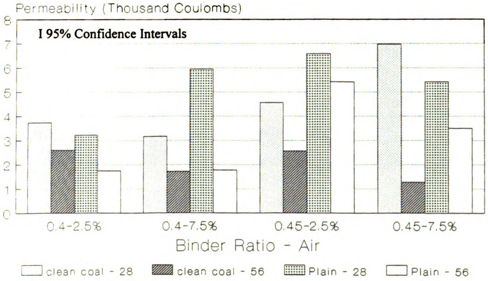
Table 7.5 Results of the Factorial Analysis of Variance.

Variables	Compressive Strength	Permeability	Scaling Resistance	Freeze-Thaw Resistance
W/C	*	**	-	-
Ash Content	-	***	-	-
Air Content	*	-	-	***
Curing Period	**	***	**	-

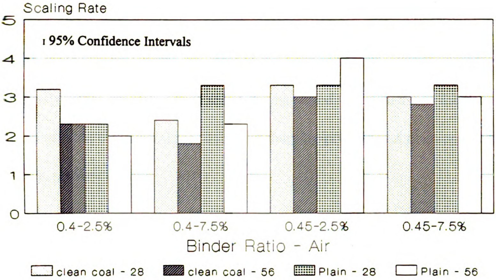
I : Significant Interaction
* : Influential at 90% confidence level
** : Influential at 95% confidence level
*** : Influential at 99% confidence level



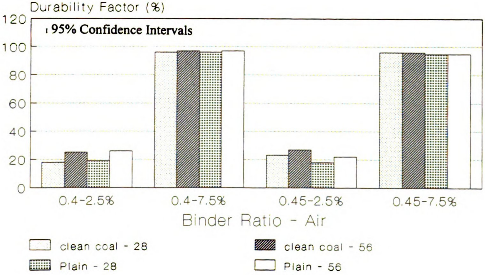
(a) Compressive Strength



(b) Rapid Chloride Permeability



(c) Deicer Salt Scaling Resistance



(d) Freeze-Thaw Resistance

Figure 7.13 Test Results (Mean & 95% confidence Interval).

7.5.1 Compressive Strength

Overall, there was no significant effect of the clean coal technology by-product on compressive strength. Prolonged moist curing period would increase the compressive strength of concretes with clean coal technology by-product and plain concrete by 14% and 19%, respectively.

7.5.2 Rapid Chloride Permeability

Statistical analysis indicates that there is a significant effect of the clean coal technology by-product on permeability. There is an average drop of 20% in permeability with the clean coal technology by-product. Prolonged moist curing benefited both clean coal technology by-product and plain concretes by reducing their permeability by 56% and 48%, respectively (Figure 7.14).

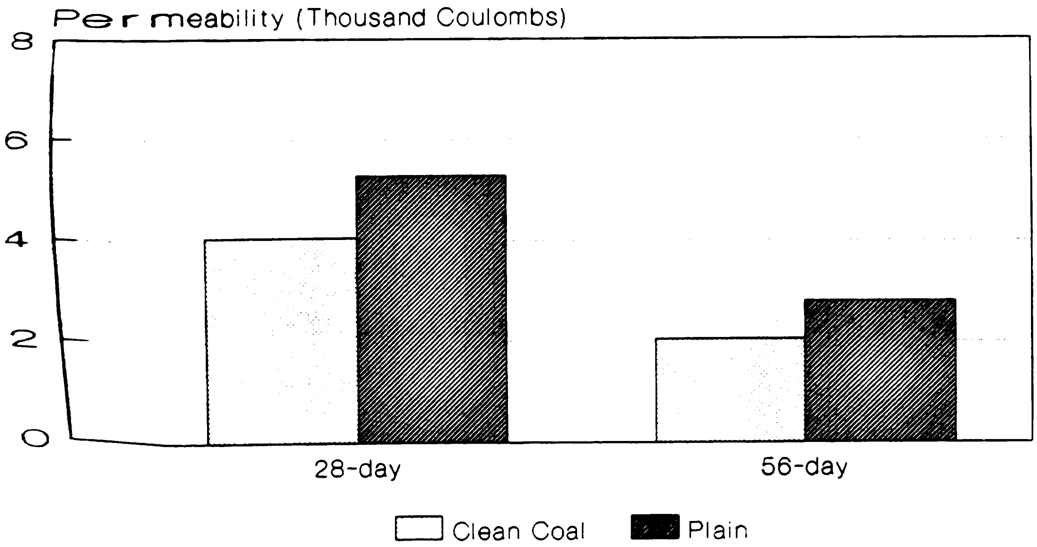


Figure 7.14 Effects of Ash Content Versus Prolonged Curing.

7.5.3 Deicer Salt Scaling Resistance

There is no statistically significant effects of the clean coal technology by-product on the scaling resistance of concrete. Prolonged moist curing would increase the scaling resistance of the clean coal technology by-product concrete by 17% and that of the plain concrete by 11%.

7.5.4 Freeze-Thaw Resistance

The analysis of results shows that the hardened concrete air content is the only key factor in determining the freeze-thaw durability of concrete.

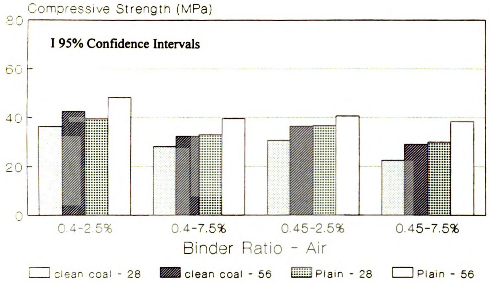
7.6 EFFECTS OF 30% CLEAN COAL TECHNOLOGY BY-PRODUCT

The overall analysis in this section focuses on the performance of plain concrete versus that with 30% replacement of cement with Class F fly ash. Table 7.6 presents the results of the analysis of variance of the test data, and Figure 7.10 shows the relevant test results.

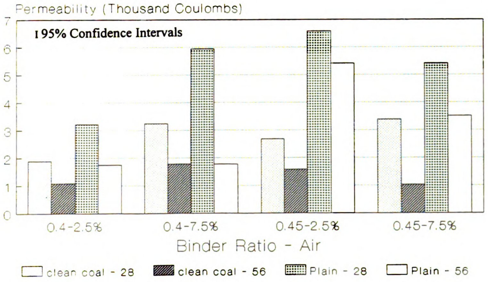
Table 7.6 Results of the Factorial Analysis of Variance.

Variables	Compressive Strength	Permeability	Scaling Resistance	Freeze-Thaw Resistance
W/C	*	*	*	-
Ash Content	***	***	-	-
Air Content	-	-	*	***
Curing Period	***	***	**	-

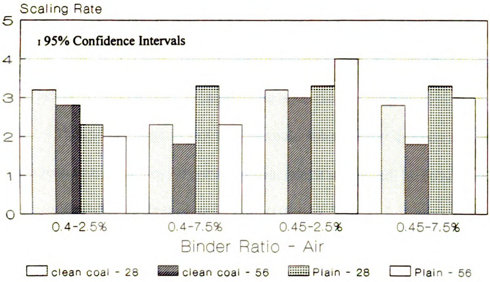
I : Significant Interaction
* : Influential at 90% confidence level
** : Influential at 95% confidence level
*** : Influential at 99% confidence level



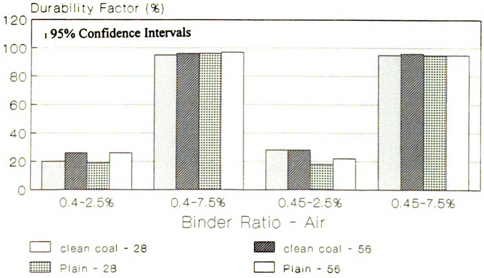
(a) Compressive Strength



(b) Rapid Chloride Permeability



(c) Deicer Salt Scaling Resistance



(d) Freeze-Thaw Resistance

Figure 7.15 Test Results (Mean & 95% confidence Interval).

7.6.1 Compressive Strength

Overall, the replacement of 30% of cement by the clean coal technology by-product has a negative effect on compressive strength; there is an average drop of 15% in compressive strength. Although prolonged moist curing would substantially increase the strength of both the clean coal technology by-product concrete, it would still be 16% lower than that of plain concrete after 56 days of moist curing (Figure 7.16)

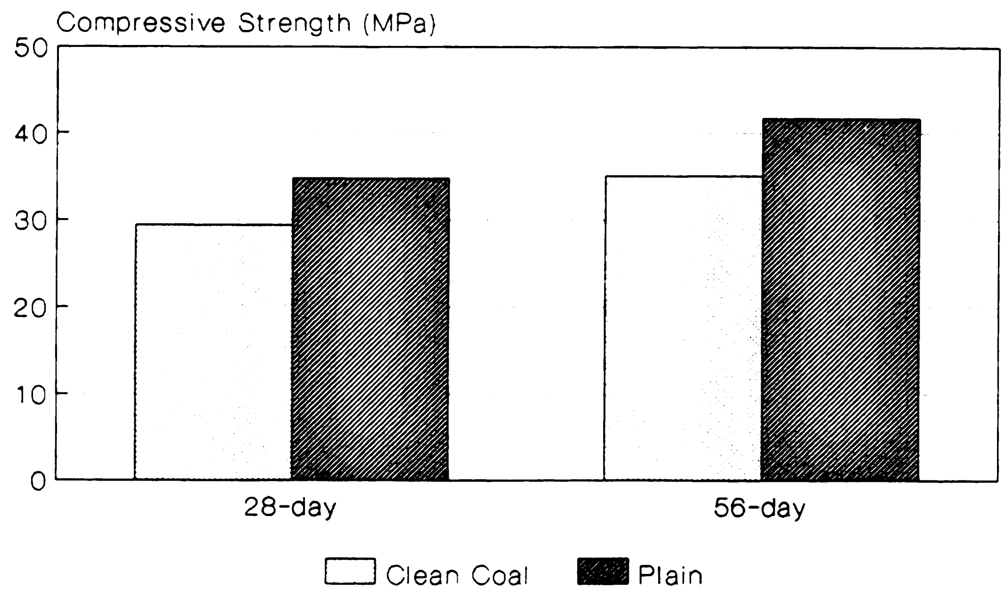


Figure 7.16 Effects of the Clean Coal Technology By-Product Versus Moist Curing Period.

7.6.2 Rapid Chloride Permeability

There is a statistically significant difference between the permeability of clean coal technology and plain concretes. The results indicates an average 50% drop in chloride permeability when using the clean coal technology by-product in concrete. Extended moist curing period reduces permeability by as much as 50% (Figure 7.17). In Figure 17, after prolonged curing, the clean coal technology by-product concrete possessed 50% less permeability when compared with plain concrete.

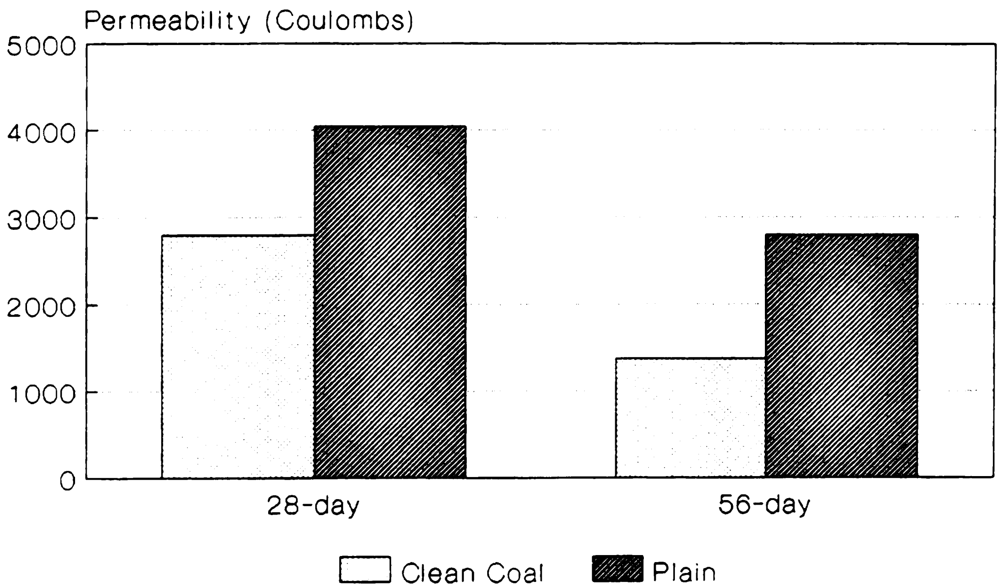


Figure 7.17 Effects of the Clean Coal Technology By-Product Versus Moist Curing Period.

7.6.3 Deicer Salt Scaling Resistance

In general, there is no statistically significant difference between the scaling resistance of the clean coal technology by-product and plain concretes. Prolonged moist curing enhanced the scaling resistance of the clean coal technology by-product and plain concretes by 18% and 8%, respectively.

7.6.4 Freeze-Thaw Resistance

The analysis of results shows that the hardened concrete air content is the only factor affecting its freeze-thaw durability.

CHAPTER 8

STRUCTURE-PROPERTY RELATIONSHIPS

8.1 INTRODUCTION

The properties of hardened concrete are mostly determined by its pore structure - typically the cement paste pore structure. There are many methods that can be used to measure the pore structure of hardened concrete. The mercury intrusion porosimetry has been the most popular and useful one.

The technique for mercury intrusion process involves forcing the mercury to penetrate into the specimen from the surface toward the inner area. During the process of intrusion, with increasing intrusion pressure, entry into the smaller pore systems can be obtained. By observing the pressure and volume of the intruded mercury, the pore entry size and the volume of different pore systems can be evaluated. Hence, the typical pore size distribution obtained by intrusion can be seen as a distribution of pore volume vs. pore entry sizes.

This pore size distribution and pore volume can be also correlated with the compressive strength and permeability. The strength of hardened concrete has a direct relationship with the pore structure. Over time, inside the hardened concrete, the unhydrated cementitious material hydrates continuously (as far as sufficient moisture is present).

This continuous reaction densifies the concrete structure, blocks the continuous capillary pores and improves the strength of concrete.

Rapid chloride permeability of hardened concrete measures the diffusion of electrical irons through the pore structure. Hence, the entry size of pores controls the quantity of ions passing through the capillary pores during the permeability test.

8.2 EXPERIMENTAL WORK

This experimental program considered plain, fly ash, and clean coal technology by-product concretes. Initial analyses are based on the general characteristics of pore structure in order to compare different cementitious materials. Subsequently, regression analyses are conducted in order to develop structure-property relationships in the form of the relationships between pore size characteristics and strength of concrete materials (irrespective of the binder composition).

8.3 PORE SIZE DISTRIBUTION

All mixes discussed in this section had a water-binder ratio of 0.4, aggregate-binder ratio of 5, and air content of 2.5%. In the case of fly ash and clean coal technology by-product concretes, the replacement level was 30%. Figure 8.1 presents the pore size distribution of Portland cement concrete at different ages. The pore system size is rather uniformly distributed at the two ages considered. Over time, pores of all size were almost equally reduced in intrusion volume as a result of continued reactions within the binder. At both ages, a peak volume of pores was observed at a pore size of approximately 0.1 micron.

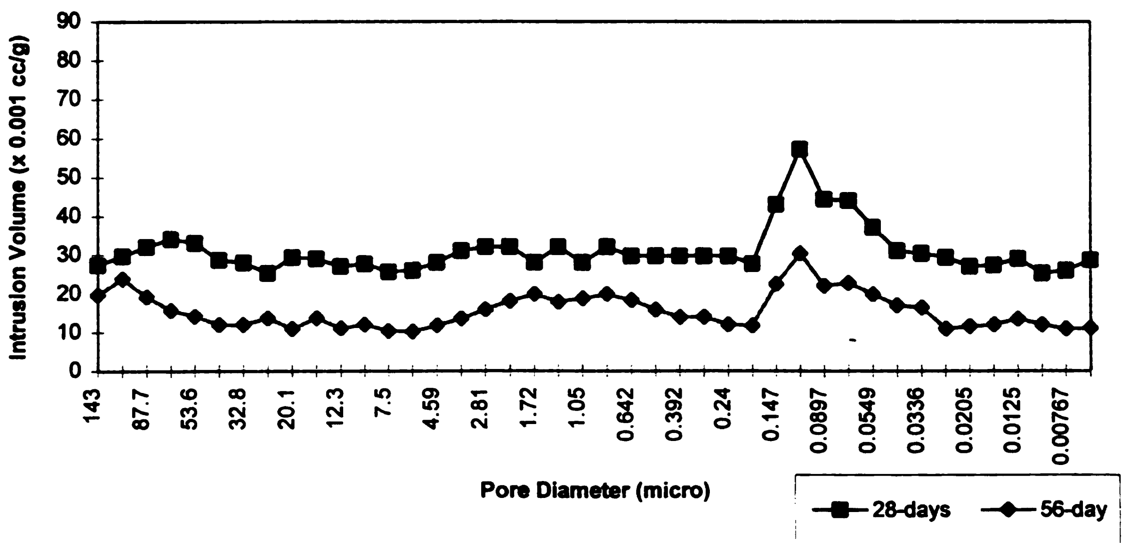


Figure 8.1 Pore Size Distribution of Portland Cement Concrete.

Figure 8.2 presents the pore size distribution of fly ash concrete. The Class F coal fly ash particles used in this study are in the range of 5 to 45 micron in size. The presence of fly ash reduced the uniformity of pore size distribution. While an increase was observed in the volume of smaller pores (<0.1 micron), the volume of larger pores was reduced. At later ages, one could see a drop in pore volume resulting from continued pozzolanic reaction. Fly ash seems to be effective in blocking the continuos capillary pore system, which should reduce the permeability of concrete. It seems that fly ash concrete benefits more than conventional concrete from prolonged curing.

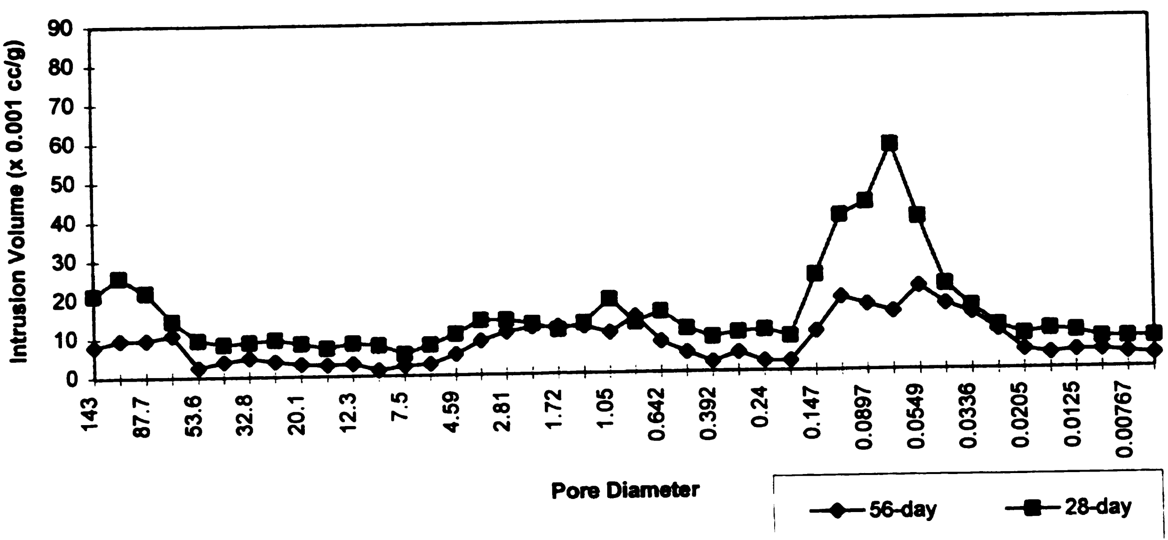


Figure 8.2 Pore Size Distribution of Fly Ash Concrete.

Figure 8.3 shows the pore size distribution of the clean coal technology by-product concrete. It can be seen that the clean coal technology by-product concrete has a relatively high volume of larger pores (~ 100 micron diameter). But this group of pores was almost diminished after prolonged curing. The overall pore size distribution was not uniform but somewhat concentrated around three areas. Although this non-uniformity may reflect the blocking effect which yields reduced permeability, the concentration of pore groups may damage the strength of concrete. Over time, the pore groups between 4 to 0.4 micron were not changed at all. This is an indication that the clean coal technology by-product is lacking a certain group of hydration systems when compared with the conventional Class F fly ash. This may be explained by the factor that the clean coal technology by-product contains, in addition to fly ash, unreacted sorbent and some reacted sorbent products. Some of these reacted products would no longer react with moisture to form hydration products. Another observation in Figure 8.3 is that prolonged curing is essential to remove the potentially problematic large-size capillary pores in the presence of the clean coal technology by-products.

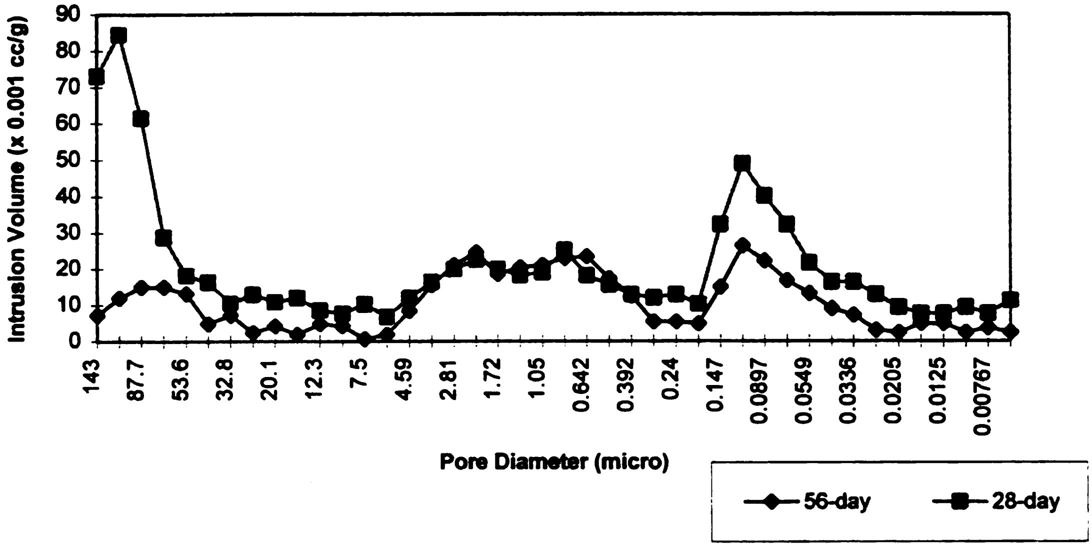


Figure 8.3 Pore Size Distribution of the Clean Coal Technology By-Product Concrete.

Figure 8.4 compares the capillary pore size distributions of Portland cement, Class F coal fly ash and clean coal technology by-product concretes after 56 days of moist curing. The clean coal technology by-product and particularly coal fly ash were effective in reducing the volume content of large capillary pores. The clean coal technology by-product produces a performance somewhat between coal fly ash and pure Portland cement. The reduction of large capillary pore volume is a key positive effect of these pozzolanic materials in concrete.

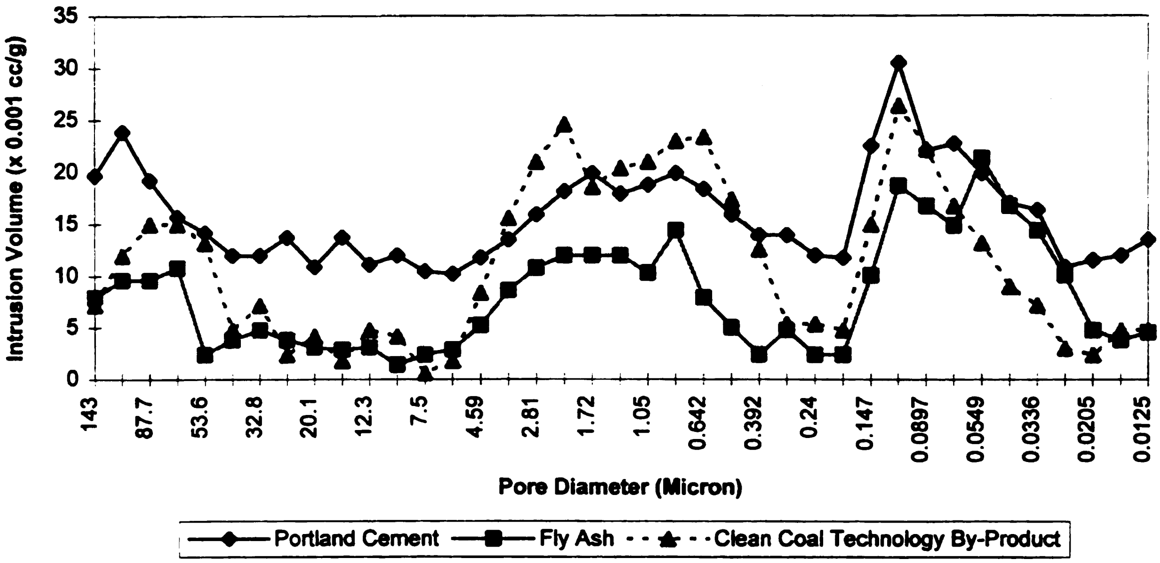


Figure 8.4 Pore Size Distribution at the Age of 56 Days.

8.4 STRUCTURE-PROPERTY RELATIONSHIP

In this section we intend to develop a relationship between the pore system characteristics and the compressive strength of concrete. Since larger pores tend to be more damaging, we have divided the capillary pore system to two groups - those larger than 1 micron, and those smaller than 1 micron. Since we intend to derive generic structure-property relationships, we have considered all mixes, irrespective of mix proportions and binder composition.

Figure 8.5 presents the relationship between compressive strength and total capillary porosity. There is a trend in compressive strength to drop with increasing capillary porosity.

The division of capillary pores to larger and smaller pores did not significantly reduce the scatter in this relationship (see Figures 8.6 and 8.7).

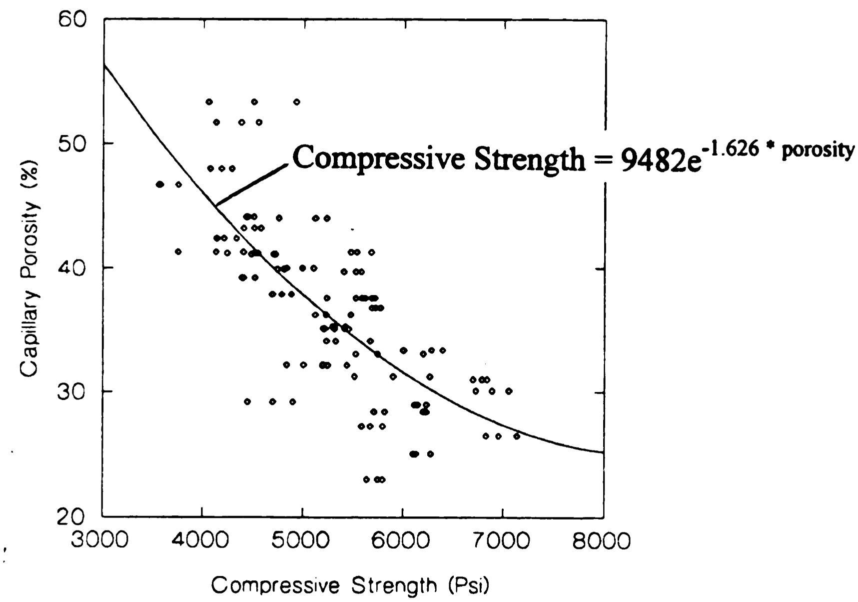


Figure 8.5 Total Porosity Versus Compressive Strength.

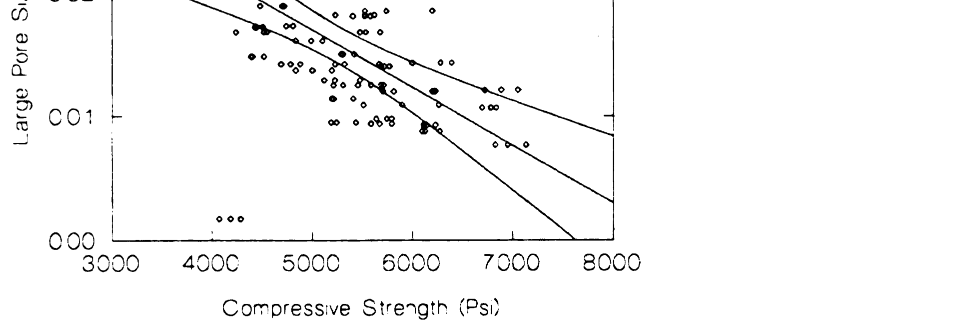


Figure 8.6 Regression Analysis Between Larger Pore Volume and Compressive Strength (Regression Line and 95% confidence region).

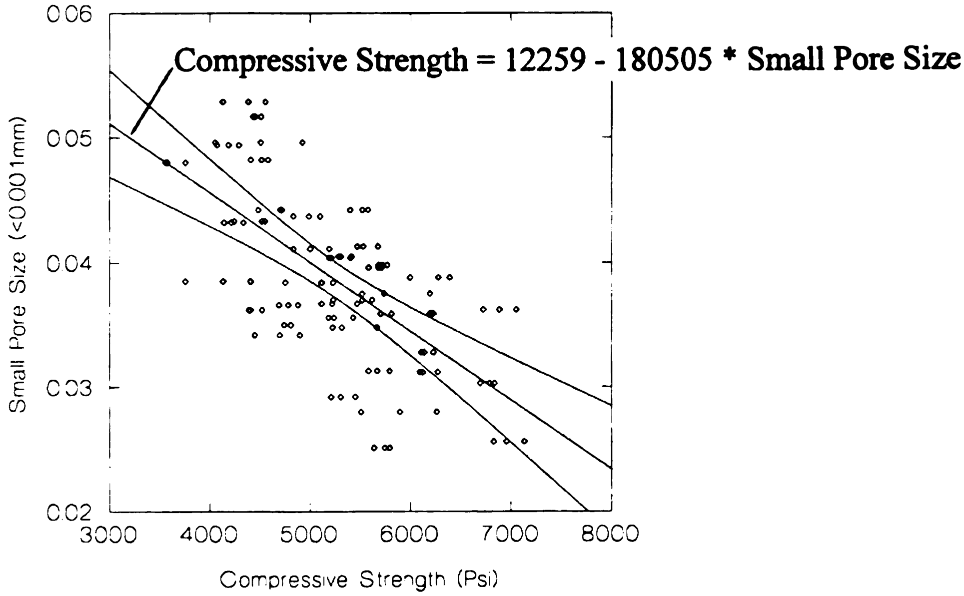


Figure 8.7 Regression Analysis Between Smaller Pore Volume and Compressive Strength (Regression Line and 95% confidence region).

CHAPTER 9

SUMMARY AND CONCLUSIONS

9.1 INTRODUCTION

Coal fly ash and clean coal technology by-products represent major volumes of solid waste. Broad implementation of clean coal combustion technologies have led to the generation of increasing volumes of clean coal technology by-products. This research determines the potential of a clean coal technology (calcium spray dryer) by-product to partially replace Portland cement in concrete. The research compares the performance of conventional coal fly ash with this clean coal technology by-product, and also addresses some key durability characteristics of concrete materials incorporating these industrial by-products.

9.2 EXPERIMENTAL PROGRAM

The experimental study investigated the effects of five variables on the engineering properties and structure of concrete in a 2^5 factorial design of experiments (with three replications):

- ash type (conventional Class F fly ash versus the by-product of the calcium spray dryer clean coal technology)

- ash content (15% and 30% replacement by weight of cement)
- water-binder ratio (0.4 and 0.45 by weight)
- moist curing period (28 and 56 days)
- air content (2.5% and 7.5%)

The concrete specimens produced based on the above experimental design were subjected to the following tests:

- Freeze-thaw durability
- Deicer salt scaling resistance
- Air void system characteristics
- Chloride permeability
- Compressive strength
- Mercury intrusion

9.3 EXPERIMENTAL RESULTS ON ENGINEERING PROPERTIES

9.3.1 Clean Coal Technology By-Product Vs. Conventional Coal Fly Ash

Compared to conventional coal fly ash, the clean coal technology by-product had lower SiO_2, Al_2O_3 and Fe_2O_3 contents but higher CaO, MgO and SO_3 contents. Its Loss On

Ignition was lower than that of coal fly ash, and it also had a somewhat higher fineness (i.e. it was slightly coarser).

Conventional coal fly ash produced concrete materials with ~ 5% higher compressive strength than the clean coal technology by-product. This could be attributed to the somewhat higher workability and compatibility of fly ash concrete. The overall performance of the clean coal technology by-product was satisfactory from the strength point of view. Compared to coal fly ash, the clean coal technology by-product produced concretes with ~9% more chloride permeability. The difference was, however, statistically insignificant. Both conventional coal fly ash and clean coal technology by-products were highly effective in reducing the chloride permeability of concrete. Their increased dosages led to further reduction of concrete permeability.

The clean coal technology by-product produced concretes with ~ 5% improvement in deicer salt scaling resistance when compared with conventional coal fly ash. Increased dosages of the clean coal technology by-product enhanced the scaling resistance of concrete while the reverse was true for conventional coal fly ash.

Both conventional coal fly ash and the clean coal technology by-product produced concretes of sufficient freeze-thaw durability as far as sufficient air content was entrained.

9.3.2 EFFECTS OF 15% AND 30% CLASS F FLY ASH

Replacement of 15% of cement with Class F fly ash generated concrete materials with comparable strength, reduced chloride permeability, improved scaling resistance, and comparable freeze-thaw durability. At 30% fly ash content, concrete materials (when compared with plain concrete) possessed reduced compressive strength, improved chloride permeability, reduced deicer salt scaling resistance, and comparable freeze-thaw durability. At both 15% and 30% replacement levels, fly ash concrete responded better to prolonged moist curing than plain concrete.

9.3.3. EFFECTS OF 15% AND 30% CLEAN COAL TECHNOLOGY BY-PRODUCT

Replacement of 15% of cement with the clean coal technology by product produced a comparable compressive strength, improved chloride permeability, and comparable scaling resistance and freeze-thaw durability. At 30% dosage of the clean coal technology by-product, concrete showed reduced compressive strength, reduced chloride permeability, and comparable scaling resistance and freeze-thaw durability. In the presence of the clean coal technology by-product, concrete responded better to prolonged periods of moist curing.

9.4. STRUCTURE - PROPERTY RELATIONSHIPS

The capillary pore size distribution of concrete was affected by the presence of fly ash and the clean coal technology by-product. Fly ash and, to some extent, the clean coal technology by-product were effective in reducing the total pore volume of concrete. This effect was more pronounced after longer moist curing periods. Fly ash concrete had finer capillary pores which could result from the filling of larger pore with the products of pozzolanic reaction. Prolonged moist curing, which promotes continued pozzolanic reaction, led to further refinement of the capillary pore system in fly ash concrete. The clean coal technology by-product reduced the uniformity of pore size distribution which may reflect on blocking of some pores. There was an increase in the volume of larger pores, which diminished with continued moist curing. The blocking of pores has positive effects from the permeability point of view, but the increase in the volume of larger pores damages strength.

Capillary porosity was found to be a dominant and fundamental property determining the compressive strength of concrete. Irrespective of the mix composition and the presence of fly ash or the clean coal technology by-product, compressive strength showed a clear drop with increasing capillary porosity.

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Chapter 3

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