SCHOOL OF
CIVIL ENGINEERING

INDIANA

DEPARTMENT OF TRANSPORTATION

JOINT HIGHWAY RESEARCH PROJECT

FHWA/IN/JHRP-89/15 - 1

Final Report

LABORATORY INVESTIGATIONS ON
LATEX MODIFIED CONCRETE

Sidney Diamond
Qizhong Sheng

PURDUE UNIVERSITY

JOINT HIGHWAY RESEARCH PROJECT

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INVESTIGATIONS IN LATEX MODIFIED BRIDGE DECK OVERLAY CONCRETE

TO: H. L. Michael, Director
Joint Highway Research Project

September 7, 1989

FROM: S. Diamond, Research Associate
Joint Highway Research Project

Project: C-36-19H
File: 5-5-8

Attached is the Final Report of the HPR Part II Study titled "Investigations in Latex Modified Bridge Deck Overlay Concrete." The report is entitled "Laboratory Investigations of Latex Modified Concrete" and is authored by Professor Sidney Diamond and Mr. Qizhong Sheng.

The objectives of the study were accomplished. It was found incorporation of either Class F or Class C fly ash into latex modified concrete produces no harmful consequences, and has the benefit of significantly reducing the chloride permeability of the resulting concrete. It was also found that the use of superplasticizer with latex modified concrete may result in major improvements in properties at very modest additional cost, or if the latex content is reduced, at less cost than the formulation.

A set of recommendations and guidelines for practical application has been included.

This Final Report is forwarded for review and acceptance by all sponsors as fulfilling the objectives of the study. With its approval and subsequent publication the Phase II referenced HPR study will have been completed.

Sincerely,

Sidney Diamond
Research Associate

SD/kr

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LABORATORY INVESTIGATIONS ON LATEX MODIFIED CONCRETE

by

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Project No.: C-36-19H

File No.: 5-5-8

for

Indiana Department of Transportation

and

Federal Highway Administration
U.S. Department of Transportation

This research was carried out by the Joint Highway Research Project, Purdue University, under the direction of the first author as principal investigator. The contents do not necessarily reflect the official views or policies of the Indiana Department of Transportation or the Federal Highway Administration. The report does not constitute a standard specification or regulation.

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West Lafayette, Indiana 47907

September 7, 1989

1. Report No. FHWA/IN/JHRP/89/15	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Laboratory Investigations on Latex Modified Concrete		5. Report Date September 7, 1989	
		6. Performing Organization Code	
7. Author(s) Sidney Diamond and Qizhong Sheng		8. Performing Organization Report No. JHRP-89/15	
9. Performing Organization Name and Address Joint Highway Research Project Civil Engineering Building Purdue University West Lafayette, IN 47907		10. Work Unit No. NCP No. 4E2a2103	
		11. Contract or Grant No. HPR-2005-(027)	
		13. Type of Report and Period Covered Final Report	
12. Sponsoring Agency Name and Address Indiana Department of Transportation Senate Office Building 100 North Senate Avenue Indianapolis, IN 46204		14. Sponsoring Agency Code	
15. Supplementary Notes Prepared in cooperation with the U.S. Department of Transportation, Federal Highway Administration. From HPR-2005-(025) study entitled "Investigations on Latex Modified Concrete."			
16. Abstract Laboratory investigations were carried out (a) to determine the effects of fly ash on the properties of latex modified concrete used for bridge deck overlays, and (b) to explore modified formulations incorporating superplasticizers, silica fume, and combinations of these with reduced latex content (for economy). It was found that incorporating either Class F and Class C fly ashes at 15% and 25% levels produced no deleterious effects, and provided positive benefits in the form of much reduced chloride permeability and the possibility of better bonding to existing concrete. Exploratory investigations of the effects of naphthalene sulfonate superplasticizer on latex modified concretes resulted in highly favorable indications. Major increases were recorded in both compressive and flexural strengths (the latter to over 2,000 psi at 180 days), and the chloride permeability was reduced by a factor of 2. It was found that reducing the latex content in half (for economy) resulted in retaining the compressive strength and chloride permeability improvements but not the increased flexural strength. Incorporating 10% silica fume with the superplasticizer treatment produced no significant increase in strength but reduced chloride permeability to extremely low values. Combining silica fume and superplasticizer with reduced latex content yielded very high compressive strengths (to over 10,000 psi at 28 days) and retained the very low chloride permeability, but degraded the flexural strength significantly. A method was developed for imaging the latex network by scanning electron microscopy. Extensive studies of the pore structures of latex modified cement pastes of various kinds were also carried out.			
17. Key words latex, concrete, overlays, bridge deck, fly ash, superplasticizer, silica fume, chloride permeability, compressive strength, flexural strength, elastic modulus, pore size, distribution, durability		18. Distribution Statement No restrictions. This document is available to the public through the National Technical Information Service, Springfield, VA 22161	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 212	22. Price

HIGHLIGHT SUMMARY

The objectives of this program were (1) to investigate the effects of incorporating fly ash as a partial replacement for portland cement in conventional latex-modified concrete used for bridge deck overlays, and (2) to explore possible modified formulations for latex-modified concrete incorporating superplasticizers, silica fume, and possible reduced contents of latex (for economy).

With respect to the first objective, latex-modified concretes were prepared containing 15% and 25% replacement levels of three different low calcium (Class F) fly ashes and a single, widely used high calcium (Class C) fly ash. Tests were carried out on fresh concrete properties, on compressive and flexural strength, on dynamic modulus of elasticity, on bond to underlying concrete, on freezing and thawing resistance, and on chloride permeability. Separately prepared latex-modified cement pastes corresponding to each concrete were examined for pore size distributions using mercury intrusion porosimetry. A method of revealing electron microscopy was developed, and the structures of the latex films in these pastes was examined.

It was found that while latex itself reduced the water demand (for 4" to 6" slump) significantly over that of ordinary concrete, incorporating fly ash resulted in further reductions, while at the same time leaving placing and finishing characteristics unchanged. There was little effect

on compressive strength; flexural strengths and dynamic elastic modulus values were reduced slightly at early ages but the effect disappeared after several weeks. Estimates of bond strength to old concrete, carried out using a new "break-off" tester suggested that fly ash possibly increased bond strength. Tests carried out using ASTM C 666 Procedure A indicated that fly ash does not degrade the excellent freezing and thawing resistance of latex concrete.

The major benefit obtained by incorporating fly ash was a highly significant reduction in chloride permeability. Fly ash also significantly reduced the total intruded pore volume of hardened latex cement pastes, while retaining their favorable pore size distribution pattern. Indications were obtained that the latex network in fly-ash bearing pastes was denser and less open-pored than that in plain latex cement paste.

Modified experimental formulations of latex concretes containing naphthalene sulfonate superplasticizer permitted batching at very low water:cement ratios (0.20 to 0.24), without changing the fresh concrete characteristics very much. Compressive and flexural strengths were significantly improved, the latter reaching the very high value of 2,000 psi by 180 days. Chloride permeability was substantially reduced, up to a factor of 2, as was the intruded pore volume of the cement paste. All of the effects were highly favorable, and the estimated marginal cost increase for such formulations was only about 4%. Much of the benefit was retained for a similar formulation except that (for economy) the latex content was cut in half. The compressive strength actually improved, and the benefit with respect to reduced chloride permeability was retained. However, the flexural strength was somewhat reduced, to about the level

of ordinary latex-modified concrete, and the pore structure revealed by mercury porosimetry was somewhat coarser. Such formulation could be placed at perhaps 15% less total cost than the present normal formulation.

Formulations with superplasticizer and silica fume provided some benefits and some drawbacks. The fresh concretes were sticky, and processing difficulties may be expected. Compressive strengths were similar to those obtained with superplasticizer alone, and flexural strengths were marginally reduced. The major effect was a very great additional reduction in chloride permeability, which paradoxically was accompanied by a substantial increase in paste pore volume intruded by mercury porosimetry. Such a treatment would be relatively expensive, and difficult to carry out in the field. If expense is reduced by reducing the latex content, some changes are observed; the compressive strengths actually increase, but the flexural strengths are degraded further. The major benefit of reduced chloride permeability is retained.

Some of these modified formulations appear to offer major benefits, but it should be emphasized that have not been tested for freezing resistance, effect on bond to underlying concrete, and other characteristics important in field service. Further testing is obviously required before they can be considered for field application.

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1. INTRODUCTION

Latex-modified concrete bridge deck overlays have been in satisfactory service for rehabilitation of deteriorated concrete bridge decks for over 30 years. The Dow Chemical Company did the pioneering work on developing a styrene-butadiene (S-B) latex-modified mortar for use on a bridge deck overlay in 1957 [1]. Only limited usage, mostly in rehabilitation, took place until the late 1960's. Usage of S-B latex-modified concrete increased in the early 1970's when deck evaluations and laboratory studies [2] indicated that the chloride permeability of the Dow S-B latex-modified concrete was significantly less than that of conventional bridge deck concrete. In 1976, the Federal Highway Administration (FHWA) authorized the use of a 1.25 inch thick layer of Dow "Modifier A" S-B latex-modified concrete as one of several approved alternative protective systems for new bridge decks constructed in deicing salt environments. Also, more widespread experimental use of the material as a rehabilitative overlay without removal of chloride-contaminated concrete was permitted.

1.1 Statement of the Problem

Recent FHWA policy has indicated that all states must authorize the use of fly ash in highway concrete as an optional bid item in accordance with Environmental Protecting Agency (EPA) RCRA requirements. Latex-

modified concrete used for bridge deck overlays were not exempted from these requirements.

The use of fly ash as a partial replacement of portland cement in the formulation of conventional concrete for various purposes has become increasingly common in recent years, and is now approaching almost a standard practice. Fly ash substitution usually results in considerable savings in the materials cost of conventional concrete, the cost of fly ash being usually only of the order of 25% or so of that of portland cement. In addition to the economic advantages, the use of fly ash can contribute significant improvements in concrete properties, especially in terms of strength development at later ages, and in various durability-related properties. In addition, mixing and placing the fresh concrete is often facilitated.

However there has been essentially no engineering evaluation or controlled research on the possible effects of fly ash when used in latex-modified concrete systems. The Indiana Department of Transportation (INDOT) initiated a small short-term laboratory investigation by the Special Studies Section of the Division of Materials and Tests, to try to establish the basic parameters of what to expect when fly ash is included in latex-modified concrete overlays. However, that study was confined to one particular fly ash, and only a limited range of properties were measured.

In these circumstances, information on the effects of fly ash incorporation in latex-modified concrete was urgently needed by INDOT and other highway agencies. The impetus of the present investigation derived from this urgent need.

Latex-modified concrete for bridge deck overlays are ordinarily batched at relatively high cement contents (of the order of 660 lbs per cu. yd.). The amount of latex used is about 15% by weight of cement (about 24 gallons of the latex dispersion per cu. yd.). The high cost of the latex renders the standard formulation of latex-modified bridge deck concrete extremely expensive by conventional concrete standards. A second impetus for the present research was to see whether modifications of the conventional S-B latex treatment could be developed that were either less expensive than the usual formulation, or alternatively were superior in technical properties.

1.2 Objectives of the Investigation

The main objective of this investigation was to investigate the probable effects that would be produced on conventional latex-modified bridge deck overlay concrete by incorporating representative Indiana fly ashes, in conformance with stated FHWA policy to permit such incorporation at the option of the contractor. Specifically, the effects of these fly ashes on workability, strength, dynamic modulus of elasticity, adhesion to concrete substrates, and durability related parameters such as freezing resistance and relative chloride ion permeability were investigated. Sulfate attack susceptibility tests were not included since sulfate attack has not been reported in highway pavements in Indiana.

A second objective was to more broadly examine the nature of physical structure developed within conventional latex-modified concrete system presently used, and based on the information derived, to attempt to develop possible modifications that could result in cheaper formula-

tions, improved performance, or both. The modifications examined included using either superplasticizer or superplasticizer plus 10% silica fume; trials were also carried out on the effects of reducing the latex content while using heavy dosage of superplasticizer.

1.3 Organization of Report

This report is divided into eight chapters. An introduction and the objectives of the research are presented in Chapter 1. Chapter 2 contains a literature review on conventional latex-modified concretes, fly ash concretes, and silica fume concretes.

The materials used in this research are described in Chapter 3, and a description of the experimental procedures used in this research is provided in Chapter 4.

The experimental results for the concrete testing are presented in Chapter 5, and those for the paste testing in Chapter 6. This is followed by a general discussion of the results obtained in Chapter 7, and the summary and conclusions are presented in Chapter 8.

2. LITERATURE REVIEW

In this chapter literature reviews are presented on the latex-modified concrete, and on the effects of fly ash, silica fume, and superplasticizer on the properties of conventional concrete. A diligent search has turned up little applicable technical literature on latex-modified concrete bearing fly ash or silica fume.

2.1 Latex-Modified Concrete

Latex is a dispersion of organic polymer particles in water. Most latices are milky fluids that are generally white to off-white in color [3].

Among the latex types that have been used with hydraulic cements are [3]:

1. Polyvinyl acetate;
2. Acrylic copolymers;
3. Styrene acrylic copolymers;
4. Vinyl acetate acrylic copolymers;
5. Vinyl acetate ethylene copolymers;
6. Vinylidene chloride and vinyl chloride copolymers;
7. Styrene butadiene copolymers;
8. Epoxy resin latex.

However, styrene butadiene copolymer latices are used in far greater

amounts than any of the other types, and constitute the main subject of concern in the present work. From this point on in the present report "latex" will be taken to refer exclusively to styrene-butadiene formulations.

Formulations of S-B latex systems in commercial practice have been standardized to meet FHWA specifications. Ohama [4] recently listed four typical formulations. All contain about 53% water by weight. About 44% of the total weight is in the form of the latex particles themselves, the latex being 60% styrene - 40% butadiene. Between 1% and 3% consists of polyoxyethylene nonyl phenol ether. In most formulations there is about 0.2% each of sodium alkyl sulfate surfactant and sodium phosphate "builder", and 0.1% ammonium persulfate. In three of the four formulations listed by Ohama there is also a very small percentage ($< 0.3\%$) of naphthalene sulfonate superplasticizer.

2.1.1 Principles of Latex Modification

When latex is used in mixes with portland cement, aggregates, and water, fresh concrete is produced with consistency and workability characteristics only slightly different from conventional concrete. After curing, the latex-modified concrete (LMC) consists of hydrated cement and aggregate, all interconnected by a continuous film of latex. It is in part this continuous film which imparts the superior physical and chemical properties to latex-modified concrete [1].

Some indication of how latex systems function to modify the internal structure of cement paste and concrete has been provided by Ohama [4]. Ohama divided the internal responses into three distinct stages, as

follows:

In the first stage, on mixing the concrete, the small spherical polymer latex particles (ca. $0.2\ \mu\text{m}$ in size) are uniformly mixed into the fresh cement paste. The small polymer particles are considered to partially coat the surfaces of the cement grains and perhaps the early hydration products as well.

In the second stage recognized by Ohama, the progress of cement hydration reduces the remaining water content; in consequence the still-undeposited polymer particles flocculate to form close packed layers on available surfaces.

In the third stage, with further depletion of water by continued cement hydration, the close-packed layers of polymer particles condense to form continuous films or membranes. These seem not to be confined to surfaces, but interpenetrate throughout the cement hydration products. Thus the fine cement paste matrix of ordinary concrete is transformed to a cement-polymer film matrix.

The details of these processes, and the length of time required for the various stages to occur remain speculative.

No mention is made by Ohama of the effect of the latex on the important "transition zone" surrounding the aggregates in concrete or mortar. It is very likely that this zone is modified, but details of the modification are not available.

2.1.2 Properties of Fresh Latex-Modified Concrete

The addition of latex generally improves the properties of fresh concrete. The very small (about $0.2\ \mu\text{m}$ in diameter) spherical polymer

particles that make up the latex may act much as entrained air bubbles to improve the workability and decrease the bleeding of paste. The surface active agents included in most formulations also tend to disperse the paste. Usually they also entrain a considerable amounts of air. According to Kuhlmann (personal communication) the Dow Modifier A formulation contains small amounts of a silicon-bearing air detrainer to counteract this effect.

The overall effect of the addition of latex allows a significant reduction in the water:cement (w:c) ratio of the concrete [5]. A workable slump (4 to 6 inches) can be achieved at a w:c ratio of 0.40 or less, including the water in the latex [6].

There is very little published experimental data on the effects of latex on the physical properties of fresh concrete. Nevertheless, there also are no reports known to the writer that mention workability of latex-modified concrete as a problem.

The results of a study on setting time of latex-modified concrete [7] indicate that latex-modified concrete did not set any faster than concrete without latex. However it does form a "crust" or relatively dry layer on the surface if exposed to dry air for prolonged period, even though the concrete underneath is still quite plastic.

Latex-modified concretes used on bridge deck overlays are almost universally mixed and placed using "concrete mobile" traveling mixers in where the concrete is mixed only briefly as it passes through an auger arrangement and deposited rapidly on the overlay site. Wallace [8] indicated that in such field applications there is only about 10 minutes to screed and finish latex-modified concrete after depositing it on the

deck.

It has been found that LMC responds badly to extended curing under wet conditions. In consequence, in the usual procedures for laboratory studies of LMC, the concrete is demolded after 1 day, but instead of further wet or fog-room curing, it is subsequently "air-cured"; that is, the concrete is merely exposed to the less-than-100% relative humidity of the laboratory air. In the present studies, air curing was carried out in an air-conditioned laboratory, where the relative humidity was typically on the order of 50%.

2.1.3 Mechanical Properties of Hardened LMC

In LMC the latex films within the cement paste increase the bonding within the structure of the hardened cement paste, and probably also at the paste-aggregate interfaces. In conventional concrete, microcracks form early when the paste is subjected to stress. These cracks expand and lead to poor tensile strength and fracture-toughness characteristics. The presence of latex in concrete results in formation of thread-like bridges across these microcracks which resist widening of the cracks. Higher flexural and tensile strengths and greater fracture-toughness thus result for latex-modified concrete.

Another important benefit of latex in concrete is improved adhesion or bond strength to various substrates.

Polymeric material is less stiff than the cement paste it replaces, thus latex incorporation results in a lower elastic modulus for mortars modified with latex [9]. Current data indicate that LMC generally develops an elastic modulus that is approximately 85% of that of

conventional concrete made of the same materials [10].

In general, modification of portland cement concrete by adding S-B latex, combined with the low w:c ratio that this permits, results in a concrete that shows somewhat decreased compressive strength, but increased flexural, tensile, and bond strengths.

Bentur [11] compared LMC with conventional concrete on an equal void-to-cement ratio basis. He found that adding S-B latex produced an increase only in flexural strength; compressive strength and tensile strength were not changed.

Popovics [12] found that wet curing LMC produced substantial reductions in compressive strength as compared to air curing, of the order of 1000 psi or more.

Flexural strength usually increases with increasing latex to cement ratio up to about 0.25 or 0.30, beyond which the flexural strength may decrease [9,13]. However, Clear and Chollar [14] found increases in flexural strength up to latex to cements ratios as high as 0.35.

2.1.4 Durability

It is now well established that latex will "seal" the cement paste or greatly reduce its permeability, depending on the amount added. Therefore the durability of the concrete should be significantly improved since deleterious substances are prevented from seeping into the paste.

Permeability, Carbonation, and Corrosion of Embedded Steel The most impressive feature of LMC is its impermeability; this is what makes it so attractive for bridge deck applications.

Generally, the water absorption and permeation of LMC are a function of the latex content; higher latex contents produced more impermeable concretes.

An even more important characteristic of LMC in bridge deck exposures is its very low "permeability" to chloride ions derived from applied de-icing salt. In an early study [15] it was indicated that this property was a function of latex content. However, the high cost of latex made latex-rich mixes not cost-effective, and it was found that the optimum latex:cement ratio in terms of a balance between reduced chloride permeability and cost was at a latex:cement ratio of about 15%.

Field tests have indicated that with such mixes, chloride ion content is significantly lower at equivalent depths below the bridge deck surface in LMC than in conventional concrete. In addition, LMC decks seemed to isolate the chloride ion intrusion near the surface of the deck, which tends to slow the onset of rebar corrosion processes significantly.

A related feature of LMC is its resistance to carbonation penetration, another corrosion-related property. Ohama and Miyake [16] reported that the carbonated layer of their LMC materials was considerably thinner than that of corresponding unmodified concrete. This was attributed to the excellent gas and fluid impermeability associated with the latex films formed inside the LMC. Subsequent ten-year outdoor exposure results by the same authors [17] confirmed the remarkably improved carbonation resistance of the LMC.

Freezing and Thawing Resistance LMC was said to exhibit improved resistance to freezing and thawing over conventional concrete at a latex-cement ratio of 5% or more [4]. This is due to the reduction of porosity

as a result of decreased w:c ratio used, to the blockage of some pores by polymer, and to air entrainment introduced by polymers and surfactants. However increasing the latex-cement ratio does not necessarily cause an improvement in the freezing and thawing durability.

However, a study on the resistance of LMC to freezing and thawing conducted by Clear and Chollar [14] showed opposite results. The LMC specimens, which were cured 1 day under wet burlap, 13 days in laboratory air, and 14 days in limewater prior to the test, were significantly damaged after 300 freezing and thawing cycles using ASTM C 666, Procedure A. Extending the dry cure period from 13 days to 27 days greatly improved freezing and thawing durability; the durability factor increasing from 34% to 87%. Their study also indicated that for LMC, an adequate air content is necessary to achieve a good freezing and thawing durability as judged by ASTM C 666, Procedure A.

2.1.5 Latex-Modified Concrete with Fly Ash

In March 1987, Smutzer and Zander [18] reported on effects of partial fly ash substitution for portland cement in LMC. This is the only report on fly ash effects in LMC found by the writer. In Smutzer and Zander's study, one Class F fly ash was used, and tests were conducted only on flexural strength, compressive strength, and chloride ion penetration. They concluded that:

1. The LMC strength gain with time does not appear to be significantly affected by the use of fly ash as a partial cement substitute.
2. The LMC strength gain data suggested that some pozzolanic

action of the fly ash was occurring. However, continuing pozzolanic action with time in an LMC overlay application may be in doubt.

3. The LMC containing fly ash as a partial cement replacement yielded equal or slightly lower chloride ion penetration as compared to ordinary LMC.

2.2 Effects of Fly Ash on the Properties of Concrete

As mentioned previously, the only paper on the effects of fly ash in LMC known to the writer was that by Smutzer and Zander [18]. However, there is a vast literature on the effects of fly ash on conventional concrete, some of which may provide useful information in the present study. Accordingly, this section provides a review of some of that information.

Fly ash is the inorganic residue that remains after powdered coal has been burned in the boilers of coal-fired power plants. The powdered coal is entrained in a hot air stream and blown into a combustion zone of the boiler. Under the high temperature of the combustion zone (about 1500°C), most of the organic matter and carbon in the coal are burned off; the mineral impurities in the coal generally melt and remain in suspension in the flue gas. The suspended droplets are quickly transported to lower temperature zones where they solidify as mostly spherical particles. Some of the mineral matter agglomerates to form bottom ash, but most of it "flies out" with the flue gas stream, and hence is called "fly ash". It is subsequently removed from flue gas by mechanical separators, electrostatic precipitators, or bag filters.

Due to its fine particle size and generally noncrystalline character, fly ash is usually classified as an artificial pozzolan. In addition, high calcium fly ashes can display self-cementing properties similar to those of portland cement.

A brief review of literature related to the influence of fly ash on the properties of concrete is presented in the following sections. A broad range of the properties of concrete is affected by the incorporation of fly ash. The review provided here emphasizes only topics germane to the present research.

2.2.1 Properties of Fresh Fly Ash Concrete

When used as a partial replacement for cement, many fly ashes have been shown to reduce the water requirement for a given consistency of concrete. Berry and Malhotra [19] cited two cases in which 30% fly ash substitution for cement was found to reduce the water requirement for constant slump by about 7%. Similar reductions (about 7% when 30% fly ash was substituted for cement) were observed by Compton and MacInnis [20], and by Pasko and Larson [21]. Based on his results of tests conducted on 20 different fly ashes available in Japan, Kokubu [22] found that these fly ashes produced water reduction ranged from 4% to 11% when they were used at a replacement level of 25%. When fly ash was substituted for cement on an equal volume basis, Brown reported a reduction in water demand ranged from 3% to 4% [23].

Not all fly ashes reduce water demand. Many investigators have observed that the use of coarse fly ashes, or fly ashes with high carbon contents (usually 10% or more) increases the water requirement instead of

reducing it [24,25,26,27,28]. Such increases were attributed by Mehta [24] to the presence of cellular particles of "coke", which are usually large in size (100 μm).

The workability of fresh concrete is one of the vital parameters related to its field application, and it is frequently influenced by incorporating fly ash into the concrete mixture. Workability depends in part on cohesiveness, which is largely controlled by the volume of the paste in concrete. An advantage of replacement of cement in concrete by an equal weight of lower-density fly ash lies in the resulting increase in the paste content. Lane and Best [29] calculated that on equal weight basis the volume of fly ash with 2400 kg/m^3 density will exceed the volume of an equivalent weight of portland cement by approximately 30%. Proportioning fly ash concrete on an equal 28-day strength basis often requires a cement replacement ratio greater than 1:1 by weight, thereby producing even a greater increase in the paste to aggregate ratio [24].

Depending on the type of fly ash used, the cement content, and the fines content of the sand, fly ash may either increase or decrease the bleeding of concretes. Fly ashes that improve workability lower the water requirement of the mix, which ordinarily results in less bleeding. In addition, the presence of fly ash may compensate for the deficiency in content of fines in a given mix and break the continuity of bleed water channels [29]. An example of such improvement in harsh mixes that are subject to bleeding was reported by Copeland [30]. The use of fly ash to reduce bleeding of fines-deficient concrete was also recommended by Johnson [28]. On the other hand, Carrette and Malhotra [27] reported increased bleeding (over that observed for plain concrete mix) for 6 out

of 11 fly ashes tested.

2.2.2 Strength of Fly Ash Concrete

The contribution of fly ash to strength is usually attributed pozzolanic reaction, which requires the presence of calcium hydroxide, a byproduct of cement hydration. Therefore it does not occur until a certain amount of time has passed. Although their early strength gain rate is usually lower, fly ash concretes frequently exhibit higher ultimate strengths than plain portland cement concrete at ages above 90 days [29,31,32,33]. The increase in strength also continues for a much longer time than in plain portland cement concrete [34]. Recently Diamond et al. [35] have questioned the extent of pozzolanic reaction that takes place during the period of most active strength gain in fly ash concretes.

Diamond and Lopez-Flores [36], using low-calcium fly ashes at 30% cement replacement by weight, found that the fly ash made no contribution to the strength of ASTM C 109 mortars tested at 1, 3, and 7 days; but by 90 days the strengths of the cement-fly ash mortars were of the same order as the reference portland cement.

Using a greater weight of fly ash than the weight of cement removed will usually help to obtain the required strength at early ages [37]. 28-day compressive strengths of fly ash concrete so batched are usually comparable to that of plain concrete [29].

The early rate of strength development of concretes containing high-calcium fly ashes seems to be affected only marginally by the fly ash. The self-cementing ability of these fly ashes often allows for achieving a strength level comparable with the strength of ash-free concrete even

as early as one day after mixing [38,39]. Using a high-alkali, high calcium fly ash as a replacement of cement up to 35%, Hooton [40] found that the strength equivalence was attained after only 7 days, and long term compressive and splitting-tensile strengths were significantly higher than the corresponding values for the portland cement control concrete.

2.2.3 Durability of Fly Ash Concrete

Permeability, Carbonation, and Corrosion of Embedded Steel The permeability of concrete is affected by size, distribution, and continuity of the pores. Incorporation of fly ashes into concrete usually favorably modifies these by reducing the amount of mixing water, increasing cohesiveness, breaking the bleeding channels, and reducing the amount of leachable Ca(OH)_2 through pozzolanic reaction by which additional amount of calcium silicate hydrate phases is produced.

Manmohan and Mehta [41] observed a significant drop in permeability of cement pastes containing 10, 20, and 30% of fly ash, and concluded that addition of fly ash to portland cement was instrumental in causing pore refinement or transformation of large pores into fine pores -- a process which had a far reaching influence on the permeability of the hardened cement paste. Reduced permeability of fly ash concretes has also been reported by other researchers [42,43].

Reduction of alkalinity of the cement paste by carbonation from atmospheric CO_2 is often the first step in the process of corrosion of steel in concrete. In a fully hydrated portland cement paste, about 20 percent of Ca(OH)_2 is present, although the pH is kept much higher than that of saturated Ca(OH)_2 solution by virtue of alkali hydroxide formation.

Nevertheless, some consider that the Ca(OH)_2 provides the "reserve basicity" necessary for steel protection. Since pozzolanic reaction consumes Ca(OH)_2 , some concerns were raised that the addition of fly ash to reinforced and prestressed concrete would cause a significant reduction in alkalinity within concrete, and so present a danger for corrosion of steel.

Massazza [44] concluded that the resistance to the carbonation of concrete does not appear to be related to the amount of calcium hydroxide in the pore solution, and indeed Diamond [45] found that pore solution in mature portland cement pastes contains little or no calcium, and that the fly ash influence on the alkalinity of pore solution is negligible. The high alkalinity of concrete pore solution is derived from alkali in the cement rather than dissolved calcium hydroxide. The effect of fly ash on this is usually too small to substantially affect the maintenance of the passivation layer present on the reinforcing steel.

The resistance of concrete to carbonation appears to be dependent primarily on physical factors such as permeability of the cement paste.

Diamond and Olek [46] found that incorporation of either Class C or Class F fly ash reduced the measured chloride permeability of concretes; low calcium fly ashes were more effective than high calcium ones, and for either type of fly ash, higher replacement led to greater reduction in measured chloride permeability. Malek et al. [47] also found that Class F fly ash is effective in increasing resistance to chloride ion migration at any replacement level; Class C fly ash blends seem to provide high resistance to chloride ion transport only at higher replacement levels. However, Malek et al. [48,49] further reported that Rockport (Class C) fly

ash is more effective in reducing chloride permeability, at lower curing temperature, than the Class F ashes.

Roy et al. [50] found that cement paste containing fly ash can also greatly reducing the chloride ion concentration in the pore fluid. Similar results were also reported by Page et al. [51].

It has been suggested that the rate of concrete carbonation should be linked to the permeability of the paste in it [52]. It has been found that when even good quality fly ash replaced a part of cement, if the amount of mixing water was not reduced to take advantage of the improved workability, increased permeability leading to more rapid carbonation of the surface region could be expected [53]. In general, reactions associated with fly ash addition decrease the permeability of the concrete while reducing the free lime present in the cement paste. Thus the overall resistance to CO_2 is improved [54].

Freezing and Thawing Resistance The freezing and thawing resistance of fly ash concrete is essentially the same as that of plain portland cement concrete with the similar strength and air content [38,55,56]. The freezing and thawing resistance is influenced by all the factors which operate on plain portland cement concrete. Therefore concrete containing fly ash must be also air-entrained to provide freezing and thawing resistance. As long as adequate air content and bubble-spacing factor are obtained, the incorporation of fly ash should not adversely affect the freezing and thawing resistance of concrete.

Yuan and Cook [38] reported that non-air entrained concrete specimens with a Class C fly ash were damaged by relatively few cycles, from 60 cycles for reference plain concrete to 140 cycles for concrete

with 50% fly ash. But their durability increased as the percent replacement of cement by fly ash increased. The same fly ash concrete specimens with 6.3 to 6.9 percent entrained air generally showed little damage even after 800 cycles. Gebler and Klieger [57] concluded that air-entrained fly ash concrete, with either Class C or Class F fly ashes, had a good resistance to freezing and thawing in water (ASTM C 666, Procedure A), with typical durability factors of about 97 percent.

2.3 Effects of Silica Fume on the Properties of Concrete

Silica fume is a byproduct of the manufacture of silicon metal or ferrosilicon alloys in electric arc furnaces. Reduction of quartz in the presence of carbon at temperature on the order of 2000°C results in the formation of silicon, but about 10-15% of the quartz in the raw material is lost in the form of Si and SiO vapors. Upon cooling the escaping SiO gas is oxidized at the top of the open electric arc furnace and condenses into extremely fine, spherical silica fume particles. The particles are composed essentially of amorphous silica with a SiO₂ content varying from about 85% to 96%, depending on what is being produced in the furnace, and having a surface area of about 20-25 m²/g (nitrogen adsorption). The particle size distribution typically ranges from 0.01 μm to 0.3 μm with about 70% < 0.10 μm [58].

Silica fume has been used in concretes as a partial replacement for Portland cement, and is known to have a great influence on the performance of concrete. The following is a brief review of the effects of silica fume on the properties of concrete.

2.3.1 Properties of Fresh Silica Fume Concrete

The major effects of condensed silica fume on the workability of concrete are to increase the cohesiveness and stability of the fresh concrete. Silica fume concrete displays a much reduced tendency to bleeding and segregation. Silica fume has been shown to increase the water requirement and to reduce the workability of the fresh concrete considerably when no water reducing agent is used. In general, the finishability is improved with the addition of silica fume [59].

In their research on three types of cement (standard Portland cement, rapid hardening Portland cement and rapid hardening Portland cement with 20% pulverized fly ash), Sellevold and Radjy [60] found that for all three cement types the water demand increased when silica fume was added to the mix if no water reducing agent was used. The water demand increased progressively with increasing silica fume content. The addition of a water reducing agent was seen to reduce the water demand much more in silica fume concrete than in the reference concrete, and the combined effect results in great reduction of the water needed for a given slump.

It has been found that equal slump does not indicate equal workability of silica fume concrete and reference concrete since the fresh silica fume concrete is generally more cohesive and "sticky". The increased cohesiveness means that a higher slump is needed to match the workability of a control concrete. It has been suggested that silica fume concrete should have 3-5 cm (1½ - 2 inches) higher slump than a corresponding plain concrete for equal workability [60].

The lack of bleeding in silica fume concrete makes it more vulnerable to plastic shrinkage cracking than ordinary concrete. Even in

moderate weather conditions, it is very important to cover the surface immediately after placing. Protective measures must be taken under conditions of high rates of evaporation from the concrete surface [61].

2.3.2 Strength of Silica Fume Concrete

Silica fume is mostly used for increasing concrete strength, but the effects of silica fume on concrete strength are rather complicated. The main contribution of silica fume to concrete strength development at normal curing temperature takes place from about 3 to 28 days [62,63,60]. Sandvik and Gjrv [64] reported that using the same water to cementitious material (w:cm) ratio the compressive strength of concrete mixes containing no silica fume and containing up to 20% silica fume were almost the same up to 7 days. After 7 days of curing at 20% silica fume content, the compressive strengths developed at 28 and 90 days were higher than that of plain portland cement concrete by about 43% and 55%, respectively.

However, the development of flexural strength of concrete incorporating silica fume is not similar to that for compressive strength, especially for higher contents of silica fume [65]. Data from Yogendran et al. [66] indicates that the 28-day flexural strength diminishes if the silica fume replacement for cement exceeds 10%. For cement mortar incorporating silica fume, Yamato et al. [63] found that at 91 days, there is an increase in the compressive strength but no increase in the flexural strength with the increasing amounts of the silica fume used above 10%.

2.3.3 Durability of Silica Fume Concrete

To make concrete durable, the transfer of dissolved substances that corrode concrete or are a cause of deterioration of concrete must be as small as possible. This transfer may be promoted by the difference of pressure, concentration, temperature and electrical potential acting on concrete. The extent of damage to concrete induced by such substances depends largely on the permeability of concrete. Concretes containing silica fume generally show noticeable improvements in all aspects of durability performance. It is also generally argued that the improved durability of silica fume concretes is a direct consequence of highly reduced water permeability [61,67].

Permeability and Corrosion of Embedded Steel The water permeability of concrete is greatly reduced by incorporation of silica fume. Even concrete with 10% of silica fume is almost impermeable at ordinary water pressures. As Gjrv [68] indicated, the most significant effect are obtained at low cement content. With concrete of 100 kg/m^3 cement content, the coefficient of water permeability was reduced from about $1.6 \times 10^{-7} \text{ m/sec}$ for plain concrete to about $4.0 \times 10^{-10} \text{ m/sec}$ for concrete with 10% silica fume.

Nagataki and Ujike [67] reported the coefficient of air permeability of concrete with condensed silica fume decreases with increasing replacement ratio of condensed silica fume.

The permeability to chloride ions has been directly related to the corrosion durability of steel in concrete. Tests using both traditional and the electrical methods of measurement showed large reductions of

chloride ion permeability for modest additions of condensed silica fume [61]. Byfors [69] reported that addition of up to 20% by weight of silica fume considerably reduced the diffusion rate of chlorides as compared with ordinary portland cement paste of the same water to binder ratio. Increasing the water to binder ratio decreased the resistance to chloride ion diffusion.

Freezing and Thawing Resistance For properly air-entrained concrete, the addition of silica fume should have no detrimental effects on the freezing and thawing resistance of the concrete [70,71,72]. However, there is conflicting evidence of increasing distress in test prisms with high contents of silica fume. Malhotra [72] reported that air-entrained concrete prisms, regardless of the w:cm ratio and containing up to 15% condensed silica fume as a partial replacement for cement, performed satisfactorily when tested in accordance with ASTM C 666 Procedures A and B. However, concrete prisms incorporating 30% of the fume and with a w:cm ratio of 0.42, performed very poorly (durability factors less than 10) irrespective of the procedure used. In another report [73], Malhotra concluded that air-entrained concrete with w:c ratio of 0.35 and 0.30 and without silica fume generally performed satisfactorily when tested in accordance with ASTM C 666, Procedure A. However, concrete prisms incorporating 10 and 20% silica fume showed poor performance in spite of having had more than 4% air in fresh concrete. Yamato et al. [63] also reported that the air-entrained concrete incorporating 20% and 30% silica fume at a w:cm ratio of 0.55 showed very poor freezing and thawing resistance, although the air-entrained control concrete without silica fume performed satisfactorily in the ASTM C 666 freezing and thawing

tests. Therefore Malhotra [72] recommended that engineers exercise caution when using high percentages of condensed silica fume as replacement for portland cement in concretes with w:cm ratios of the order of 0.40, if these concretes are to be subjected to repeated cycles of freezing and thawing.

For non-air entrained concretes of low w:cm ratio the data is controversial. Yamato et al. found that non-air entrained concrete prisms with a w:cm ratio of 0.25 and showed excellent freezing and thawing resistance regardless of the amount of silica fume used. However the use of non-air entrained silica fume concrete with w:cm ratios greater than 0.35 was not recommended when it is to be subjected to repeated cycles of freezing and thawing [63]. Sorenson also obtained good freezing and thawing resistance with non-air entrained concretes with 10 and 20% silica fume and with a w:cm ratio of 0.38 [70]. On the other hand, Malhotra et al. [73] found that non-air entrained concrete prisms, regardless of w:cm ratio and irrespective of the condensed silica fume content, show very low durability factors and excessive expansions when tested in accordance with ASTM C 666 (Procedure A or B). The test prisms appeared to show somewhat increasing distress with increasing amounts of the silica fume.

2.4 Effects of Superplasticizer on the Properties of Concrete

Superplasticizers, also known as high-range water reducers, constitute a class of polymeric materials used to "plasticize" concrete; that is, to disperse the individual particles completely and produce a relatively fluid concrete at low water contents.

Naphthalene sulfonate based superplasticizers and melamine sulfonate

based superplasticizers constitute the major families, although modified lignosulfonates are sometimes elevated to this category.

Reviews of their manufacture, structure, and effects on concrete have been published by Rixom and Mailvaganam [74], Ramachandran and Malhotra [75], and others.

Naphthalene sulfonate (NS) based products appear to presently dominate the market in American practice, and have been used exclusively in the present study. Accordingly, the remainder of this section will be concerned mostly with the effects of this class of superplasticizer, although the effects of melamine sulfonate (MS) based superplasticizer are broadly similar.

NS products are produced by sulfonating naphthalene with sulfur trioxide (or oleum); polymerizing the resulting naphthalene sulfonate with formaldehyde, and then neutralizing the sulfonate groups on the polymer chain with sodium hydroxide [74]. While commercial products have a range of molecular weights (or degree of polymerization), the higher molecular weight fractions (degree of polymerization of the order of 10 or above) are needed to prevent unwanted air entrainment effects.

Normal dosage levels for such materials are in the range of 1% to 3% of the weight of cement, i.e. 16 to 48 oz./100 lbs; the higher dosages are used primarily for specialized concretes where the water content needs to be maintained at a very low level.

Superplasticizers, especially NS based products, are often used with fly ash or especially, with silica fume in concrete. As indicated earlier [60] silica fume by itself increases the water demand to unacceptably high levels. On the other hand, the combination of silica fume and superplas-

ticizers often provides a synergistic effect, and reduces the water demand more than the corresponding dosage of superplasticizer alone.

NS (and MS) based superplasticizers effectively disperse cement paste in concrete by a combination of effects on the zeta potential [76] and so-called "steric stabilization" induced by the presence of the polymer chains between the particles. In any event, there is a loss in dispersion with time that manifests itself in concrete as slump loss. This can be mitigated by using higher than normal dosages of superplasticizer or by several repeated doses added at intervals [77].

While NS based superplasticizers entrain some additional air, the presence of the superplasticizer facilitates escape of air bubbles on handling, especially if repeated doses are used [75].

When superplasticizers are used to reduce the water content otherwise needed for a given slump, the reduced w:c ratio usually results in substantial increases in both compressive and flexural strengths. Compressive strength values of the order of 8,000 psi at 28 days are readily attained by this effect for high dosages of superplasticizer [74,78]; Corresponding flexural strengths of about 1,000 psi are usually attained [75].

Shrinkage and creep of superplasticized concretes are generally similar to those of ordinary concretes at the same w:c ratio [75], except that the relationship between moisture loss (from the saturated condition) and shrinkage is somewhat different [79] in that the superplasticized concrete shrinks more per unit loss of water content.

The durability of superplasticized concrete is in general at least as good as that of ordinary concrete at the same w:c ratio. This is true

with respect to sulfate attack [80,81], salt scaling [82], and steel corrosion [83]. The effect of superplasticizers on freezing resistance is complicated; in general there is increases bubble spacing, but despite this, standard freeze-thaw tests give satisfactory results [75].

If comparisons are not carried out at the same w:c ratio, but rather at the same slump value or workability, heavily-superplasticized concretes, having a much lower w:c ratio and reduced porosity and permeability, can be expected to be much more durable to most concrete problems.

3. MATERIALS

In this chapter the properties of the materials used in this study are described. Some of the indicated measurements were provided by manufacturers or suppliers; most were measured by the writer. In the later case, methods used for the measurements are briefly described.

3.1 Portland Cement

ASTM Type I portland cement, produced at the Lone Star Industries, Inc., plant in Greencastle, IN, was used throughout this study. This cement is widely used in the northwestern part of Indiana, and is as representative Type I cement.

The chemical composition and the physical characteristics of this cement are presented in Table 3.1-1. All the data reported in the table were measured by the cement manufacturer and provided at the time of the shipment.

The composition of the cement is in the normal range for Type I portland cement. The potential C_3S content for this cement is about 61%, somewhat higher than that for some of Type I cements, and the potential C_2S content lower than usual, about 13%. The potential C_3A content is about 10%, which is higher than in some Type I cements. A relatively high early age reactivity might consequently be expected.

Table 3.1-1 Chemical Composition and Physical Characteristics of Cement Used in This Study

CHEMICAL ANALYSIS, %		PHYSICAL DATA	
SiO ₂	20.41	Normal Consistency, %	24.5
Al ₂ O ₃	5.20	Expansion, %	0.002
Fe ₂ O ₃	2.22	Air Entrained, %	10.1
CaO	64.35		
MgO	1.58	Setting Time:	
SO ₃	2.94	Gillmore	
Na ₂ O	0.12	Initial, Hr:Min	2:20
K ₂ O	0.73	Final, Hr:Min	4:10
T.A. as Na ₂ O	0.60	Vicat, Min	105/200
Ignition Loss	2.06		
Insol. Residue	0.31	Fineness:	
		#325, %Passing	85.0
		Wagner, cm ² /g	1860
		Blain, cm ² /g	3680
Potential Compound Composition, %		Compressive Strength, psi	
C ₃ S	60.95	1 Day	2000
C ₂ S	12.62	3 Days	3470
C ₃ A	10.03	7 Days	4555
C ₄ AF	6.76	28 Days	5865
CaSO ₄	5.00		

3.2 Latex Admixture

Specifications for styrene-butadiene latex emulsions for bridge deck overlay concrete require that the latex emulsion have the following properties [14]:

Solids Content:	46.5 to 49.0 percent
Butadiene Content of Polymer:	34 ± 1½ percent
Styrene Content of Polymer:	66 ± 1½ percent
pH value:	9.5 to 11.0

Average Polymer Particle Size: 1,900 to 2,500 Å

The latex used in this study was the current Dow Modifier A styrene-butadiene formulation obtained from Modified Concrete Suppliers, Inc., Indianapolis, IN, through the courtesy of Mr. R.K. Smutzer, INDOT.

The solid content of the latex used was measured by drying the latex emulsion in the oven at 105°C to constant weight. In this case, the solid content is equal to the quantity of polymer particles plus the solid portion of any additive contained in the latex emulsion. The measured solid content for the latex used was 47 ± 0.5 percent, which is the average of the measurement results of seven samples from two different batches.

According to the specification provided by manufacturer, the latex emulsion had a particle size ranging from 2,100 to 2,400 Å.

3.3 Fly Ash

Fly ashes from four power stations were selected for use in this study to represent a wide range of chemical and physical properties of fly ashes available in Indiana. The single Class C fly ash used (from the Rockport Station of the Indiana and Michigan Electric Co.) is an excellent fly ash and is utilized widely in Indiana concrete. The three Class F fly ashes used have varying characteristics. The Schahfer fly ash (from the Schahfer Station of Northern Indiana Public Service Company) is an extremely fine fly ash and is thought to be unusually reactive because of this. The Stout fly ash (from the Stout Station of the Indianapolis Power and Light Co.) is a typical fair quality Class F fly ash representative of many in the State. The Gibson fly ash (from the Gibson Station of

Table 3.3-1 Chemical and Physical Properties of the Fly Ashes Used in This Study

Generating Plant Symbol Used	Rockport (R)	Schahfer (A)	Stout (T)	Gibson (G)
SiO ₂ (%)	35.8	59.9	49.8	48.2
Al ₂ O ₃ (%)	19.6	23.7	22.9	22.0
Fe ₂ O ₃ (%)	6.36	5.73	21.0	16.0
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃ (%)	61.8	89.3	93.7	86.2
CaO (%)	26.8	1.69	4.14	1.79
MgO (%)	3.30	1.20	0.85	1.90
Loss of Ignition (%)	0.34	2.43	3.40	6.50
Pozzolan Activity				
Index with Cement (%)	116	136	57	78
Magnetic Particles (%)	0.60	1.60	20.1	12.6
Specific Gravity	2.61	2.00	2.37	2.35
Mean Size, μm	14	19	26	16
% > 45 μm	21	2	31	24

Public Service Indiana, Inc.) is a relatively coarse fly ash with a high content of magnetic particles, which are thought to be generally non reactive in concrete. Such high iron content fly ashes are unusual in the most parts of the world but fairly common among Indiana fly ashes. Selected chemical and physical properties of these four fly ashes are listed in Table 3.3-1 [46].

3.4 Silica Fume

Microsilica EMS 900 silica fume supplied by Elkem Chemicals, Inc., Pittsburgh, PA, was used in this study. The data provided by supplier show that this product contains mainly amorphous SiO₂ and carbon, with small contents of oxides and salts of Al, Fe, Mg, Ca, Na, and K. The content of amorphous SiO₂ is stated as being 90-98 percent by weight. The primary particles of microsilica are essentially submicron in size (less

than 1 micrometer). It has a bulk density of 12-22 lbs/ft³, and a specific gravity of 2.2.

3.5 Aggregates

ASTM standard procedures were followed to determine the properties of the aggregates, including the following test methods:

1. ASTM C 136-80 for particle size distribution of sand and coarse aggregate;
2. ASTM C 127-80 for bulk specific gravity and absorption of coarse aggregate;
3. ASTM C 128-79 for bulk specific gravity and absorption of fine aggregate;
4. ASTM C 29-78 for dry rodded unit weight of both fine and coarse aggregate.

Table 3.5-1 Physical Properties and Gradation of Fine Aggregate

Fineness Modulus FM = 2.59		
Bulk Specific Gravity (surface saturated dry) BSG _{SSD} = 2.62		
Absorption A = 1.74%		
ASTM Sieve Designation	Cumulative weight percent	
	Retained	Passing
3/8"	0	100
No. 4	0	100
No. 8	5	95
No. 16	23	77
No. 30	52	48
No. 50	83	17
No. 100	96	4
Pan	100	0

Table 3.5-2 Physical Properties and Gradation of Coarse Aggregate

Bulk Specific Gravity (surface saturated dry) $BSG_{SSD} = 2.73$		
Dry Rodded Unit Weight $DRUW = 96.7 \text{ lbs/ft}^3$		
Absorption $A = 1.28\%$		
ASTM Sieve Designation	Cumulative weight percent	
	Retained	Passing
1/2"	0	100
3/8"	19	81
No. 4	78	22
Pan	100	0

The results are given in Tables 3.5-1 and 3.5-2.

The fine aggregate used in this study was local siliceous pit sand. The selected physical properties and sieve analysis data for the sand used in this study are given in Table 3.5-1.

No. 11 aggregate ($d_{max} = 1/2 \text{ in.}$) was used in this study as coarse aggregate. The aggregate used was clean crushed limestone supplied by Verplank Concrete & Supply Inc., of West Lafayette, IN. The selected physical properties and sieve analysis results of this aggregate are shown in Table 3.5-2.

The fine and coarse aggregates were combined at a Fine/(Fine+coarse) ratio of 0.575 by weight for concrete mixing.

3.6 Admixtures

A neutralized vinsol resin (Master Builders MBVR) was used as the air entraining admixture in this study. The quantity of air entraining agent used was adjusted as necessary to give 4-6% of air in the fresh

concrete mix, after correction for the aggregate void content.

A naphthalene sulfonate type superplasticizer (Master Builders Rheobuild 1000), was used in this study. The actual dissolved solids content of the superplasticizer admixture was approximately 40% by weight. The normal dosage rate range recommended by manufacturer is 10 to 25 fl. oz. per 100 lb (0.65 to 1.6 litre per 100 kg) of cementitious materials.

4. EXPERIMENTAL PROCEDURES

The experimental procedures used in the course of this study are described in this chapter. Some of the methods used are ASTM standard methods which are commonly used. For such methods, only the ASTM designation codes are given. Where the test method is not a standard ASTM procedure, or for less commonly used ASTM standard methods, a detailed description is provided so that the measurement can be unambiguously repeated.

4.1 Preparation of Concretes

Sixteen concrete mixes were prepared for this study. They were divided into five different groups which are described as follows:

1. Conventional portland cement concrete (OPC) as a reference;
2. Conventional latex-modified concrete (LMC) also as a reference;
3. LMC with each of the different types of fly ash at cement replacement levels of 15% and 25%;
4. LMC with a naphthalene sulfonate superplasticizer, at one of several dosage rates, and either full or half normal latex contents;
5. LMC with 10% silica fume and a naphthalene sulfonate superplasticizer, also at several dosage rates, and either

full or half normal latex contents.

All the mixes other than two reference concretes were coded using a four-part description. The first letter of the description indicates the type of solid mineral admixture used. Code letters used to distinguish the different types of fly ash are given in Table 3.3-1. For silica fume the code letter is S; for "no mineral admixture" the code letter is N.

The second element of the code is a two digit number, indicating the replacement level, in percent. The third code entry is a letter indicating the latex content in the concrete. Here F stands for the usual latex content (30% liquid latex product by weight of cement), and H for half of usual latex content. The fourth element of the code is a two digit number representing the dosage of superplasticizer in fl. oz. per 100 lbs of cementitious materials. For example, N00H38 means that no mineral admixture was used, the latex content was half of usual latex content, and 38 fl. oz. of superplasticizer admixture per 100 lbs of cement was added.

The basic LMC mix design incorporated about 30 percent of the latex liquid product (equivalent to about 14% solids) by weight of cement, and a cement factor of 657 lbs/yd³. Fly ash or silica fume were added in some mixes as a replacement of equal weight of the cement. Water:cementitious material (w:cm) ratios were adjusted to give a slump between 4 and 6 in. The plain concrete had a cement factor of 657 lbs/yd³, and a w:c ratio of 0.48 to give the slump required.

The specific compositions of each of the 16 mixes used in this study is given in Table 4.1-1.

Table 4.1-1 Batch Weight Compositions of Mixes Used in the Study

Mix	Materials (lbs)								SP (ml)
	w:c	Cement	Fly Ash	Silica Fume	Latex	Water	Sand	Coarse Aggregate	
OPC*	0.48	42.6	-	-	-	20.5	111.6	82.5	-
LMC	0.29	42.6	-	-	13.3	5.7	111.6	82.5	-
A25F00	0.25	34.1	10.7	-	13.3	4.1	111.6	82.5	-
T25F00	0.27	34.1	10.7	-	13.3	5.0	111.6	82.5	-
R25F00	0.26	34.1	10.7	-	13.3	4.6	111.6	82.5	-
G25F00	0.27	34.1	10.7	-	13.3	5.0	111.6	82.5	-
A15F00	0.26	37.5	6.4	-	13.3	4.4	111.6	82.5	-
T15F00	0.28	37.5	6.4	-	13.3	5.2	111.6	82.5	-
R15F00	0.27	37.5	6.4	-	13.3	4.8	111.6	82.5	-
G15F00	0.27	37.5	6.4	-	13.3	4.8	111.6	82.5	-
N00F15	0.24	42.6	-	-	13.3	3.2	111.6	82.5	189
N00F30	0.20	42.6	-	-	13.3	1.5	111.6	82.5	378
N00H30	0.22	42.6	-	-	6.7	5.9	111.6	82.5	378
S10F23	0.24	38.4	-	4.3	13.3	3.2	111.6	82.5	284
S10F38	0.20	38.4	-	4.3	13.3	1.5	111.6	82.5	473
S10H38	0.23	38.4	-	4.3	6.7	6.3	111.6	82.5	473

* Air entraining agent (MBVR) was added to bring the air content of the fresh concrete to the level similar to that in the LMCs.

The OPC concrete was prepared from the same cement and aggregates used in the same proportion as the reference LMC concrete, and batched using the water content necessary to achieve a 5 in (+ 1 inch) slump. The resulting w:c ratio, 0.48, was somewhat higher than the 0.443 value specified for Class C structural concrete by INDOT.

All concrete mixes were prepared in the laboratory using a Lancaster pan type mixer (4.0 ft³ nominal capacity). The volume of the concrete mixed at a given time was about 1.75 ft³ (50 dm³). It should be noted that pan mixing probably produces a greater degree of mixing uniformity than is achieved in field applications using the auger mixing characteristic of concrete mobile units.

The plain concrete was mixed in accordance with the standard ASTM C

192 procedure. Prior to starting rotation of the mixer, coarse aggregate and about 1/3 of the mixing water was placed in the mixing pan. After the mixer was started, sand, cement, and water were added sequentially while the mixer were running. The air entraining agent (MBVR) was dissolved in the mixing water before it was added into the mixer. After all of the ingredients were in the mixer, the concrete was mixed for 3 minutes followed by a 3 minute rest period; a 2 minute final mixing completed the mixing operation.

A modified mixing procedure [14] was followed for all of the latex-modified concretes. The total mixing time for each batch was 3.5 minutes, and the ingredients were combined as follows:

1. the coarse aggregate and latex were combined and mixed for 1/2 minute;
2. the sand and cement, and fly ash or silica fume (if used), were added and mixed for 1 additional minute; and
3. the water (containing dissolved superplasticizer, if used) was added and mixed for 2 additional minutes.

The slump of each mix was measured immediately after completion of mixing and again 5 minutes after completion of mixing, in accordance with ASTM C 143. The unit weight of the concrete was then determined in accordance with ASTM C 138. Finally the air content of each freshly mixed concrete batch was measured using the standard pressure method, ASTM C 231.

4.2 Casting and Curing of Concrete Specimens

For strength testing purposes, five 3 x 6 in. compressive test cylinders were cast in plastic molds, and four 3 x 3 x 15 in. flexural

test beams were cast in steel molds from each mix. Three individual batches of each mix were required. After the tests for slump, unit weight, and air content described previously, the fresh concrete was placed into molds in two layers and consolidated by rodding each layer 25 times using a steel rod 3/8" in diameter.

For the chloride permeability test, freshly-mixed concrete was placed into 3.75 x 12 in. steel cylindrical molds in three layers. Each layer was consolidated by rodding 25 times using a 3/8" thick steel rod.

For freeze-thaw testing, three 3 x 3 x 15 in. beams were cast in the same way used for strength test specimens.

After casting, the specimens of latex-containing concrete were covered with plastic sheets and kept in a fog room in the molds for 24 hours. In accordance with normal practice for LMC, they were then demolded and allowed to hydrate in laboratory air until testing time. The plain concrete specimens were covered with plastic sheets and kept in laboratory air in the molds for 24 hours, but then they were demolded and transferred to a fog room (100% RH) until testing time.

4.3 Preparation of Pastes

All of the paste used in this study were prepared using the same Lone Star Industries Type I portland cement from Greencastle, IN as used for the concretes. A reference portland cement paste was prepared with only the cement and water. An "LMC" paste was prepared containing this cement and latex, and modified LMC pastes were prepared using fly ash, superplasticizer, or superplasticizer and silica fume. The latex content, the fly ash or silica fume content, and the w:cm ratio in each case was the same as those in the corresponding concrete mixes. The batch

composition of each paste is given in Table 4.3-1.

Table 4.3.1 Components and Proportions of Paste Used in the Study

Mix	Weight of Components (g)						
	w:cm	Cement	Latex	FA	SF	Water	SP (ml)
OPC	0.48	900	-	-	-	432	-
LMC	0.29	900	283	-	-	120	-
A25F00	0.25	720	283	225	-	87	-
T25F00	0.27	720	283	225	-	106	-
R25F00	0.26	720	283	225	-	97	-
G25F00	0.27	720	283	225	-	106	-
A15F00	0.26	792	283	135	-	92	-
T15F00	0.28	792	283	135	-	111	-
R15F00	0.27	792	283	135	-	101	-
G15F00	0.27	792	283	135	-	101	-
N00F30	0.20	900	283	-	-	32	18
N00H30	0.22	900	142	-	-	125	18
S10F38	0.20	810	283	-	90	32	23
S10H38	0.23	810	142	-	90	133	23

A standard Hobart mixer (model N-50, capacity 4.73 dm³) was used in mixing the pastes. The ASTM C 305 Standard Method for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency was followed in the preparation of the pastes.

All the mixing water, and latex and superplasticizer (if used) was placed in the bowl, and the cementitious materials were added. After a period of 30 seconds for the absorption of the water, mixing was started at low speed (145 ± 5 rpm) for 30 seconds. It was followed by a waiting period of 15 seconds, during which the paste was scraped down into the batch from the sides of the bowl. The mixing was then continued for additional 1 minute at medium speed (285 ± 10 rpm).

The freshly mixed pastes were placed into 1 x 1 x 10 in. steel molds, covered with plastic sheets, and kept in the laboratory air for 24

hours. They were then demolded. The paste bars containing latex were then continuously kept in the laboratory air; the paste bars without latex was transferred to the fog room for conventional curing.

4.4 Testing of Hardened Concrete

A description of each of the various tests performed on hardened concrete is provided in this section.

4.4.1 Compressive Strength

Compressive strength testing was carried out according to the ASTM C 39 Standard Method. The 3 x 6 in. cylinder specimens were capped prior to testing with a commercial sulfur mortar capping compound, following the general procedure given in ASTM C 617.

The specimens with fly ash were tested using a Forney hydraulic compressive testing machine (Model FT-0040-DR) of 250,000 lbs capacity. The loading rate used was about 60,000 lbs/min. The specimens with superplasticizer or silica fume, prepared later in the program, were tested with a Satec hydraulic universal testing machine (Model M100BTE) of 100,000 lbs capacity, newly equipped for computer controlled operation. The loading rate used was 15,000 lbs/min. (about 35 psi/sec.).

4.4.2 Flexural Strength

Flexural strength testing was carried out using 3 x 3 x 15 in. concrete beams, following the procedure provided in ASTM C 78-84 (third-point loading). Specimens with fly ash were tested using a Southwark-Emery hydraulic universal testing machine of 60,000 lbs

capacity; subsequent tests on specimens with superplasticizer or silica fume were tested using the Satec hydraulic universal testing machine (Model M100BTE) of 100,000 lbs capacity. The loading rate used was 2000 lbs/min. in both cases.

When the fracture in the specimens initiated in the tension surface within the middle third of the span length, the modulus of rupture was calculated using the following formula:

$$R = Pl/bd^2$$

where: R = modulus of rupture, psi

P = maximum applied load indicated by the testing machine, lbf

l = span length, in.

b = average width of specimen, in.

d = average depth of specimen, in.

When the fracture in the specimen occurred on the tension surface outside of the middle third of the span length by no more than 5% of the span length, the modulus of rupture was calculated using the following formula:

$$R = 2Pa/bd^2$$

where: a = average distance between line of fracture and the nearest support measured on the tension surface of the beam, in.

4.4.3 Statistical Evaluation of Strength Data

Strength values obtained as functions of concrete age as described in Section 4.4.1 and 4.4.2 are secured using necessarily small number of replicate specimens at each age. In this work, the compressive strength at each age tested was evaluated using 5 replicates, and the flexural strength using 4 replicates each.

Since there are often individual values recorded that seem to be outside the normal range of variation expected, the question always arises as to whether it is justified to discard specific outlying values in a set of 4 or 5 replicates.

The usual statistical criterion applied to make such decisions is to first determine the variance and standard deviation of each set, and to discard only those values that are more than two standard deviations from the mean.

However, it is difficult to place undue reliance on such a procedure unless the true variance of the individual set is itself known with reasonable accuracy. Computation of the variance (and standard deviation) based on only 4 or 5 replicates does not properly provide a sufficiently reliable estimate of these parameters.

A way out of this difficulty is attainable if it can be shown that the all the data subsets (e.g. compressive strength at one age) in the entire data set (e.g. compressive strengths at all ages) have equal variance. If this is the case, the estimate of variance on the entire, much larger, data set can be applied to the problem of eliminating individual outlying values for the computation of any particular average.

A method of testing to see whether the variance of the entire data set is equal has been provided by V.L. Anderson and R.A. McLean [84]. The procedure consists of transforming each data value to its common logarithm and then computing the variance for each transformed data subset (i.e. particular age). A "Burr-Foster Q-Test of Homogeneity" is then applied as follows:

(1) The q statistic is calculated according to the following equation:

$$q = \frac{\sum (S^2)^2}{(\sum S^2)^2}$$

where S^2 is the variance of each transformed data subset.

(2) The calculated q value is then compared to the critical values which are given in the table of percentile points for Q-Test [84]. The critical value is based on (a) degree of freedom of data subset and (b) number of total data point. Large values of q lead to rejection of the hypothesis of equal population variances. If the calculated q value is less than criterion provided in the table, the variance of the all subsets can be considered as equal within a specified degree of probability. The critical values are provided at probability of 0.99 and 0.999 level. In the present application the critical value for the probability of 0.999 level was used.

If the transformed data subsets are shown by this procedure to have equal variances, the overall variance is estimated by averaging the individual transformed data subset variances. This average is the best estimate of the variance of the entire transformed data set.

Having established this value, each transformed data subset is treated individually. Transformed values more than two standard deviations from the average of the transformed subset are rejected. The corresponding data points of the original data subset are then rejected, and the average of the remaining data points is computed and used as the best estimate for the average of that particular subset.

This procedure has been applied to the calculation of the average values at each age for compressive strength (Tables 5.2-1 and 5.2-3), and flexural strength (Tables 5.2-2 and 5.2-4). At first, the Q-Test was carried out on each individual mix to see whether the variances of strength data at different ages have equal variance after transformation. For both the compressive and flexural strengths, the strength data at different ages for each mix showed an equal variance. The Q-Test was then further carried out on all mixes to see whether the variances of the strength data at different ages and in all mixes were equal. This was true for all flexural strength tests, and for all compressive strength tests except for those concretes containing fly ash. Accordingly, individual data points were discarded if their transformed values were more than two standard deviations from the mean of the subset, with the standard deviation being based on the overall variance. For the fly ash concrete compressive strength data, the same procedure applied, except that the standard deviation used in each subset was based on the variance of that subset only.

4.4.4 Tests of Bond between LMC and Old Concrete

One of important properties of any overlay concrete material is its ability to bond well with the existing concrete surface. Field experience indicates that LMC generally presents no difficulties in this regard. However, it is important to establish whether the modifications to the basic LMC system considered in this work might cause bond problems to develop.

Unfortunately, testing bond of an overlay material to existing concrete presents some technical difficulties. There is no generally accepted method of test, although various shear and tensile bond test procedures do exist.

A new form of test device, called the "Break-Off Tester" by its manufacturer, A/S Scancem, of Slemmested, Norway, was considered to offer potential for this kind of test, and after some preliminary trials, was adopted for use in this project.

The break-off tester was originally designed to mainly test the in-situ compressive strength of concrete. The principle of the method is to apply a cantilever bending moment on a concrete core so as to induce a fracture located at a designated depth below and parallel to the upper specimen surface, as illustrated in Figure 4.4-1. The designated depth of the surface of fracture in this device is 70 mm.

The device can be used to test bond of LMCs to base concrete if a specimen is so designed that the surface of contact between the two is at this depth.

The testing apparatus consists of a dual range loading device connected by a flexible hose to a hand held hydraulic pump as shown in

Figure 4.4-1 Section Across Specimen to Illustrate the Operating Principle of Break-Off Test

Figure 4.4-2. As the user manually increases the hydraulic pressure, the loading device (or hydraulic jack), which fits in the test seat (or slit), applies a cantilever force at the top of the latex concrete specimen. This creates a maximum bending moment at the designated fracture plane. This bending moment is resisted by the circular cross section at the 70 mm level, which is the plane of the bond. The applied pressure is increased incrementally until the core fractures, and the maximum "break-off value" (manometer reading) is observed and recorded.

In the usual application for compressive strength estimation, the corresponding compressive strength is estimated from the "break-off value" using the manufacturer's correlation curves.

Figure 4.4-2 Break-Off Tester

In the present investigation, break-off test was used to estimate the bonding strength between the overlay concrete and base concrete. Specimens were designed to insure that the plane of maximum bending moment was the plane at which the LMC overlay material was bonded to previously-cast concrete. The specimen preparation and the testing procedure used in this application are described as follows.

Specimen Preparation The base concretes were ordinary portland cement concrete. They were cast into specially-designed 6 x 6 plastic cylindrical molds. A plastic insert filled with previously melted and cooled sulfur was pre-positioned so as to create a cylindrical space or hole into which the LMC concrete would later be cast. This space was 70 mm in depth; below this space the remaining depth of concrete was about 82 mm

(3.2 in.). The upper surface of this 3.2 in. layer constitutes the projected boundary surface against which the LMC concrete would be placed, and also the plane of maximum bending moment.

This insert was removed when the base concretes were demolded, 24 hours after casting. The base concretes was then cured in a fog room for over one month before proceeding to the next step of the preparation procedure. Figure 4.4-3 shows a base concrete with the insert removed to show the empty space into which the LMC concrete will later be cast.

The next step of the procedure was to sandblast this surface, to simulate the usual treatment of concrete to which an overlay is to be applied.

The surface was then wetted, and an annular insert was placed so as to provide an annular space within which the LMC will be cast. This

Figure 4.4-3 Base Concrete

insert is slightly thicker at the top than the bottom, to facilitate removal. The LMC concrete is then cast into the remaining space in two layers, and compacted in the usual manner. For LMC concrete, the assemblage was covered with a plastic sheet and placed in a fog room for 24 hours. It was then removed from the fog room and exposed to laboratory air for an additional 29 days before testing.

Several specimens in which the bond to be tested was that of plain concrete to old plain concrete were also prepared. For these specimens, the procedure was identical except that they were covered and kept in laboratory air for 24 hours; then the cover was removed and the assembly placed in a fog room for 29 days of additional curing at 100% RH.

Figure 4.4-4 shows a specimen which was ready for the testing.

Tests were carried out on the bond between plain concrete and old

Figure 4.4-4 A Specimen Ready for Break-Off Testing

plain concrete, ordinary LMC and old plain concrete, and LMCs containing fly ash and plain concrete. The LMC concretes tested had the same mix proportions as those used for the other types of testing carried out in this research.

Testing Procedure Before testing, the device was calibrated as recommended by the manufacturer. In the actual testing, the loading unit (which contains the hydraulic jack-driven load actuator, visible as the separate segment of the bottom of the cell in Figure 4.4-2) was placed in the slit, as shown in Figure 4.4-5. The load was then applied at the rate of about 100 psi per stroke, with a stroke of the hydraulic ram being delivered each second. This rate of loading was maintained until rupture occurred across the bond surface. The manometer reading at failure was recorded, and the rupture surface was examined to see whether the failure surface occurred properly, that is, at the interface of the test concrete and base concrete. This was found to be the case in all trials.

In these tests, the higher of the two loading ranges built into the Tester was always used.

In the presented application with respect to bond strength, the failure mode is actually closest to flexural bond testing rather than to compressive strength testing, and some means must be taken to convert the apparent "compressive strength" obtained from the calibration curve to the equivalent flexural bond strength.

Reasoning that the bond strength would be controlled primarily by the LMC (and not the concrete substrate it is bonded to), we examined the relationship between flexural strength and compressive strength for the LMC and LMCs containing fly ash in our testing program. The data for ages

Figure 4.4-5 Break-Off Testing

between 3 days and 28 days fell on a single straight line with reasonable consistency; those for the 1 day old samples did not. Accordingly, we neglected the 1-day data and established the approximate relationship between flexural and compressive strength of LMC as

$$\text{Flexural Strength (psi)} = \frac{\text{Compressive Strength (psi)} - 1000}{4.4}$$

This equation was then applied to the apparent compressive strength provided by the calibration curve for the hydraulic pressure need to cause failure of bond for LMC.

However, since the relationship between flexural and compressive strength is different for OPC from that for LMC, it was considered that a separate calibration equation was needed for the corresponding bond

tests of OPC bonded to old concrete. Since our own results for OPC are much too few in number to establish a relationship, we used the well-established relationship given as Figure 15.12 in the standard concrete text by Mindess and Young [5] for this purpose.

4.4.5 Density

The density of concrete was determined using broken beams from the flexural test. Each broken beam was crushed into small pieces about one inch in size. About ten pieces from each broken beam were used in a given determination. Four beams for each of the concretes tested were separately evaluated. The specimens were submerged in water for 24 hours, then placed in a container submerged in water and weighed. The specimens were then dried at a temperature of 105°C for 24 hours, cooled and then reweighed.

The density of concrete was calculated as follows:

$$D = D_w \times \frac{W_d}{W_d - W_b}$$

where: D = density of concrete, g/cm^3

D_w = density of water, 1 g/cm^3

W_d = weight of oven-dry specimens in air, g

W_b = weight of saturated specimens in water, g.

4.4.6 Dynamic Modulus of Elasticity

The dynamic modulus of elasticity of the concretes were determined using the pulse velocity method.

The instrument used is a portable V-meter (Model C-4901), manufactured by James Instruments, Inc. It generates low frequency ultrasonic pulses, and measures the time taken for them to pass through the material interposed between the two transducers. The measurements were made with 54 kHz frequency transducers, and the time readings were considered accurate to 0.1 μ sec. An instrument zero was checked prior to each measurement using the standard reference bar supplied with the apparatus. The pulse transit time for the reference bar was 26 μ sec.

The measurements were performed on the 3 x 3 x 15 in. beams at ages of 1, 3, 7, 28, 90, 180 and 360 days. The transmitting and receiving transducers were placed in contact with the opposite ends of the beam being tested to provide a direct transmission of pulses through the beam. In order to assure proper coupling, a lubricant grease was applied to each of the transducer faces before placing them in contact with the specimen surface. The transducers were then pressed hard against the ends of the concrete beams and held continuously against them until a constant reading was obtained on the display.

4.4.7 Chloride Permeability

The chloride permeability of concretes was measured according to AASHTO Designation T 277-83I "Interim Method of Test for Rapid Determination of the Chloride Permeability of Concrete". This method provides a

measurement for the "permeability" to chloride ions of conventional portland cement concrete and specialized concretes, e.g., latex-modified and polymer concretes. It consists of monitoring the amount of electrical current passed through 3.75 in. diameter by 2 in. long cores when one end of the core is in contact with a 3.0 percent NaCl solution, the other in contact with a 0.3N NaOH solution, and a potential difference of 60 V DC is maintained across the specimen for 6 hours. The total charge passed, in coulombs, is the actual parameter measured, and this is used as a relative measure of the chloride permeability.

One 2 in.-thick slice was cut from each of the 3.75 in. diameter cylinders at given age and used as the test specimen in the chloride permeability test. The sides of the specimens were coated with rapid setting epoxy (CIBA brand GY-6010 resin and HY-9225 hardener mixed at 1:1 by weight). Then the specimen was placed in a 1000 ml beaker in a vacuum desiccator and kept under vacuum for 3 hours. While vacuum was maintained, previously boiled deionized water was added to cover the specimen, and then vacuum was kept on for 1 additional hour. Then air was allowed to reenter the desiccator, and the specimen was soaked under water in the beaker for 18 ± 1 hours.

The specimen, prepared as above, was then mounted in the test cell. The left (-) side of cell was filled with 3.0 percent NaCl solution and right (+) side of cell with 0.3N NaOH solution. Then 60 ± 1 V DC was applied to the test cell. The resulting current flow was recorded for six hours and was integrated over time to give the total charge passed in six hours.

The measurements and the integration were done automatically by a Model 159 Chloride Permeability Test Set produced by RLC Instrument Co., Akron, Ohio. The apparatus provides a printout of time, current, and accumulated charge passed at 30 minute intervals, and automatically terminates the test at the end of six hours.

4.4.8 Freeze-Thaw Resistance

The determination of freeze-thaw resistance of concrete was performed by Materials and Test Division of the Indiana Department of Transportation at their test facility located in Indianapolis.

The concretes used for freezing and thawing were the fly ash-bearing latex-modified concretes, and two reference concretes. The mix designs of these concretes were the same as corresponding concretes used for strength testing, but they were mixed separately. All the specimens were air cured for 13 days after demolding, then cured in water for several weeks prior testing.

Two series of freezing and thawing test were carried out. For the first series of test, no air entraining agent was added to the latex-modified concretes. The observed air contents of the freshly mixed concrete were less than 4 percent. For the second run, sufficient air entraining agent was added to bring the actual measured air contents to between 4 and 6 percent.

The freezing and thawing tests were carried out in accordance with ASTM C 666. For the first series of test, because of the freezer malfunction, the first 12 cycles were carried out per Procedure A, and followed by 288 cycles per Procedure B. For the second series, the entire

test was carried out per Procedure A.

In the test chamber the specimens were oriented vertically; and were rotated 180° at the time of each fundamental transverse frequency reading. The fundamental transverse frequency were measured at intervals of approximately every 30 cycles, at the end of a thaw cycle. The tests were continued for the full 300 cycles recommended by ASTM C 666.

4.5 Cement Paste Analyses

A description of each of the various tests performed on cement paste is provided in this section.

4.5.1 Contact Angle Measurement

To measure the pore size distribution of the pastes, the contact angle between mercury and the pastes is a very important parameter. To the knowledge of the writer, no prior contact angle measurements have been reported for latex-modified concretes. To interpret measurements of the pore structures of the various latex-modified cements, the effective contact angle between mercury and each type of paste used in this study was measured. The measurement procedure is described as follows.

The specimens used for contact angle measurement were small prisms of 90 day old paste with a dimension of approximately $1 \times 0.5 \times 0.25$ in. These prisms were cut from the paste bars and immersed in acetone to stop hydration. The samples were subsequently dried in vacuum desiccator under rotary vacuum pump evacuation for three months or more. About 90 holes were then drilled in one side of each specimen using a micro-drill with

a diameter about 400 μm . The diameter of the holes was measured using a microscope; 20 individual holes being actually measured for each specimen. The average value of these 20 diameters measured was used as the representing diameter of the holes in that specimen.

Each specimen prepared as above was inserted into a penetrometer, which was then evacuated to a pressure of less than 10 $\mu\text{m Hg}$. The penetrometer was then filled with mercury to completely surround the specimen. Then the pressure of the system was increased stepwise using successive increments of about 2 mm Hg pressure steps. The volume of mercury intruded and the pressure were recorded at each step. The measurement was continued until a sudden jump of volume of mercury intruded, corresponding to the entry and filling of the cylindrical holes, was completed. The cumulative intrusion of mercury was then plotted versus pressure to find the pressure under which the intrusion jump started. Using this pressure the contact angle was calculated using the formula:

$$\cos \theta = - Pd/4\Gamma$$

where: θ = contact angle between mercury and the pastes
 P = pressure under which intrusion jump takes place, dyne/cm^2
 d = diameter of the holes drilled on the specimen, cm
 Γ = surface tension of mercury, 484 dyne/cm

4.5.2 Pore Size Distribution Measurement

The pore size distribution for each of the pastes was measured by mercury porosimetry. Mercury porosimetry is based on the capillary law governing liquid penetration into small pores. This law, for the case of a non-wetting liquid like mercury and cylindrical pores, is expressed by

$$P = - 4\Gamma \cos \Theta / d$$

where: P = required external pressure
 Γ = surface energy of the mercury
 Θ = contact angle between mercury and the paste
 d = diameter of the pore.

The pore diameter range measurable by this method runs from about 500 μm (or more, if special precautions are taken), down to about 20 $\text{\AA}$, depending on the contact angle between the specific paste and mercury.

The instrument used was Autopore II 9220 porosimeter manufactured by Micromeritics Instrument Corp. The porosimeter consists of 4 low pressure ports and 2 high pressure ports. The low pressure measurement runs from 0 to 30 psia, and high pressure measurement runs from 0 to 60,000 psia. The data collection is done by computer automatically.

Two 1 x 0.5 x 0.25 in. prisms were cut from the paste bars at given ages using an Isomet diamond saw manufactured by Buehler Ltd. The chunks were put into acetone for three days to stop hydration, and then were dried under vacuum in a desiccator under continuous rotary pump evacuation for two weeks or more prior to testing.

At the time of testing, the specimen was inserted into a penetrom-

meter, which was then inserted into the low pressure port, evacuated to less than 20 μ m Hg pressure, and filled with mercury to completely surround the specimen. After the low pressure run was completed, the penetrometer was transferred to the high pressure port for high pressure mercury intrusion. The intrusion was carried out following a preset pressure schedule, to a maximum pressure of 60,000 psia. At each pressure stop, the pressure was held 15 seconds to allow intrusion equilibrium in the specimen.

4.5.3 Scanning Electron Microscopy Examination

The 3-month old specimens used for SEM examinations were placed into acetone for 3 days to stop hydration, and then evacuated continuously under rotary pump evacuation until they were to be examined. At the time of examination, the specimens were fractured into small pieces, mounted on aluminum stubs with plastic cement, and coated with a gold-palladium alloy using a Hummer II Plasma Coater manufactured by Technics, Inc.

Some specimens were treated with 1:4 HCl repeatedly until they turned entirely white. Examinations disclosed that all of the cement paste had been dissolved, leaving over only the latex film for examination.

The morphology examinations were conducted with ABT-55 scanning electron microscope, manufactured by International Scientific Instruments, Inc., using an ETP SEMRA Robinson backscatter detector. A Tracor Northern Series II x-ray microanalysis system, manufactured by Tracor Northern, Inc., was used for energy-dispersive x-ray analysis (EDXA).

5. EXPERIMENTAL RESULTS

The study was carried out in two parts. In the first part, which was the major part of this work, the effects of fly ash on the properties of latex-modified concrete were studied. In the second, less intensive part of the study, superplasticizer and silica fume were introduced into latex-modified concrete to study the effects of these components and to secure information on the possibility of reducing the latex content. Accordingly, the experimental results are discussed in two separate parts, followed by a brief comprehensive discussion.

5.1 Properties of Fresh Concretes

5.1.1 Water:Cementitious Materials Ratio

In developing the mix designs for this study, the usual criterion of 4 to 6 inch slump was used to adjust the water content of the concrete. Trial mixes were carried out to find the w:cm ratios which yield a slump in this range with the materials being batched. These w:cm ratios were used for mixing all of the corresponding concretes.

5.1.2 Properties of Fresh Latex-Modified Concretes with Fly Ash

The properties of the fresh LMCs containing fly ash, with the two reference concretes (OPC and LMC1) are summarized in Table 5.1-1. Each

value in the table represents an average of four measurements performed on separate batches of the same composition. The air content reported in this table is the actual air content after the correction for aggregate void space.

From the data presented in Table 5.1-1, it is obvious that latex admixture used had a substantial water reducing action. The w:cm ratio needed for the conventional LMC to give a slump of 4-6 in. was 0.29, compared to a ratio of 0.48 for the ordinary portland cement concrete made with the same cement and aggregate mix.

Incorporation of the fly ashes into the mix reduced the water demand still further. The water:cementitious materials (w:cm) ratios were between 0.25 and 0.28 for the LMCs containing the different fly ashes.

Based on the slump measurement results, all the concrete mixes had essentially same workability. Thus, incorporation of the different types

Table 5.1-1 Summary of Properties of Fresh Latex-Modified Concretes with Fly Ash

Mix	w:cm	Slump (in.)*		Unit Weight (lbs/ft ³)	Air Content (%)
		S ₁	S ₂		
OPC	0.48	6.0	5.1	147	4.42
LMC1	0.29	5.5	5.4	149	3.61
R15F00	0.26	6.0	5.6	151	2.54
R25F00	0.25	5.6	5.1	147	3.57
A15F00	0.27	5.3	5.0	149	3.14
A25F00	0.26	5.6	5.3	150	2.57
G15F00	0.27	5.8	5.5	150	2.79
G25F00	0.27	5.4	4.8	149	3.31
T15F00	0.28	6.3	5.8	150	3.32
T25F00	0.27	5.3	4.4	149	3.24

* S₁ is the slump immediately after completion of mixing;
S₂ is the slump 5 minutes after completion of mixing.

of fly ash did not change the workability of LMC significantly. The LMCs containing fly ash showed no increased difficulty in placing and finishing compared to those without fly ash. All concretes prepared were reasonably workable over a period of about 25 minutes.

All of the unit weights determined for the LMCs were within ± 2 lbs/ft³ of the reference LMC. Thus incorporation of fly ash into these mixes had no significant effect on unit weight.

Air contents for LMCs do not have quite the significance that they do with normal concretes. It was found that the reference LMC had an air content of 3.6%. Incorporation of the fly ashes resulted either in no change or in a reduction of as much as 1% in this value.

5.1.3 Properties of Fresh Latex-Modified Concretes with Superplasticizer or Superplasticizer Plus Silica Fume

The properties of fresh LMCs batched with superplasticizer or superplasticizer plus silica fume are summarized in Table 5.1-2. Each value in the table represents an average of two measurements performed on separate batches of the same composition. The air contents reported are actual air contents after correction of aggregate void space.

With the addition of superplasticizer or superplasticizer plus silica fume, the slump of fresh concrete was a little difficult to control. With the same w:cm ratio, the slumps of two separate batches of the same composition sometimes were quite different from each other. The slump reduction 5 minutes after completion of the mixing was considerably greater for the mixes with silica fume than for the others. The fresh concretes with silica fume were cohesive and unusually sticky, which made

Table 5.1-2 Summary of Properties of Fresh Latex-Modified Concretes Batched with Superplasticizer or Superplasticizer Plus Silica Fume

Mix	w:cm	Slump (in.)*		Unit Weight (lbs/ft ³)	Air Content (%)
		S ₁	S ₂		
LMC2	0.29	7.0	6.3	148	4.30
N00F15	0.24	6.5	5.8	148	4.40
N00F30	0.20	6.3	4.5	148	5.40
N00H30	0.22	7.3	3.5	141	> 9.20
S10F23	0.24	4.3	1.9	146	5.40
S10F38	0.20	7.5	5.0	144	6.90
S10H38	0.23	5.3	2.0	145	6.90

* S₁ is the slump immediately after completion of mixing;
S₂ is the slump 5 minutes after completion of mixing.

consolidation somewhat difficulty. Nevertheless, all of the fresh concretes had reasonably good workability over a period of about 20 minutes. Even for those mixes which had slumps as low as 2 inches (measured 5 minutes after completion of mixing), there was no additional difficulty in placing and finishing compared to the others.

As seen in Table 5.1-2, the unit weights of some of the concretes were slightly lower than those of the reference LMC. One of them, the concrete with reduced latex content and no silica fume, had a particularly low measured unit weight (141 lbs/ft³), attributable to particular difficulty in rodding consolidation of this concrete. Generally speaking, inclusion of superplasticizer increased the air content significantly; incorporation of silica fume led to additional air entrainment. The very sticky, low unit weight concrete with reduced latex content mentioned earlier had a measured air content of well over 6 percent. Most of this extra air is undoubtedly in large air voids and it does not necessarily represent a better air void system with respect to

prevention of freezing damage.

5.2 Strength

Each strength value reported represented an average of the test results of five individual cylinders for compressive strength, and an average of the test results of four individual beams for flexural strength. Individual test results are provided in Appendix A. As indicated in Section 4.4.3, outlying values were rejected if their transformed values were more than two standard deviations from the transformed mean.

5.2.1 Strength of the Latex-Modified Concretes with Fly Ash

Compressive and flexural strength tests were carried out for all the concretes with fly ash and two reference concretes at ages of 1, 3, 7, 28, 90, 180, and 360 days. A summary of the test results is presented in

Table 5.2-1 Compressive Strength of Latex-Modified Concrete with Fly Ash

Mixes	Compressive Strength (psi) at:						
	1 day	3 days	7 days	28 days	90 days	180 days	360 days
OPC	2180	3710	4770	6180	5380	6510	7230
LMC1	3310	5040	6210	7390	7850	7890	8210
R15F00	2760	4950	6410	7870	8160	7680	8620
R25F00	2990	5120	6440	7610	8180	7400	8460
A15F00	2760	5290	6080	7600	7800	7570	8550
A25F00	2460	4790	6050	7140	7510	7490	8280
G15F00	2790	5160	6110	7480	8120	6980	8720
G25F00	2620	4890	5930	7170	8010	7370	8950
T15F00	2100	4410	5640	6810	7470	7200	8160
T25F00	2710	4340	6110	6640	7480	7290	8220

Table 5.2-2 Flexural Strength of Latex-Modified Concretes with Fly Ash

Mixes	Flexural Strength (psi) at:						
	1 day	3 days	7 days	28 days	90 days	180 days	360 days
OPC	520	710	860	960	1000	1090	1080
LMC1	710	1040	1090	1470	1710	1750	1740
R15F00	620	960	970	1400	1820	1860	1750
R25F00	730	950	1180	1440	1860	1800	1820
A15F00	580	860	970	1380	1470	1710	1740
A25F00	540	860	950	1370	1680	1840	1870
G15F00	560	900	1020	1320	1570	1860	1860
G25F00	570	840	950	1260	1710	1710	1800
T15F00	460	850	900	1400	1530	1770	1690
T25F00	620	760	910	1280	1550	1660	1850

Table 5.2-1 for compressive strength and Table 5.2-2 for flexural strength.

The strength testing results are presented graphically in Figures 5.2-1 and 5.2-2 for compressive strength of the concretes with 15% fly ash and 25% fly ash respectively, and Figures 5.2-3 and 5.2-4 for flexural strength of the concretes with 15% fly ash and 25% fly ash respectively.

Compressive Strength The effects of incorporating fly ash into LMC are shown in Figures 5.2-1 and 5.2-2.

From Figures 5.2-1 and 5.2-2, it is apparent that the compressive strengths of all LMCs are higher than that of the plain reference concrete at all ages.

The effects of the different fly ashes on compressive strength of the LMC are somewhat complex to describe.

In ordinary concrete, fly ash typically reduces early strength. In the present data for LMC, most of the fly ashes produced significant

Figure 5.2-1

Compressive Strength versus Time for Latex-Modified Concrete with 15% Fly Ash, Plain Concrete, and Latex-Modified Concrete

Figure 5.2-2 Compressive Strength versus Time for Latex-Modified Concrete with 25% Fly Ash, Plain Concrete, and Latex-Modified Concrete

Figure 5.2-3 Flexural Strength versus Time for Latex-Modified Concrete with 15% Fly Ash, Plain Concrete, and Latex-Modified Concrete

Figure 5.2-4 Flexural Strength versus Time for Latex-Modified Concrete with 25% Fly Ash, Plain Concrete, and Latex-Modified Concrete

compressive strength reduction at 1 day. However by three days the effect was negligible (about 3.5% reduction in average), and subsequently there was no strength reduction, with a single exemption. The Stout fly ash, batched at 15%, somewhat degraded the compressive strength of LMC, the reduction being about 400-800 psi. However even here, by 1 year the effect disappeared.

Individual comparisons of compressive strength between the concretes with 25% fly ash replacement and concretes with 15% fly ash replacement are shown in Figures 5.2-5 through 5.2-8. In general, increasing the fly ash replacement level from 15% to 25% produced almost no change in compressive strength.

In the compressive strength testing time series shown in Figures 5.2-1 and 5.2-2, all of the fly ash bearing LMCs and the reference OPC show an apparent strength drop at 180 days, which was reversed by 360 days. No corresponding drop was noted in flexural strength.

Nevertheless, examination of the results for dynamic modulus of elasticity at the same age (Figures 5.3-1 and 5.3-2) showed corresponding changes in that parameter as well. Since the two tests are independent of each other, it was concluded that the effect was real, although its cause is unknown.

Flexural Strength LMCs have substantially higher flexural strengths than plain concrete, as indicated in Figures 5.2-3 and 5.2-4. As seen in Figure 5.2-3, incorporation of the different fly ashes at the 15% replacement level resulted in a little flexural strength reduction for periods up to 28 days. At later ages, this reduction became less significant, and for Rockport fly ash (by 90 days) and Gibson fly ash (by

Figure 5.2-5 Comparison of Compressive Strength versus Time between Latex-Modified Concretes with 25% and 15% Substitutions of Rockport Fly Ash

Figure 5.2-6 Comparison of Compressive Strength versus Time between Latex-Modified Concretes with 25% and 15% Substitutions of Schahfer Fly Ash

Figure 5.2-7 Comparison of Compressive Strength versus Time between Latex-Modified Concretes with 25% and 15% Substitutions of Gibson Fly Ash

Figure 5.2-8 Comparison of Compressive Strength versus Time between Latex-Modified Concretes with 25% and 15% Substitutions of Stout Fly Ash

Figure 5.2-9 Comparison of Flexural Strength versus Time between Latex-Modified Concretes with 25% and 15% Substitutions of Rockport Fly Ash

Figure 5.2-10 Comparison of Flexural Strength versus Time between Latex-Modified Concretes with 25% and 15% Substitutions of Schahfer Fly Ash

Figure 5.2-11 Comparison of Flexural Strength versus Time between Latex-Modified Concretes with 25% and 15% Substitutions of Gibson Fly Ash

Figure 5.2-12 Comparison of Flexural Strength versus Time between Latex-Modified Concretes with 25% and 15% Substitutions of Stout Fly Ash

180 days), the flexural strength had even overtaken that of the reference LMC.

As seen in Figures 5.2-3 and 5.2-4, incorporation of the various fly ashes at the 25% replacement level slightly degraded the flexural strengths at intermediate ages as compared to those obtained at the 15% replacement level. The effect was gone by six months, however.

Individual comparisons of the effects at 25% replacement with those at 15% replacement for each fly ash are provided in Figures 5.2-9 through 5.2-12. It is apparent that the effects of increasing the fly ash replacement level are not very significant.

There were some consistent differences among the flexural strength effects produced by the different fly ashes. With Rockport fly ash, there was a small net increase over the reference LMC at early ages (before 28 days), but this effect became negligible at later ages. With Schahfer fly ash, there was a slight increase at later ages (after 28 days). With Gibson and Stout fly ash, there were slight flexural strength reductions at all ages.

5.2.2 Strength of the Latex-Modified Concretes with Superplasticizer or Superplasticizer Plus Silica Fume

Compressive and flexural strength tests were carried out for all the LMCs with superplasticizer or superplasticizer plus silica fume treatments, and for reference LMC at ages of 1, 7, 28, and 180 days. A summary of the test results for compressive strength is presented in Table 5.2-3, and for flexural strength in Table 5.2-4. Individual test results are provided in Appendix A.

Table 5.2-3 Compressive Strength of Latex-Modified Concrete with Silica Fume

Mixes	Compressive Strength (psi) at:			
	1 days	7 days	28 days	180 days
LMC2	2950	5160	6930	7820
N00F15	3280	6040	7690	9070
N00F30	3570	6270	7940	9480
N00H30	4870	7060	9210	9570
S10F23	3590	5830	8410	9350
S10F38	2990	6450	8450	9270
S10H38	3850	8300	10270	11050

The strength testing results are presented graphically in Figure 5.2-13 for compressive strength, and Figure 5.2-14 for flexural strength.

Compressive Strength The measured compressive strength of all the concretes contain superplasticizer (with or without silica fume) were higher than those of the reference LMC.

The addition of superplasticizer to LMC at a normal dose rate (15 fl. oz. per 100 lbs cementitious materials) significantly increased the compressive strength of the concrete, especially at later ages. Higher-

Table 5.2-4 Flexural Strength of Latex-Modified Concrete with Silica Fume

Mixes	Flexural Strength (psi) at:			
	1 days	7 days	28 days	180 days
LMC2	740	1060	1160	1480
N00F15	780	1090	1300	1760
N00F30	800	1200	1220	2030
N00H30	700	1010	1120	1300
S10F23	670	970	1200	1550
S10F38	600	980	1280	1550
S10H38	690	950	1180	1330

than-normal superplasticizer dosage (30 fl. oz. per 100 lbs cementitious materials) provided only small compressive strength improvement over that with the normal dose, even though the w:cm ratio was reduced from 0.24 to 0.20.

Incorporation of 10% silica fume with the superplasticizer also provided no further compressive strength improvement above that provided by the superplasticizer alone.

However, and somewhat surprisingly, reducing the latex content to half of normal latex content and using a high dose (30 fl. oz. per 100 lbs cementitious materials) of superplasticizer provided an obvious improvement (about 2000 psi) to the normal LMC compressive strength at all ages. The simultaneous incorporation of 10% silica fume provided even further compressive strength improvement, with compressive strength well over 10,000 psi being recorded by 28 days.

It appears that the normal dosage rate of latex is significantly higher than optimal for compressive strength development if superplasticizer or superplasticizer and silica fume combinations are to be used. It is also apparent that compressive strengths of LMCs batched with superplasticizer greatly exceed those batched with fly ash as the only amendment. This result is at least partly due to the lower water content achieved by adding superplasticizer.

Flexural Strength The effects of superplasticizer, silica fume, and latex content are less significant for flexural strength than for compressive strength. Using a normal dosage (15 fl. oz. per 100 lbs cementitious materials) of superplasticizer provided a small but consistent flexural strength increase at all ages as compared to normal LMC. Doubling the

Figure 5.2-13 Compressive Strength versus Time for Latex-Modified Concretes with Superplasticizer or Silica Fume and Superplasticizer, and Latex-Modified Concrete

Figure 5.2-14 Flexural Strength versus Time for Latex-Modified Concretes with Superplasticizer or Silica Fume and Superplasticizer, and Latex-Modified Concrete

dosage of superplasticizer makes the increase substantially larger. Using silica fume with superplasticizer provides a very small additional flexural strength improvement (less than 100 psi) at all ages. Reducing the latex content produces a small but consistent flexural strength reduction which becomes more significant at later ages. Adding silica fume while reducing latex content provides essentially no flexural strength change as compared to that without silica fume.

5.2.3 Overall Assessment of Strength Characteristics of Latex-Modified Concretes

The incorporation of latex into concrete produces a significant increase in both compressive and flexural strength. Is this increase due to the lower w:cm ratio that the latex makes possible, or to the presence of latex itself? To help clarify this point, strength comparisons between concretes with normal dosage of latex and with half of normal dosage of latex are presented in Figure 5.2-15 for compressive strength and in Figure 5.2-16 for flexural strength. Note that all except the reference LMC are superplasticized.

With respect to compressive strength (Figure 5.2-15), the LMC at half the normal dosage of latex shows consistently higher strength than that at the normal dosage level, with w:cm being almost the same. This is true up to 1 year, when the difference disappears.

On the other hand, similar comparisons for flexural strength (Figure 5.2-16) indicate that cutting the dosage of latex in half reduces, rather than increases, the strength. Indeed the flexural strength of the half-latex content LMC is slightly below that of the reference LMC batched at

Figure 5.2-15 Compressive Strength versus Time for Latex-Modified Concrete, Latex-Modified Concrete with Reduced Latex Content, Latex-Modified Concrete with Superplasticizer

Figure 5.2-16 Flexural Strength versus Time for Latex-Modified Concrete, Latex-Modified Concrete with Reduced Latex Content, Latex-Modified Concrete with Superplasticizer

a much higher w:cm ratio (0.29 as compared to 0.22). Thus it appears that the normal dosage of latex is needed for high flexural strength in these systems.

In general terms, incorporation of fly ash at up to 25% replacement level in LMC does not significantly degrade either compressive strength or flexural strength. Different fly ashes have slightly different effects on the strength, but in practical terms both the compressive and the flexural strength developed by concrete with all of the fly ashes tested are close to that of the unmodified LMC, and all would be satisfactory.

Using superplasticizer alone does improve both compressive and flexural strengths of LMC, especially flexural strength. Using heavy dosage of superplasticizer in the LMC produces very high flexural strength at later ages (about double of that of reference LMC at 180 days).

Addition of silica fume in the LMC with superplasticizer does improve the compressive strength, but does not improve the high flexural strength already achieved by LMC with superplasticizer. A possible reason for lack of improvement in flexural strength might be the lack of moisture due to the dry curing provided to the LMC.

5.3 Bond Strength of LMC to Old Concrete

Tests of bond strength using the "Break-Off Tester" as described in Section 4.4.3 were carried out for OPC, normal LMC, and LMCs containing 15% and 25% of each of the four fly ashes used in this research. Each determination was carried out in triplicate.

The appearance of the failure surface of typical latex-bearing concrete samples is shown in Figure 5.3-1, and it is evident that failure

Figure 5.3-1 Failure Surface of Typical Latex Concrete Specimens

Figure 5.3-2 Failure Surface of a Latex Concrete Specimen and Base Concrete Assembly from which It Was Separated

has indeed taken place along the bond surface. Figure 5.3-2 shows a failed latex concrete specimen and the base concrete assembly from which it was separated. There is a single aggregate piece that projected at the top of the base concrete after sandblasting, which was cleaved in failure and came off partly attached to the LMC.

The overall results are provided in Table 5.3-1. Included in the table are (1) the actual manometer readings at failure for each specimen, (2) the equivalent average compressive strength, as given in the manufacturer's calibration curve, and (3) the equivalent average flexural strength (bond strength) as estimated from the compressive strength in the manner described in Section 4.4.3.

All of the values obtained for LMCs are in the range of 170 to 450 psi.

While these are very low values in ordinary terms, they are very similar to the range of values obtained recently by Knab and Spring of NIST (formerly NBS) [85]. These authors found average values of 293 psi for LMC tested using the tensile bond method with friction grips, and 393 psi using the tensile bond method using pipe nipple grips. These values were almost an order of magnitude lower than found by the same authors using the slant shear method, 2100 psi.

Thus, our estimates of tensile bond strength are at least of the correct order of magnitude.

However, as can be seen in Table 5.3-1, the variation between replicate values of manometer pressure at failure is very wide. Thus even the average of the three replicates, used to compute the estimated bond strength, is not considered very reliable number.

Table 5.3-1 Break-Off Testing Results

Mixes	Replicate	Manometer Reading at Failure	Average Manometer Reading	Corresponding Compressive Strength ¹ , psi	Estimated Flexural Bond Strength ² , psi
OPC	A	68	65	2080	250
	B	72			
	C	56			
LMC	A	50	57	1730	170
	B	60			
	C	62			
R15F00	A	68	73	2550	300
	B	62			
	C	88			
R25F00	A	64	69	2250	280
	B	58			
	C	84			
A15F00	A	80	76	2620	370
	B	74			
	C	74			
A25F00	A	82	80	2850	420
	B	-			
	C	78			
G15F00	A	98	80	2970	450
	B	64			
	C	78			
G25F00	A	58	73	2520	350
	B	74			
	C	88			
T15F00	A	66	74	2580	360
	B	84			
	C	72			
T25F00	A	52	61	1850	200
	B	68			
	C	64			

1. From manufacturer's calibration curve.

2. From equation, Section 4.4.3 for all latex bearing concretes and relation of Figure 15.12 [5] for OPC.

Nevertheless, we interpret the results obtained as indicating:

- (1) that the incorporation of fly ash certainly does not degrade, and may actually increase, the bond strength between LMC and old concrete;
- (2) that for a given type of fly ash, the LMC incorporating 15% fly ash seems to show slightly better bond than the corresponding LMC incorporating 25% fly ash.

The data suggest that the bond for OPC is actually better than that for ordinary LMC, although since the two are derived from different relationships between compressive and flexural strengths, they probably should not be directly compared. It is of interest that Knab and Spring [85] found almost identical bond strength between their plain concrete and their LMC in each of the three methods of test that they employed.

5.4 Dynamic Modulus of Elasticity

The dynamic modulus of elasticity of the concretes was determined using the pulse velocity method described in section 4.4.4. The values of dynamic modulus of elasticity were calculated using the following formula [86]:

$$E_d = 0.000216 V^2 p [(1+\mu)(1-2\mu)/(1-\mu)],$$

where E_d = dynamic modulus of elasticity (psi)

V = longitudinal wave velocity (ft/sec)

p = density of concrete (lbs/ft³)

μ = Poisson's ratio of concrete, 0.22.

5.4.1 Dynamic Modulus of Elasticity of Latex-Modified Concretes with Fly Ash

The values of dynamic modulus of elasticity calculated for LMCs with fly ash are presented in Table 5.4-1. Values are also presented for plain concrete (OPC) and for LMC without fly ash (LMC1). These values are also graphically presented in Figure 5.4-1 for the concretes with 15% fly ash and in Figure 5.4-2 for the concretes with 25% fly ash. Each data point reported represents an average of determination results on four separate replicate specimens. Individual test results are provided in Appendix B.

It was found that the LMC had a different pattern of the development of the dynamic modulus of elasticity (E_d) than did the plain concrete. The E_d value for LMC at 1 day was very high, 6.05×10^6 psi. It increased with time up to 90 days, and then decreased a little with time. The E_d value for LMC attained at 360 days was 7.45×10^6 psi. The increase in E_d

Table 5.4-1 Dynamic Modulus of Elasticity of Latex-Modified Concretes with Fly Ash

Mix	Dynamic Modulus of Elasticity (ksi) at:						
	1 day	3 days	7 days	28 days	90 days	180 days	360 days
OPC	5610	6300	6910	7610	8030	7720	8560
LMC1	6050	6670	7000	7360	7570	7380	7450
R15F00	5680	6600	6760	7310	7440	7540	7590
R25F00	5870	6670	7000	7360	7570	7380	7450
A15F00	5640	6630	6760	7340	7360	7030	7330
A25F00	5520	6540	6680	7210	7370	6960	7380
G15F00	5410	6670	6810	7200	7450	7210	7460
G25F00	5600	6700	6840	7270	7600	7300	7450
T15F00	4970	6440	6780	6980	7240	7260	7340
T25F00	5710	6340	6960	7220	6680	7290	7340

Figure 5.4-1

Dynamic Modulus of Elasticity versus Curing Time for Latex-Modified Concretes with 15% Fly Ash, Latex-Modified Concrete, and Plain Concrete

Figure 5.4-2

Dynamic Modulus of Elasticity versus Curing Time for Latex-Modified Concretes with 25% Fly Ash, Latex-Modified Concrete, and Plain Concrete

between 1 day and 360 days was about 21%. For plain concrete, the E_d value at 1 day was only 5.61×10^6 psi, about 7% lower than that for LMC. However, it increased with time more rapidly, and had overtaken that for the LMC by 7 days. At 360 days, the measured E_d value for plain concrete was 8.56×10^6 psi, which was about 53% higher than that at 1 day and 15% higher than that for LMC at the same age.

As seen in Figure 5.4-1, incorporating fly ash into LMC at a 15% replacement level gave a lower E_d value at 1 day for all of the fly ashes used. But this difference disappeared for all four fly ashes after 3 days of curing. Similar behavior was also observed at a 25% replacement level (Figure 5.4-2).

It is apparent, from Figures 5.4-1 and 5.4-2, that the development pattern of dynamic modulus of elasticity is not significantly affected by the individual fly ash used.

5.4.2 Dynamic Modulus of Elasticity of Latex-Modified Concretes with Superplasticizer or Superplasticizer Plus Silica Fume

The E_d values calculated for the LMCs with superplasticizer or superplasticizer plus silica fume are presented in Table 5.4-2, and in Figure 5.4-3. Each value in Table 5.4-2 represents the average calculated from determinations on four separate replicate specimens.

As shown in Figure 5.4-3, adding superplasticizer at normal dosage (15 fl oz per 100 lbs cementitious materials) into LMC produced a small but consistent increase in E_d value at all ages. The increase in E_d values was about 0.4×10^6 psi at 1 day and about 0.2×10^6 psi at later ages. Doubling the dosage of superplasticizer produced no further increase in

Table 5.4-2 Dynamic Modulus of Elasticity of Latex-Modified Concretes with Superplasticizer or Superplasticizer Plus Silica Fume

Mix	Dynamic Modulus of Elasticity (ksi) at:			
	1 day	7 days	28 days	180 days
LMC2	5840	6820	7230	7310
N00F15	6250	7090	7340	7510
N00F30	6240	7150	7390	7470
N00H30	6080	6890	7160	7210
S10F23	5680	6380	6730	6810
S10F38	5480	6510	6770	6980
S10H38	5470	6940	7130	7220

E_d value.

Incorporating 10% silica fume as a replacement of cement with superplasticizer at either the lower dosage used (23 fl oz per 100 lbs cementitious materials) or the higher dosage used (38 fl oz per 100 lbs cementitious materials) reduced the E_d value at all ages. The decrease of E_d value ranged from about 0.16×10^6 to about 0.5×10^6 psi.

Reducing the latex content to half the usual latex content for LMC produced different effects on the E_d value depended on the compositions of the concretes. For LMC amended with superplasticizer only, reducing latex content reduced E_d values at all ages; but for the LMC with superplasticizer plus silica fume, reducing latex content increased E_d value at all ages. The E_d values in both cases were about the same as those of reference LMC at 7 days and beyond.

The results indicate that incorporating fly ash into LMC at either 15% or 25% replacement level does not significantly influence the elastic behavior of the concrete as measured by dynamic modulus of elasticity after 3 days of curing. In contrast, incorporation of 10% silica fume

Figure 5.4-3 Dynamic Modulus of Elasticity versus Curing Time for Latex-Modified Concretes with Superplasticizer or Superplasticizer Plus Silica Fume, Latex-Modified Concrete, and Plain Concrete

with superplasticizer significantly decreases the dynamic modulus of elasticity of the LMC at all ages. Reducing the latex content brings the dynamic modulus of elasticity back to the level of reference LMC for LMCs batched with superplasticizer or superplasticizer plus silica fume.

5.5 Chloride Permeability

The chloride permeability of the concrete was measured in accordance with AASHTO Designation T 277-83I "Interim Method of Test for Rapid Determination of the Chloride Permeability of Concrete". This test was originally developed as an indicator of the effective resistance of saturated concrete to migration of chloride ions. The test results are evaluated using the presumed relationship between the chloride permeability and the charge passed as given in Table 1 of AASHTO T 227-83I. This table is reproduced as Table 5.5-1.

Table 5.5-1 Chloride Permeability Based on Charge Passed

Charge Passed (coulombs)	Chloride Permeability	Typical of
>4,000	High	High water:cement ratio, conventional (≥ 0.6) portland cement concrete
2,000-4,000	Moderate	Moderate water:cement ratio, conventional (0.4-0.5) portland cement concrete
1,000-2,000	Low	Low water:cement ratio, conventional (< 0.4) portland cement concrete
100-1,000	Very Low	Latex-modified Concrete Internally sealed concrete
<100	Negligible	Polymer impregnated concrete Polymer concrete

5.5.1 Chloride Permeability of Latex-Modified Concrete with Fly Ash

The test results for LMCs with fly ash at different age are presented in Table 5.5-2. Two specimen slices were tested for each concrete. The individual testing results are listed in Appendix C. Two 3.75 in. diameter cylinders were cast for each concrete; one was 12 in. in height, the other 6 in. in height. The positions of the specimen slices in the cylinders are shown in Figure 5.5-1. Each value reported in Table 5.5-2 represents the average of the results from these two tests. The same data are also plotted schematically for comparison purposes in Figure 5.5-2.

For plain portland cement concrete, the average total charge passed in the period of 6 hours was about 2900 coulombs at about 3 months of wet curing. This falls into the "moderate" permeability category of the AASHTO classification (2000-4000 coulombs), which is typical of conven-

Table 5.5-2 Results of Chloride Permeability Test on Latex-Modified Concretes with Fly Ash

Mix	Relative Chloride "Permeability" (coulombs) at:		
	3 months	6 months	12 months
OPC	2901	1894	1655
LMC1	567	190	127
R15F00	425	146	99
R25F00	346	107	89
A15F00	476	128	101
^D5F00	374	103	56
G15F00	366	116	156
G25F00	330	89	79
T15F00	515	145	89
T25F00	414	110	69

Figure 5.5-1 Positions of Specimen Slices for Chloride Permeability Test in the Sample Cylinders

tional portland cement concrete with moderate w:c ratio (0.4-0.5). The corresponding figure at 6 months was down to about 1900 coulombs, and it was further reduced to about 1650 coulombs at 12 months. Thus the chloride permeability for 6 months and beyond falls into the "low" category (1000-2000 coulombs).

As expected, the reference LMC showed a much lower chloride permeability than the ordinary portland cement concrete, averaging about 570 coulombs after 3 months of air curing. This falls into the "very low" permeability category of the AASHTO classification (100-1000 coulombs), which is typical of LMC. Additional air curing reduced the value even further, to 190 coulombs at 6 months and 127 coulombs at 12 months.

Thus LMC intrinsically develops a much lower chloride permeability than ordinary portland cement concrete.

It was found that incorporation of fly ash in LMC resulted in further reductions of the measured permeability as compared to the

Figure 5.5-2

Total Charge Passed in a Period of 6 Hours for Latex-Modified Concretes with Fly Ash, Latex-Modified Concrete, and Plain Concrete Tested at Various Ages

Table 5.5-3 Reduction of Average Chloride Permeability of Latex-Modified Concretes with Fly Ash (As Compared to the Reference Latex-Modified Concrete)

Fly Ash Type	Replacement Level (%)	Permeability Reduction (%) at:		
		3 months	6 months	12 Months
Rockport	15	25	23	22
	25	39	44	30
Schahfer	15	16	33	20
	25	34	46	56
Gibson	15	35	39	-
	25	42	53	38
Stout	15	9	24	30
	25	27	42	46

reference LMC. The effects of different fly ashes on the chloride permeability were slightly different at 3 months. The Rockport and Gibson fly ashes were clearly more effective in this regard than Schahfer and Stout fly ashes. However at later ages these differences between fly ashes tended to disappear.

Furthermore, it appears that incorporation of fly ash at the 25% replacement level confers somewhat greater improvement in chloride permeability than at the 15% replacement level. This appears to be true at all ages. Table 5.5-3 provides the percentage reduction of chloride permeability for the LMC containing each fly ash as compared to reference LMC. It is apparent that increasing the fly ash replacement level provides significant additional effect on the reduction of chloride permeability.

5.5.2 Chloride Permeability of Latex-Modified Concretes with Superplasticizer or Superplasticizer Plus Silica Fume

The test results for LMCs with superplasticizer or superplasticizer plus silica fume at different age are presented in Table 5.5-4. Two specimen slices from two 3.75 x 12 inch cylinders were tested for each concrete. The individual testing results are listed in Appendix C. The position of the specimen slices on the cylinders was different at different ages. After cutting off a 5-mm layer of the very top surface material, 2-in. thick slices were cut from the top of the cylinders for the 3 month test. Another 2-in. thick slice was cut from the top of the remainder of each cylinder for the 6 month test. One 2-in. thick slice was cut from the remainder of each cylinder for the 12 month test. Each value reported in Table 5.5-3 represents the average of the results from these two tests. The same data are also plotted schematically for comparison purposes in Figure 5.5-3.

Adding superplasticizer to LMC at normal dosage (15 oz/100 lbs cement) improved the already substantial impermeability achieved by

Table 5.5-4 Results of Chloride Permeability Test on Latex-Modified Concretes with Superplasticizer or Superplasticizer Plus Silica Fume

Mix	Relative Chloride "Permeability" (coulombs) at:	
	3 months	6 months
LMC2	567	303
N00F15	361	188
N00F30	255	164
N00H30	296	144
S10F23	80	68
S10F38	77	59
S10H38	63	67

Figure 5.5-3

Total Charge Passed in a Period of 6 Hours for Latex-Modified Concretes with Superplasticizer or Superplasticizer Plus Silica Fume, and Reference Latex-Modified Concrete Tested at Various Ages

conventional LMC. The concrete (coded N00F15) showed a 36% of reduction in chloride permeability as compared to the reference LMC at 3 months, and a 38% reduction at 6 months. Presumably these reductions are at least partly due to the lower water content ($w:c=0.24$ compared to $w:c=0.29$ for the conventional LMC) made possible by the use of the superplasticizer.

Doubling the dosage of superplasticizer (concrete coded N00F30) provided further reduction in chloride permeability. The total charge passed was only about half that of reference LMC at both ages. For this concrete the $w:c$ ratio was 0.20.

Incorporating 10% silica fume into LMC with superplasticizer, dramatically reduced the chloride permeability of the concrete even further than did the superplasticizer alone. The measured chloride permeability of all the concretes containing silica fume were "negligible" (less than 100 coulombs) at as early as 3 months.

The LMC formulated with half of normal latex content (N00H30) was only a little more permeable at 3 months than the corresponding LMC with normal latex content, by 6 months its permeability was actually lower. Thus a high latex content is not necessary for impermeability to chloride, and reducing it may actually be beneficial in this regard.

For LMCs with superplasticizer plus silica fume, reducing the latex content by a factor of 2 produced no significant effects on the chloride permeability up to 6 months, apparently because of the negligible chloride permeability intrinsic to this kind of concrete.

From the above discussion, the following points are made:

- (1) LMC has a very low chloride permeability even at 3 months, and its chloride permeability decreases to almost negligible levels by

12 months.

(2) The incorporation of fly ash in LMC makes the chloride permeability even lower. The different fly ash types and replacement levels (15% and 25%) give almost the same results.

(3) Reducing the w:cm ratio (by adding superplasticizer) does improve the already very low permeability to chloride ions shown by LMC.

(4) Superplasticized concrete with only half the normal content of latex gives a chloride permeability substantially lower than ordinary LMC.

(5) The incorporation of 10% silica fume with superplasticizer gives the LMC a chloride permeability which is so low as to be rated "negligible" as early as 3 months; this is true for concrete with reduced latex content as well as for that with normal latex content.

5.6 Freezing and Thawing Resistance

During the period of this investigation, the apparatus for conducting standard freezing and thawing tests at Purdue University was inoperative. Accordingly, and through the kind courtesy of Mr. Richard Smutzer of the Indiana Department of Transportation, concrete specimens for the standard freezing and thawing test (ASTM C 666) were prepared at Purdue University and conveyed to the laboratory of the Division of Materials and Tests, INDOT, where the actual freezing and thawing tests were carried out.

Tests were carried out only for LMCs with fly ash and for the corresponding reference latex-modified and plain concretes. In these

tests the fundamental transverse frequency of the specimens was measured before the first cycle of freezing and thawing, and the measurements were then repeated after approximately every 30 cycles of freezing and thawing. The fundamental transverse frequencies measured were used to calculate the relative dynamic modulus of elasticity (P_c) according to the following formula [87]:

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

where:

P_c = relative dynamic modulus of elasticity, after c cycles of freezing and thawing, in percent;

n = fundamental transverse frequency at 0 cycle of freezing and thawing;

n_l = fundamental transverse frequency after c cycles of freezing and thawing.

According to the ASTM procedure, the tests should be continued until the specimens have been subjected to 300 cycles, or until their relative dynamic modulus of elasticity drops to 60 percent of the initial modulus, whichever occurs first. The durability of the concrete is then assessed by calculating the durability factor (DF) using the expression [87]:

$$DF = PN/M$$

where:

DF = durability factor of the test specimen,

P = relative dynamic modulus of elasticity at N cycles, percent,

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

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

A series of specimens for freezing and thawing tests were delivered to INDOT on April 12, 1987. This set is referred to herein as the "first series".

In accordance with normal practice for LMC, no air entraining agent was used in batching these concretes. A normal vinsol resin air entraining agent was used for the reference plain portland cement concrete. As indicated in Table 5.6-1, the actual measured air content of this reference plain concrete was 5%, those of the LMCs were typically less than 3%, with some less than 2%.

The tests were to be conducted by INDOT along with their own routine testing activities. INDOT ordinary uses ASTM C 666 Procedure A. During the course of these tests it was reported to us that a number of testing difficulties were experienced by the INDOT personnel actually carrying out the tests, due at least in part to equipment malfunction.

Despite these difficulties, all of these concrete specimens were tested to 300 cycles.

The results conveyed to us indicated that all of the specimens (the reference plain concrete, the reference LMC, and the LMCs with fly ash) showed similar patterns. Only modest reduction in dynamic modulus were

reported for the first 170 cycles, but after 240 cycles severe and progressive reductions apparently took place. The results reported indicates that all of the concretes had dynamic modulus reductions of between 55% and 58.5% at 300 cycles.

Table 5.6-1 Air Contents of Concrete Specimens for Freezing and Thawing Test

Mix	Actual Air Content (%)	
	First Series	Second series
OPC	5.04	7.24
LMC	2.64	4.14
R15F00	1.84	4.64
R25F00	2.74	4.24
A15F00	2.84	4.34
A25F00	1.84	4.74
G15F00	2.84	4.84
G25F00	2.94	5.99
T15F00	2.74	4.54
T25F00	3.54	4.44

It is believed that these results were erroneous, especially since examination of the concrete specimens after the conclusion of the tests showed no weight loss and no observable damage.

Accordingly, a second series of specimens was prepared for testing and delivered to INDOT on December 1, 1987. In preparing the second freezing and thawing test series it was decided to incorporate a standard dosage of air entraining agent in each mix, despite the fact that use of air entraining agents is not common with LMC.

As indicated in Table 5.6-1, use of this air entraining agent increased the measured air contents significantly. Air contents of the LMCs ranged between 4% and 6%.

The second series of tests was run by INDOT strictly according to ASTM C 666 Procedure A, and no difficulties were reported.

The relative dynamic modulus of elasticity and durability factors obtained from the second series of tests are presented in Table 5.6-2. The relation between the relative dynamic modulus of elasticity of concretes and the number of freezing and thawing cycles is presented in Figure 5.6-1.

It appears that all the concretes, including the LMCs with all of the fly ashes, at both 15% and 25% replacement levels, exhibited very good durability according to ASTM C 666. The indicated durability factors at 302 cycles were all over 90 percent. The durability factors were all

Table 5.6-2 The Average Durability Factor, and Relative Dynamic Modulus of Elasticity of LMCs with Fly Ash, Reference LMC, and Reference OPC

	LMC	R15	R25	A15	A25	G15	G25	T15	T25	OPC
Number of Cycles	Relative Dynamic Modulus of Elasticity (%)									
0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
21	99.5	97.1	97.7	97.4	97.6	97.6	97.4	97.9	96.6	95.3
50	95.5	94.8	96.8	96.2	97.2	96.2	97.2	97.4	94.0	93.9
65	93.0	94.7	97.2	95.5	96.4	95.5	97.1	96.5	94.4	93.9
83	93.3	94.4	96.6	94.9	96.1	95.4	96.6	96.1	93.0	93.0
96	92.8	94.4	96.3	94.6	96.1	95.0	97.4	96.1	92.5	92.9
117	92.6	94.1	94.9	95.5	96.2	95.0	96.7	95.5	93.3	95.0
148	93.3	94.9	95.4	95.3	96.4	95.7	96.6	95.6	93.6	93.0
177	93.6	95.9	95.9	94.5	95.3	94.7	97.7	96.1	93.8	94.6
204	94.8	95.7	95.9	94.3	96.5	94.5	97.4	96.3	94.6	94.6
229	93.7	95.3	95.9	93.8	95.8	95.2	96.5	96.8	94.3	94.0
247	94.0	96.0	95.6	93.3	96.5	95.6	97.6	96.8	93.8	93.6
280	93.3	95.5	95.5	94.6	96.4	95.8	97.1	97.3	93.1	93.1
302	92.3	95.3	96.7	93.8	95.3	94.3	97.5	95.6	92.5	91.5
Durability Factor (%)										
	92.3	95.3	96.7	93.8	95.3	94.3	97.5	95.6	92.5	91.5

between 91.5 and 97.5 percent.

The indicated durability factors for the LMCs with fly ash, at either 15% and 25% replacement levels, are equal to or somewhat higher than those of the reference LMC and the reference plain concrete. It can also be seen in Figure 5.6-2, that all the LMCs with fly ash had a similar pattern of reduction in the relative dynamic modulus of elasticity.

In addition to the numerical results of the durability factor measurement, visual assessment of the physical appearance of all of the specimens was carried out. This confirmed that no visually observable damage could be detected on the surface of any of the specimens.

Figure 5.6-1

Relative Dynamic Modulus of Elasticity versus Number of Freezing and Thawing Cycles for Latex-Modified Concretes with Fly Ash, Reference Latex-Modified Concrete, and Reference Plain Concrete

6. PROPERTIES RELATING TO THE PERFORMANCE OF LATEX-MODIFIED CONCRETES WITH FLY ASH OR SILICA FUME

In this chapter, the results of the tests and investigations on certain properties relating to the performance of latex-modified concretes with fly ash or silica fume are presented. All of the tests and investigations described in this chapter were carried out on the pastes batched from the same constituents and proportions as used in the concretes, but without aggregate.

6.1 Porosity and Pore Size Distribution

Many concrete durability problems involve diffusion or mass transfer of deleterious chemical components from outside the concrete. Also, the resistance to freezing and thawing is in partly related to the pore characteristics of the concrete, although freezing and thawing problems may generally be prevented by the inclusion of an adequate air bubble system. Therefore porosity and pore size distribution are often cited as a prime index of the potential resistance of a given concrete to the durability problems. In this study, the porosity and the pore size distribution of the pastes were measured by mercury porosimetry.

6.1.1 Contact Angle Measurements

In order to measure the pore size distribution of a given paste, it

is necessary to know the contact angle between mercury and that specific solid material. To some extent, contact angles vary between different cement systems, and with method of drying.

In the present study, the presence of latex in most of the pastes to be studied may cause difficulties if heating pretreatments are used. Accordingly, the method of drying adopted was to immerse the specimen in acetone to stop hydration, and then to continuously evaporate in a vacuum desiccator for long periods of time. For the contact angle measurements, pumping was continued for at least three months.

Measurements were carried out for the reference OPC paste, and for specimens of latex-containing pastes of all of the types studied in this work.

The contact angle found for the OPC (in a single determination) was 115° , essentially identical with that found for cement paste by Winslow and Diamond [88] after vacuum oven drying.

The contact angles found for the latex-bearing pastes were very much higher. Essentially all values were between about 140° and 160° for the various pastes, with the mean value of the entire set of 12 materials being 149° . Some trends were observed, in that the materials without added solids -- fly ash or silica fume -- tended toward lower values within this range. However, only single values are available, and this trend may not hold up under further investigation. The fly ash - bearing pastes, in particular, showed considerable apparent variation, with the Schahfer ash pastes showing low values (143° and 147° for the 15% and 25% replacement levels, respectively); the others were all higher.

Fortunately, for contact angles in the general range, the relation between pressure of intrusion and pore size ($P = -4\Gamma\cos \theta/d$) is only marginally affected by changes in the contact angle used to make the calculation. To illustrate this point, Figure 6.1-1 shows 4 plots of the pore size distribution found for the unmodified LMC paste. The contact angles used in the four separate calculations were respectively 143° , 149° , 154° , and 160° , leading to the four separate lines, going from left to right. As can be easily seen from the plot, there is essentially no difference in the results of the pore size distribution calculations with changes in contact angle in this range.

Accordingly, in calculating the pore size distributions to be reported in the following section, the contact angles used were 115° for OPC paste (without latex), and the average value for all of the latex-bearing pastes, 149° , for each of these latex-bearing specimens.

6.1.2 Pore Size Distribution and Porosity Measurements

The pore size distribution measurements were carried out each of the pastes at the ages between 1 day and 6 months. Each of the determinations were carried out at least in duplicate, and if the duplicates were not in sufficiently close agreement, additional runs were carried out. The weight average of all of the results measured for each paste was used as representing the pore size distribution for that paste.

The total intrusion of mercury up to the high pressure limiting value of the instrument (60,000 psi) provides a measure of "intrudable pore volume" characteristic of the material. This is not necessarily total pore volume, since some pores are not able to be intruded.

Figure 6.1-1

Comparison of Mercury Intrusion Pore Size Distribution Curves of the LMC Paste Using Different Contact Angles

In these determinations, each specimen was continuously evacuated at room temperature for periods of at least two weeks prior to the determination.

Ordinary Portland Cement Paste The measured pore size distribution (psd) for the reference portland cement paste (OPC) at age of 3 months is presented in Figure 6.1-2. The following features can be observed:

- (1) The total intruded pore volume (to a high-pressure limit of 20 Å) is $0.186 \text{ cm}^3/\text{g}$, about one-third of which is in the pores of nominal diameters less than 100 Å.
- (2) There is a definite, sharp break-through diameter (i.e. nominal diameter at which major intrusion starts) is about 2,600 Å ($0.26 \text{ }\mu\text{m}$).
- (3) The volume mean diameter of the indicated pore system is about 290 Å.
- (4) The slope of the curve at the high pressure end indicates that there probably is additional pore volume in nominal diameters below the 20 Å minimum diameter intrudable.

Figure 6.1-3 provides a comparison of the mercury pore size distribution curves for this paste at ages of 1, 7, 28, 90, 180 days. The shapes of the psd plots are similar to those of Winslow and Diamond [88] for ordinary cement pastes, as are also (1) the decreasing volume intrudable with increasing age, and (2) the decreasing value of the break-through diameter with increasing age.

In the present data, intrudable pore volume decreased from $0.35 \text{ cm}^3/\text{g}$ at 1 day to approximately $0.19 \text{ cm}^3/\text{g}$ at 90 days, and thereafter was essentially unchanged.

Figure 6.1-2

Mercury Intrusion Pore Size Distribution Curve for
Reference Portland Cement Paste

Figure 6.1-3

Mercury Intrusion Pore Size Distribution Curves for Reference OPC Paste at Different Ages

Latex-Modified Cement Paste Figure 6.1-4 provides a comparison of the psd curves for reference LMC paste and reference OPC paste at 90 days. The following differences are apparent:

- (1) The LMC paste has a lower total intruded pore volume, about $0.095 \text{ cm}^3/\text{g}$. However, the minimum diameter intrudable here is only $40 \text{ \AA}$. For comparative purposes, one can compare this value with the pore volume down to $40 \text{ \AA}$ in the OPC paste, which was $0.157 \text{ cm}^3/\text{g}$. Thus even in this comparasion the LMC paste has lower porosity. This is not surprising given the much lower w:c ratio of the LMC paste (0.29 as compared with 0.48).
- (2) The break-through diameter for LMC paste is much less definite than it is for OPC paste.
- (3) Except for a small "tail" at the bottom of the plot, the psd curve for LMC paste is displaced to the finer-pore-size side of the pore size distribution curve for OPC paste. This indicates that LMC paste has a generally finer pore system than that in OPC paste. However, the indicated mean pore diameter in LMC paste is about $360 \text{ \AA}$, which is significantly greater than that of the OPC paste, which is only about $290 \text{ \AA}$.
- (4) There is very little indicated pore volume below $50 \text{ \AA}$ in LMC paste.

These differences suggest that the addition of latex admixture has greatly reduced the porosity in the paste and modified the pore system in such a way as to either eliminate the finest pores or the keep them from

Figure 6.1-4 Comparison of Mercury Intrusion Pore Size Distribution Curves for Reference Latex-Modified Cement Paste and Reference Portland Cement Paste

being intruded.

Figure 6.1-5 shows the measured psd for the reference LMC at 1, 7, 28, 90, and 180 days, to illustrate the time-dependent changes taking place. A number of things are apparent from the figure:

- (1) The shapes of the plots are similar to each other, and quite different from those of the OPC paste at any age.
- (2) The 7-day old paste has a significantly lower intrudable pore volume than the 1-day old paste (about $0.11 \text{ cm}^3/\text{g}$ compared with $0.14 \text{ cm}^3/\text{g}$); subsequently, however, there is little further reduction.
- (3) There is no indication of a progressive reduction in break-through diameter with age, as was seen for reference OPC paste in Figure 6.1-3. For these pastes, the break-through phenomenon is not sharp, the curves being rounded out, but it is evident that the start of major intrusion is not progressively delayed to higher pressures (smaller diameters) with age.
- (4) After 7 days, there are only very minor changes in the psd curve itself.

Thus it is evident that the results of mercury intrusion psd measurements for latex-modified pastes are quite different in character from those of ordinary cement pastes without latex.

Latex-Modified Cement Pastes with Fly Ash In Figure 6.1-6, the pore size distribution curves at 90 days for LMC pastes with different fly ashes are shown together with that for the reference LMC paste to permit general comparison. The comparison shows that:

Figure 6.1-5

Mercury Intrusion Pore Size Distribution Curves for Reference LMC Paste at Different Ages

- (1) the total intruded pore volume (greater than 40 Å) ranges from 0.064 to 0.083 cm³/g for the fly ash bearing LMC pastes, all of which are significantly less than that in the unmodified LMC paste (0.095 cm³/g)...
- (2) the indefinite break-through pattern previously seen for LMC persists for the LMC pastes containing fly ash.
- (3) the mean pore diameter in the LMC pastes containing fly ash ranges from 300 to 450 Å, which is close to that in unmodified LMC paste (360 Å).
- (4) there is very little indicated pore volume below 50 Å in any of the LMC pastes containing fly ash, an observation also made for the unmodified LMC paste.

As described above, incorporating fly ash produced a less porous pore system at 90 days than was present in the LMC paste. However the effects of fly ash were somewhat different when different fly ash type and fly ash replacement level were used.

At 15% replacement level, as seen in Figure 6.1-7, the total intruded pore volume in the latex-modified cement pastes was reduced about 15% by incorporating Gibson or Stout fly ash, and about 27% by incorporating Rockport or Schahfer fly ash. At 25% replacement level, as seen in Figure 6.1-8, the total intruded pore volume in the LMC paste was reduced about 18% by incorporating Gibson or Stout fly ash, only about 13% by Schahfer fly ash, and about 32% by Rockport fly ash.

Generally speaking, increasing fly ash replacement level from 15% to 25% reduces the total intruded pore volume about 3-6% further except in the case of Schahfer fly ash. When Schahfer fly ash was used, the

Figure 6.1-6

Comparison of Mercury Intrusion Pore Size Distribution Curves for LMC Pastes Containing Fly Ash, Reference LMC Paste, and Reference OPC Paste

Figure 6.1-7

Comparison of Mercury Intrusion Pore Size Distribution Curves for LMC Pastes with 15% Fly Ash, Reference OPC Paste, and Reference LMC Paste

Figure 6.1-8

Comparison of Mercury Intrusion Pore Size Distribution Curves for LMC Pastes with 25% Fly Ash, Reference OPC Paste, and Reference LMC Paste

total intruded pore volume was for some reason significantly greater at 25% replacement level than at 15% replacement level.

Figures 6.1-9 through 6.1-16 are results of mercury psd determinations for LMC pastes containing each of four fly ashes at 15% and at 25% replacement levels, each for ages of 1, 7, 90, and 180 days.

The pattern developed for the Rockport fly ash (a Class C high calcium fly ash) is somewhat different from those developed with the other fly ashes, all of which are Class F low-calcium fly ashes.

Figures 6.1-9 and 6.1-10 show the psds for the LMC paste with Rockport fly ash at the 15% replacement and at the 25% replacement levels, respectively.

At both levels, the psd patterns are different from the others in that the results for 7 days are almost identical to the results for 1 day; the implication is that the early hydration was somewhat faster for this paste. For both levels of fly ash, there is a significant drop in pore volume intruded between 7 and 90 days. Subsequently there is a difference: the paste with 15% fly ash shows a further drop with additional aging to 180 days, but that with 25% fly ash does not; instead there is an increase in volume, which is due to increased pore space intruded in the finest pore sizes intrudable. This is a characteristic that also is followed with the Class F fly ashes, to be described subsequently.

The shapes of the distribution curve at all ages are similar to that for the reference LMC paste and generally similar to those for pastes containing the other fly ashes. The total amounts intruded at a given age is considerably less than that for the reference LMC pastes, as was discussed previously for the comparison at 90 days.

Figure 6.1-9

Mercury Intrusion Pore Size Distribution Curves for LMC Paste containing 15% Rockport Fly Ash at Different Ages

Figure 6.1-10

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Containing 25% Rockport Fly Ash at Different Ages

Figure 6.1-11

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Containing 15% Schahfer Fly Ash at Different Ages

Figure 6.1-12

Mercury Intrusion Pore Size Distribution Curves for LMC Paste containing 25% Schahfer Fly Ash at Different Ages

Figure 6.1-13

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Containing 15% Gibson Fly Ash at Different Ages

Figure 6.1-14

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Containing 25% Gibson Fly Ash at Different Ages

Figure 6.1-15

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Containing 15% Stout Fly Ash at Different Ages

Figure 6.1-16

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Containing 25% Stout Fly Ash at Different Ages

Figures 6.1-11 and 6.1-12 show the psds for the Schahfer fly ash; Figures 6.1-13 and 6.1-14 for the Gibson fly ash; and Figures 6.1-15 and 6.1-16 for the stout fly ash.

All of the psd curves are similar in shape, and are very much like those of the reference LMC paste and of the LMC pastes containing Rockport fly ash.

The total volume intruded at 1 day in all cases is significantly less than that for the reference LMC paste, ranging from slightly less than $0.12 \text{ cm}^3/\text{g}$ to slightly less than $0.13 \text{ cm}^3/\text{g}$, as compared to $0.14 \text{ cm}^3/\text{g}$.

At 7 days, all of these fly ash bearing pastes show significantly reduced total intruded pore volumes, in contrast to the lack of such reduction with the Rockport fly ash pastes.

There was also a further significant reduction in intruded pore volume in going from 7 days to 90 days with the possible exception of the 15% replacement paste with Stout fly ash.

In going from 90 to 180 days, there was the same difference with level of replacement found previously for the Rockport fly ash. At the 25% level, there is increased porosity at the extreme fine end of the distribution; at the 15% level, this was usually not the case.

Latex-Modified Cement Pastes with Superplasticizer Figure 6.1-17 shows the psd curves at 90 days for LMC pastes with superplasticizer (N00F30 and N00H30 pastes) together with those for two reference cement pastes (LMC and OPC), previously shown.

The total intruded pore volume in the heavily-superplasticized LMC paste (N00F30) at 90 days is only $0.052 \text{ cm}^3/\text{g}$, which is only a little more

Figure 6.1-17

Comparison of Mercury Intrusion Pore Size Distribution Curves for LMC Pastes with Superplasticizer, Reference LMC Paste, and Reference OPC Paste

Figure 6.1-18

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Amended with Superplasticizer at Different Ages

Figure 6.1-19

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Amended with Superplasticizer and Reduced Latex Content at Different Ages

than half that found in the unmodified LMC paste at the same age. The volume mean pore diameter is substantially lower, about 280 Å as compared to about 360 Å. Thus use of the superplasticizer (and the lower w:c ratio it permits) results in a much reduced and finer pore system.

On the other hand, reducing the usual latex content by half (N00H30) provides a much coarser pore structure. The total volume intruded at 90 days is 0.16 cm³/g, almost 70% higher than that in the LMC paste, and about 3 times that in the N00F30 full latex content paste. Reducing the latex content increases the volume mean pore diameter at 90 days by about 3 times, from 360 Å for normal LMC paste to about 1,200 Å. Despite the fact that the w:c ratio in this paste was very low (0.22), the pore structure that developed was coarse, even coarser than that of the reference OPC paste cast at more than twice the w:c ratio.

The development of the psd with time for these pastes is illustrated in Figures 6.1-18 and 6.1-19. For the full latex dose, superplasticized paste (N00F30) it is evident that even at 1 day the total pore volume intruded was exceedingly small, only 0.11 cm³/g; by 7 days it dropped to only about 0.05 cm³/g, and there was almost no subsequent change.

The corresponding psds for the half latex dose superplasticized paste (N00H30) are very different in terms of total pore volume but similar in pattern of development over time. There was a great reduction in total pore volume in going from 1 day to 7 days, but very little subsequent change.

Latex-Modified Cement Pastes with Silica Fume The psd curves for the LMC pastes with superplasticizer and silica fume (the S10F38 and S10H38 pastes) are shown in Figure 6.1-20 together with those for two previously

Figure 6.1-20

Comparison of Mercury Intrusion Pore Size Distribution Curves for LMC Pastes with Silica Fume Plus Superplasticizer, Reference LMC Paste, and Reference OPC Paste

shown reference cement pastes (LMC and OPC).

The full latex content superplasticized silica fume bearing paste (S10F38) at 90 days showed a dramatically higher intruded pore volume than the reference LMC paste, $0.15 \text{ cm}^3/\text{g}$ as compared to $0.10 \text{ cm}^3/\text{g}$. However, the mean pore diameter was slightly smaller than that in LMC paste, $290 \text{ \AA}$ as compared to $360 \text{ \AA}$. Most of the "extra" pore volume in the silica fume bearing paste seems to be in the fine pore size range, between $200 \text{ \AA}$ and $100 \text{ \AA}$ in diameter.

When the latex content was cut to half normal with silica fume present (S10H38), the total intruded pore volume at 90 days was even higher, about $0.19 \text{ cm}^3/\text{g}$. This is almost double that in the LMC paste and about the same as that in OPC paste. However the mean pore diameter remained about the same as for the full latex content paste.

It is evident that at 90 days the heavily superplasticized pastes showed substantial extra pore volume in the range between about $300 \text{ \AA}$ and $100 \text{ \AA}$ as compared to the LMC paste.

Figure 6.1-21 shows the pattern of development of psd with time for the full latex dose, heavily superplasticized silica fume bearing paste (S10F38). The total intruded pore volume at 1 day was very high, $0.20 \text{ cm}^3/\text{g}$; it was only somewhat reduced (to $0.16 \text{ cm}^3/\text{g}$) at 7 days. There was very little further reduction at 28 and 90 days, and surprisingly, at 180 days there was a significant increase, back to the original $0.20 \text{ cm}^3/\text{g}$ that was found at one day. This behavior is entirely unexpected and unexplained.

On the other hand, the pattern for development with age of the psd for the half latex dose superplasticized paste with silica fume (S10H38)

Figure 6.1-21

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Amended with Superplasticizer and Silica Fume at Different Ages

Figure 6.1-22

Mercury Intrusion Pore Size Distribution Curves for LMC Paste Amended with Superplasticizer and Silica Fume, and Reduced Latex Content at Different Ages

is more normal (Figure 6.1-22). The very high 1-day total intruded pore volume ($0.25 \text{ cm}^3/\text{g}$) was reduced by 7 days to about $0.18 \text{ cm}^3/\text{g}$. There was little subsequent reduction.

The shapes and general characteristics of all of these psds are similar to each other, and similar to those of unmodified LMC and of the fly ash bearing LMCs as well.

6.2 Microstructure

Scanning electron microscopy (SEM) examinations were carried out on paste samples prepared in the same way as those used for mercury porosimetry. All these pastes had been allowed to hydrate for 3 months before being sampled for the examinations.

A Robinson backscatter detector was used for all these micrographs. The operating voltage was 15 kV.

6.2.1 Microstructure of Reference Portland Cement Paste

Several SEM micrographs were taken for reference ordinary portland cement paste (OPC) to serve as background for interpretation of any change induced by the presence of latex or latex and fly ash.

Figure 6.2-1 shows a typical morphology of 90 day old hardened OPC paste at a magnification of 500 X. The smooth-textured areas are calcium hydroxide crystals and, in a few cases, residual clinker grains. They are embedded in a porous surrounding mass of CSH gel, the details of which cannot be seen at this magnification.

Figure 6.2-1 Scanning Electron Micrograph of Reference Portland Cement Paste

Figure 6.2-2 is a dual magnification micrograph of a similar area. The left side was taken at 500 X; the right side is the area enclosed in the rectangle in the left-side micrograph, enlarged to 2,500 X. The region is mostly CSH gel. The fibrous habit of some of the CSH gel is evident, as is the large proportion of unoccupied space. A similar pair of micrograph from a different area is shown in Figure 6.2-3.

6.2.2 Microstructure of Reference Latex-Modified Cement Paste

SEM examinations were also carried out on 90 day old reference latex-modified cement (LMC) paste. A typical view of the morphology of hardened LMC paste is shown in Figure 6.2-4. Figure 6.2-4 shows a somewhat less porous microtexture than seen for the OPC.

Figure 6.2-2 Scanning Electron Micrograph of Reference Portland Cement Paste

Figure 6.2-3 Scanning Electron Micrograph of Reference Portland Cement Paste

A dual magnification view of a CSH gel area, analogous to Figures 6.2-2 and 6.2-3 for OPC paste, is shown in Figure 6.2-5. It is evident that the CSH gel microstructure here is somewhat different from that in OPC paste. Most of the material visible is in the form of regular porous gel masses; comparatively few fibrous particles can be seen, and the individual fibers are shorter. There is still significant void space visible in these areas. A similar pair of micrographs of the same paste is shown in Figure 6.2-6.

No latex films could be distinguished in these examinations.

To attempt to secure formation about the nature of the latex films in the hardened LMC paste, the fracture surface of a small piece of LMC paste was etched repeatedly with 1:4 hydrochloric acid to remove the cement paste without dissolving the latex films. This was continued until

Figure 6.2-4 Scanning Electron Micrograph of Latex-Modified Cement Paste

Figure 6.2-5 Scanning Electron Micrograph of Latex-Modified Cement Paste

Figure 6.2-6 Scanning Electron Micrograph of Latex-Modified Cement Paste

the sample was entirely white, i.e. until essentially all of the solid paste components were dissolved. The specimen was then coated in the same way as had been done for the previous specimens, and examined with SEM and EDXA.

Figure 6.2-7 shows the typical morphology of HCl-leached fracture surface of hardened LMC paste at 500 X. The examination results indicate that latex formed a continuous porous network in the hardened LMC paste, and unhydrated cement particles and hydration products were embraced within the network. Spaces, or pores, in the network ranged from less than 1 μm up to 30-40 μm .

The specimen examined in Figure 6.2-7 was also examined using EDXA, with the pattern secured in Figure 6.2-8. Only three significant elemental peaks were found; peaks for Au and Pd from the metallic coating

Figure 6.2-7 Scanning Electron Micrograph of Latex-Modified Cement Paste Etched with HCl

Figure 6.2-8

EDXA Result for the HCl Etched Fracture Surface of
Latex-Modified Cement Paste

Figure 6.2-9 EDXA Result for the Fracture Surface of a Oven Dried Latex Sample

applied to the specimen, and a peak for Si. No peaks for Ca, the major component of hydrated cement, was detected. Accordingly, it was concluded that all of the cement had been dissolved in the acid washing procedure, leaving behind the undamaged latex film network.

The silica detected in the acid-washed specimen could have been secondary material precipitated from the acid dissolution. However, a separate EDXA spectrum was secured from a dried sample of the latex material itself, dried at 105°C in a separate mass. The dried latex yielded the spectrum shown in Figure 6.2-9, which showed the same three peaks. Accordingly, the silica detected in Figure 6.2-7 could have partly come from a minor silica bearing component of the latex product. Clear and Chollar [14] have indicated that such a component, in the form of polymethylsiloxane, is present in some S-B formulation. On further inquiring Kuhlmann (personal communication) indicated that the silica bearing component in the Dow Modifier A formulation used in this work was air-detainer.

6.2.3 Microstructure of Latex-Modified Cement Pastes with Fly Ash

The 90 day old LMC pastes with two types of fly ashes were examined with SEM. One was R25F00, the paste with Rockport Class C fly ash at 25% replacement level; the other was G25F00, the paste with Gibson Class F fly ash also at 25% replacement level.

Morphology of R25F00 Paste Figure 6.2-10 shows the typical morphology of 90 day old hardened R25F00 paste. The morphology shown in Figure 6.2-10 is similar to that shown in Figure 6.2-4 (for hardened LMC paste), except

that in this figure several spherical fly ash particles and several "sockets" remaining after the mechanical removal of residual fly ash particles can be clearly seen. An example of a fly ash particle is shown below the "a" mark in the figure, a socket is indicated a "b". There is no visible evidence of hydration on the surface of any of the fly ash particles.

In Figure 6.2-11, the writer was able to observe, for the first time, some latex strands in the original unetched paste. These were detected at the bottom of a large (160 μm diameter) air void in another area of the paste shown in Figure 6.2-10. These latex strands are shown at higher magnification in Figure 6.2-12, and additional details are visible. Similar features were found to occur in most air voids of this paste. However, it was not possible to detect them in the fracture

Figure 6.2-10 Scanning Electron Micrograph of Latex-Modified Cement Paste with 25% Rockport Fly Ash

Figure 6.2-11 Scanning Electron Micrograph of Latex-Modified Cement Paste with 25% Rockport Fly Ash

Figure 6.2-12 Scanning Electron Micrograph of Latex-Modified Cement Paste with 25% Rockport Fly Ash

surfaces away from the air voids.

The morphology of an HCl-etched fracture surface of this hardened R25F00 paste is shown in Figure 6.2-13. Again the sponge-like latex network is observed, this time with some fly ash particles embraced in it. The sponge-like latex network appears to be significantly more dense than that of the LMC paste (Figure 6.2-7). The residual fly ash particles seem to be firmly embedded in the latex network, even after HCl treatment. They seem to show little evidence of dissolution under the acid washing treatment.

Morphology of G25F00 Paste A typical morphology of 90 day old hardened G25F00 paste (with Class F fly ash) is shown in Figure 6.2-14. The microstructure is similar to that seen in Figures 6.2-10, both types of

Figure 6.2-13

Scanning Electron Micrograph of HCl Etched Surface of Latex-Modified Cement Paste With 25% Rockport Fly Ash

Figure 6.2-14 Scanning Electron Micrograph of Latex-Modified Cement Paste with 25% Gibson Fly Ash

fly ash producing latex-modified paste of similar morphology.

Figure 6.2-15 is a dual magnification micrograph of this paste. At the higher magnification (2,500 X) it appears that the residual spaces between the hydration product masses may be smaller in size and less extensive than in the reference LMC paste. Few elongated CSH gel particles are visible.

Figure 6.2-16 shows another area of the same paste at higher magnification. Fly ash particles with diameters from about 4 μm to 10 μm are visible, and a socket previously occupied by a fly ash particle is also apparent. Again there is no evidence of any reaction on the either the surfaces of the fly ash particles or in the bottom of the empty socket.

Figure 6.2-15 Scanning Electron Micrograph of Latex-Modified Cement Paste with 25% Gibson Fly Ash

Figure 6.2-16 Scanning Electron Micrograph of Latex-Modified Cement Paste with 25% Gibson Fly Ash

7. SUMMARIES AND GENERAL DISCUSSIONS

In this chapter, summaries and general discussions are presented of the experimental results reported for each of the specific tests in previous two chapters.

7.1 Properties of Normal Latex-Modified Concrete

As batched in this laboratory (with a Lancaster pan mixer), we found that "normal" LMC mixed with Dow Modifier A styrene-butadiene latex has characteristics as described below. It should be recalled that this laboratory mixing procedure is quite different from that used in most field applications; the mixer is more efficient and the mixing time is longer. Thus the results obtained may not be precisely characteristics of field LMC mixes.

7.1.1 Workability

The portland cement, sand, and coarse aggregate used to prepare all of the LMCs were such that the w:c ratio needed to prepare an ordinary portland cement (OPC) reference concrete at the specified 4 to 6 in. slump was 0.48.

Using the same components and the standard dosage of Dow Modifier A latex, it was found that the latex itself provided a highly significant

water reduction effect; the w:c ratio necessary to meet the same slump criterion was only 0.29, a 40% reduction. While some water reduction was expected, based on previously reported results like those of Clear and Chollar [14] and Smutzer and Hockett [7], we had expected w:c ratios of the order of 0.35 to 0.40.

Water reduction produced by the latex system is likely due to a combination of the effects of the very small (about 0.2 μm) latex spheres acting more like entrained air bubbles, and to chemical dispersing effects of the surfactants used in the latex modifier mix.

For the reference LMC concrete, the actual slump measured immediately after completion of mixing was 6 in. The concrete remained reasonably workable for about 25 minutes, and there was no difficulty in placing or finishing specimens during this period. There was no noticeable bleeding and no segregation.

As reported by Kuhlmann [6], fresh LMC tend to form an apparently dry "crust" on its surface. We found such a crust formed at about 25 minutes after the completion of the mixing, even though the concrete underneath was still quite plastic.

7.1.2 Compressive Strength

The compressive strengths of the LMC were all quite high in comparison with that expected from the literature at various ages. The measured strengths exceeded 3000 psi at 1 day, 6200 psi at 7 days, and reached 7400 psi at 28 days. Subsequently the compressive strengths increased to about 8000 psi at 1 year.

From Figure 5.2-1, it is obvious that the compressive strengths of

LMC are significantly higher than those of reference OPC at all ages, the differences being in the range of 1000 to 2000 psi, or generally in the range of 20% or so. Since the latex itself does not increase compressive strength [11], the higher compressive strength of LMC is mainly due to the much reduced w:c ratio.

7.1.3 Flexural Strength

As shown in Figure 5.2-3, the LMC concrete was much stronger in flexural than the ordinary portland cement concrete made from the same materials. The difference was about 200 psi (about 30%) over the first week, but it increased substantially thereafter. At 28 days the LMC was more than 50% stronger in flexure. By six months its flexural strength had reached 1700 psi, about 70% higher than that of the OPC. This difference was maintained subsequently.

It is evident that the latex concrete is stronger than the corresponding OPC in both compression and flexure, but it is much stronger in flexure while only marginally stronger in compression. The much enhanced flexural strength is likely associated with the continuous porous network formed by the latex, as shown for example in Figure 6.2-8. According to Manson [89] such a continuous latex film network appears to possess the capacity to intercept growing microcracks and dissipate the fracture energy by forming microfibrils across them. Instead of the energy induced by the flexural loading serving to propagate the crack, it is dissipated by stretching the microfibrils, and crack growth is minimized. Such a mechanism would clearly improve flexural (or tensile) behavior much more than compressive behavior.

7.1.4 Dynamic Modulus of Elasticity

Polymer is less stiff than cement paste it replaces, and so latex incorporation can be expected to result in a lower elastic modulus [9]. Nevertheless, as shown in Figure 5.3-1, the measured dynamic modulus of elasticity (E_d) of LMC was higher than that of OPC at 1, 3, and 7 days. However it cross over after 7 days, and by a year, it was only about 85% of that for OPC. This is in agreement with findings by Kuhlmann [10] that LMC generally develops an elastic modulus that is approximately 85% of that of conventional concrete made of the same materials.

7.1.5 Durability

Chloride Permeability The most impressive feature of LMC is its impermeability; this is what makes it so attractive for bridge deck applications. The reference LMC used in this study had a very low chloride permeability (570 coulombs) at 3 months, and its chloride permeability was progressively reduced to an almost but not quite negligible level (ca. 130 coulombs) at 12 months.

Impermeability is usually associated with low porosity. Separately-prepared hardened cement paste of LMC showed very low intrudable porosity ($0.15 \text{ cm}^3/\text{g}$) as early as 1 day; its porosity decreased to about $0.10 \text{ cm}^3/\text{g}$ at 7 days, and remained about same afterward. This suggests that the formation of the pore structure in the latex-modified cement paste is essentially complete by 7 days, and that the latex film network has been well established at this age. This appears to conflict with the

observation that the chloride permeability of LMC decreases with curing age even after 6 months. The explanation may lie in a progressive decrease in the pore structure of the interfacial zone around aggregate grains in the concrete.

Freezing and Thawing Resistance The excellent field service history of latex-modified concrete for bridge deck overlays indicates that the freezing and thawing resistance is not a problem for this kind of concrete in the field [14]. Also the extensive review of the performance history of latex-modified concrete overlays did not even mention freezing and thawing damage as a potential problem [1].

Latex-modified concrete studied in this work exhibited excellent freeze-thaw durability according to ASTM C 666. The indicated durability factor at 302 cycles was 92 percent, which was essentially the same as that for referee OPC. Visual assessment of the physical appearance of the specimens confirmed that no visually observable damage could be detected.

7.1.6 Summary of LMC Properties

The latex modified concrete prepared as a reference material in this research was batched at w:c of 0.29, a low value. It had an initial slump of almost 6 in., was workable for almost 1/2 hour and then formed a crust, and exhibited no bleeding and no visible segregation.

The hardened LMC was somewhat stronger in compression than ordinary concrete made of the same materials without latex, but it was very much stronger in flexure. The elastic modulus was slightly higher than the ordinary concrete at first, but it was only about 85% of that of the

ordinary concrete by the end of a year. the measured chloride permeability for the LMC was very low initially and dropped progressively with age to about 130 coulombs. Separately-batched LMC paste showed a low volume of pores intrudable in mercury porosimetry, and this mostly in fine pore size. The ASTM C 666 freeze-thaw test results for the LMC were highly satisfactory.

7.2 Effects of Fly Ashes on LMC

As has been mentioned earlier, the original focus of this investigation was to establish the behavioral effects of fly ashes of various types on LMC.

As indicated in the test results documented in Chapter 5 and 6, effects of fly ash replacement for part of the cement used in LMC were almost invariably favorable, but usually relatively small in magnitude. In this section we summarize and discuss these effects and attempt to interpret the behavior of the various fly ash-bearing LMC concretes.

7.2.1 Effects of Fly Ashes on Workability of LMC

It was quickly established that replacement of cement with fly ash at both 15% and 25% levels permitted a reduction of the w:c ratio of LMC, already low, to somewhat lower levels at constant slump. The w:cm ratios needed to get a 4 to 6 in. slump were between 0.25 and 0.28, compared to the 0.29 for the reference LMC.

None of the fly ashes used (three Class F ashes and one Class C ash) changed the actual workability of the LMC very much. All of the LMC

concretes with fly ash remained reasonably workable over a period of about 25 minutes.

It is well established that most fly ashes do reduce the w:c ratio necessary to get a given slump value for ordinary concrete; and generally the effects on the physical characteristics of the fresh concrete are moderately favorable. It is reassuring that these characteristics seem to carry over to LMC as well.

7.2.2 Effects of fly Ashes on Compressive Strength of LMC

One of the possible complications we were originally concerned about was the possibility that strength gain with fly ash bearing LMC might be substantially reduced because of the effects of the air curing necessary with LMC. The results of Chapter 5 show that this concern was unwarranted, and that the rate of gain of compressive strength with fly ash-bearing LMC was comparable to that of ordinary LMC without fly ash. The slow early strength gain found in plain concretes with most fly ashes did not seem to occur with LMC.

Instead, comparing LMC with fly ash (at both 15% and 25% levels) to ordinary LMC, after 1 day all of the strengths were similar with a single exception. Incorporating the Stout fly ash into LMC consistently degraded compressive strength. However the magnitude of the effect was relatively small (around 400 to around 700 psi), and even this small effect disappeared at 1 year.

7.2.3 Effects of Fly Ashes on Flexural Strength of LMC

For flexural strength, as indicated in Chapter 5, incorporating the fly ash did slightly degrade performance at early ages (up to 28 days), but the effect practically disappeared afterward. There were some variations among the effects of the different fly ashes. With Rockport fly ash there was a small increase before 28 days which became negligible afterward; with Schahfer fly ash there was a slight flexural strength enhancement after 28 days; with Gibson and Stout fly ashes, there were slight reductions at all ages.

Generally speaking, the effects of fly ash on flexural strength of LMC were too small to be of any significance, and the great improvement of LMC over conventional concrete in this characteristic was maintained.

As indicated earlier, for example in Figure 6.2-12, incorporating fly ash appeared to change the latex film structure by making it denser and less porous. If the film structure is responsible for the large increase in flexural strength shown by LMC over ordinary concrete, one might expect a substantial change in flexural strength due to the changed character of the latex film. No such effect on flexural strength was observed.

7.2.4 Effects of Fly Ashes on Dynamic Modulus of Elasticity of LMC

It was found that incorporating fly ashes into LMC reduced the dynamic modulus at 1 day, but by 3 days the effect had essentially disappeared and no significant effect was observed thereafter. There were no significant differences in the effects produced by the different fly

ashes or with replacement level.

These results for dynamic elastic modulus somewhat parallel the corresponding result for compressive strength. This is not surprising, since it is generally accepted that the modulus of elasticity of concrete is closely associated with its compressive strength.

7.2.5 Effects of Fly Ashes on Durability-Related Properties of LMC

Chloride Permeability As shown in Chapter 5, all of the fly ashes produced significant reductions in the chloride permeability of LMC, which was already very low. While there were small individual variations between fly ashes, and the reduction was slightly greater at the 25% replacement level, these differences between effects of different ash treatments are not large enough to cause observable differences in field performance, in the opinion of writer.

There was a strong effect of age. All of the fly ash-bearing LMCs showed progressive decreases in value with increasing age, down to negligible values (less than 100 coulombs) by 1 year. This result may be contrasted with results for mercury intrusion pore size distribution measurements for separately-batched pastes. In those measurements the total pore volume intruded, and the pore size distribution curves, changed very little after 7 days. This difference in developing pattern on aging reinforces the earlier suggestion that the progressive reduction in chloride permeability of LMC system might involve changes in the interfacial zone around aggregates rather than changes in the bulk paste.

Freezing and Thawing Resistance All the fly ash containing LMC exhibited excellent freezing and thawing durability according to ASTM C 666. The indicated durability factors at 302 cycles were all over 90 percent.

All the LMCs containing fly ashes have a similar pattern of very slight reduction in the relative dynamic modulus of elasticity with increasing number of freeze-thaw cycles. From Figure 5.5-2, it is obvious that all fly ash containing LMCs have a somewhat higher relative dynamic modulus of elasticity than reference LMC and OPC during the whole freezing and thawing test procedure, even though the differences may not have practical significance.

Visual assessment of the physical appearance of all of the specimens confirmed that no visually observable damage could be detected.

Therefore, it is apparent that fly ash incorporation should not lead to freezing and thawing difficulties if an adequate air content is maintained.

Pore Structure Separately-batched LMC paste has a tight pore structure. As indicated in Chapter 6, by 7 days the pore structure, as measured by mercury porosimetry, changes little. The total intruded volume is only about $0.10 \text{ cm}^3/\text{g}$, and the mean pore size only about $400 \text{ \AA}$.

Incorporation of fly ash produces changes that are generally favorable. The total intruded pore volume, already small, is reduced further (to 0.06 to $0.08 \text{ cm}^3/\text{g}$), and in some case the mean pore diameter is reduced somewhat. There are small differences among the effects produced by the different fly ashes and levels of replacement, but the basic pore structure, as indicated by the shape and characteristics of the pore size distribution curve, is not greatly affected.

Microstructure The same general interpenetrating latex film structure is developed with fly ash, except that it appears to be denser and somewhat less porous. There seems to be almost no visible reaction on the surfaces of the individual fly ash particles, suggesting that very little pozzolanic reaction had taken place in the 3-month old specimens examined.

7.2.6 Effects of Fly Ashes on Bond Strength

While the reproducibility of the bond strength measurements carried out is not of the highest, the results shown in Chapter 5 indicate that fly ash increases the bond strength of LMC to previously-prepared concrete substrates considerably. Improved bond strength values were obtained for all of the fly ashes. There were apparent differences among the different fly ashes, although the actual significance of these differences is in doubt.

7.2.7 Summary of the Effects of Fly Ashes on LMC

It has been established that the effects of fly ash on the measured properties of LMC mixed with a laboratory pan mixer are either negligible or favorable.

It has been found that the w:cm ratio can be reduced somewhat at the same slump, and that the workable time and the physical characteristics of the fresh concrete are not impaired. The fly ash bearing concretes are similar to unmodified LMC in both compressive and flexural strengths, and the dynamic modulus of elasticity is relatively unchanged.

Chloride permeability, already low, is reduced still further,

especially at later ages. Freezing resistance is unaffected. The pore structure of separately-batched paste is only slightly affected, and the effects are marginally favorable. The microstructure of the latex films developed is apparently denser.

Bond strength measurements show improvements over conventional LMC, although the reproducibility of these measurements was not completely satisfactory.

7.3 Effects of Modification of Latex System: Effects of Superplasticizer

7.3.1 Effects of Superplasticizer on Workability of LMC

With the addition of superplasticizer, the w:c ratio needed to give a 4-6 in. slump was greatly reduced, from 0.29 for reference LMC to 0.24 or 0.20 depended on the dosage of superplasticizer. The actual slumps measured immediately after completion of mixing were 6.5 inches for a "normal" dose (15 oz./100 lbs cement) and 6.3 inches a for heavy dose (30 oz./100 lbs cement). The slumps measured 5 minutes later did not show a significant slump loss.

The reduced water contents produced no difficulty in placing and finishing. The thin, relative dry "crust" ordinarily produced with LMC was also observed in this case, starting at about 20 minutes after the completion of the mixing. Nevertheless, the freshly mixed concretes were reasonably workable over a period of 20 minutes.

7.3.2 Effects of Superplasticizer on Compressive Strength of LMC

Reducing the w:c ratio by adding the normal dosage of superplasticizer significantly improved compressive strength at all ages, the increases ranging from about 10% to about 17%. The greater w:c ratio reduction made possible by using higher superplasticizer dosage provided only small further compressive strength improvement, about 200 to 300 psi.

7.3.3 Effects of Superplasticizer on Flexural Strength of LMC

Using a normal dosage of superplasticizer provided a small but consistent flexural strength increase at all ages. Doubling the dosage of superplasticizer made the increase even larger. The increases became more significant at later ages in both cases, and a value close to 2000 psi is reached 1 year for the heavily dosed system.

It is considered that these increases may be due to a denser latex film expected to be formed in the reduced void space available. However, this would suggest that film development proceeds continuously even up to late ages, which is doubtful.

7.3.4 Effects of Superplasticizer on Dynamic Modulus of Elasticity of LMC

Adding superplasticizer to LMC produced a small but consistent increase in E_d value at all ages. The increase in E_d value was about 0.4×10^6 psi at 1 day, and about 0.2×10^6 psi at later ages. Doubling the dosage of superplasticizer produced no further increase in E_d value. These are in accord with the increase of compressive strength with the addition

of superplasticizer.

7.3.5 Effects of Superplasticizer on Durability-Related Properties of LMC

Chloride Permeability Reducing the w:c ratio (by using superplasticizer) does improve the already very low permeability to chloride ions shown by LMC. The measured chloride permeability was reduced by about 35% when the normal dosage of superplasticizer was used, and by about 50% when superplasticizer dosage was doubled. Despite those reductions, the resulting values are still in the "very low" range at 6 months, and are not "negligible".

Pore Structure The effect of a high dosage of superplasticizer on the pore size distribution of separately-batched LMC paste was highly favorable. The total intruded porosity was reduced by a factor of almost 2, to about $0.05 \text{ cm}^3/\text{g}$. This is an exceedingly low value. The shape and the other characteristics of the pore size distribution remain similar to those of LMC paste without superplasticizer.

7.3.6 Summary of Effects of Superplasticizer

Incorporation of superplasticizer into LMC was found, as expected, to reduce the water demand sufficiently that the concrete could be batched at very low w:c ratios. There was little effect on placing and finishing characteristics. The concrete produced was, as expected, substantially stronger in compression - with most of the increase occurring at a normal dosage level of superplasticizer. The concrete was also substantially

stronger in flexure, but this required a high superplasticizer dose. A small increase in dynamic elastic modulus was observed in either cases.

Use of the superplasticizer produced substantial reduction in chloride permeability, and at the higher level, substantially reduced the pore space intrudable by mercury porosimetry.

7.4 Effects of Modification of Latex System: Effects of Joint Addition of Superplasticizer and Silica Fume

7.4.1 Effects on Workability of LMC

Incorporating 10% silica fume with superplasticizer treatment made fresh concretes cohesive and unusually sticky. This made consolidation by rodding somewhat difficult. However all these concretes had a reasonably good workability for a period of about 20 minutes, and showed no additional difficulty in placing and finishing compared to the others.

7.4.2 Effects on Compressive Strength of LMC

The effect of the silica fume addition on the compressive strength of heavily superplasticized LMC was not as significant as it usually is on that of ordinary portland cement concrete. In fact, incorporation of 10% silica fume with either normal or heavy dosage of superplasticizer provided essentially no further compressive strength improvement over superplasticizer used alone.

7.4.3 Effects on Flexural Strength of LMC

Incorporation of 10% silica fume with superplasticizer surprisingly

reduced the flexural strengths somewhat as compared to superplasticized concretes without silica fume. This was true at all ages tested.

7.4.4 Effects on Dynamic Modulus of Elasticity of LMC

Even though incorporation of 10% silica fume into superplasticized LMC had little effect on compressive strength as compared to superplasticized concretes without silica fume, using the silica fume unexpectedly reduced the dynamic modulus of elasticity values at all ages. The decrease in the E_d values obtained was substantial. This decrease in E_d value may be caused by the relatively poor consolidation accomplished with these sticky concrete mixes.

7.4.5 Durability-Related Effects of Silica Fume Addition

Chloride Permeability Incorporation of silica fume into the superplasticized LMC concrete had a major effect on the chloride permeability. The permeability values, already "very low", were reduced to "negligible" values (less than 100 coulombs) as early as 3 months. The actual values were about 80 at 3 months and 60 to 70 at 6 months, as low as any ever recorded, to the knowledge of the writer.

Pore Structure Rather surprisingly in view of the above, the effect of incorporating silica fume into separately-batched superplasticized LMC paste was to substantially increase the total intrudable pore volume, from 0.05 to 0.15 cm³/g. Again the shape of the pore size distribution curve was similar to those of the other LMC pastes, but the volume intruded was not only higher than that of superplasticized LMC paste, but even

substantially higher than that of normal LMC paste. The source of this added porosity is not understood.

7.4.6 Summary of Effects of Silica Fume Addition to Superplasticized Concrete

Addition of 10% silica fume to superplasticized concrete resulted in the present case in a sticky mix that was difficult to consolidate by rodding, but that otherwise had reasonable workability characteristics. Surprisingly, compressive strength was not improved, and the flexural strength and elastic modulus slightly reduced, perhaps due to imperfect consolidation. The pore volume of the separately-batched paste was dramatically higher than those of other LMC pastes. Despite this, the chloride permeability of the concrete was quickly reduced to "negligible" values, a considerable improvement over even that of superplasticized LMC concrete.

7.5 Effects of Radical Modification of Latex System Involving Reduction of Latex Content

7.5.1 Effects on Workability of LMC

Halving the latex content while using a heavy dosage of superplasticizer produced a fresh concrete with workability similar to reference LMC.

Incorporating 10% silica fume in such a half-latex content superplasticized LMC produced fresh concrete of similar workability to silica fume containing LMC with the full latex content, i.e. a sticky mix exhibiting some difficulty in consolidation.

7.5.2 Effects on Compressive Strength of LMC

As shown in Figure 5.2-15, reducing the latex content by half in a heavy superplasticized mix provided very high compressive strengths at all ages. This was so even though the reduced latex content concrete had a higher w:c ratio than the normal latex content superplasticized concrete.

Adding 10% silica fume to such reduced latex content mixes increased compressive strength still further, and values in excess of 10,000 psi were recorded at 28 days. It thus appears that compressive strength benefits expected for silica fume require a mix with substantially less latex than normally used.

7.5.3 Effects on Flexural Strength

In contrast to its beneficial effect on compressive strength, reducing the latex content by half in a heavily superplasticized mix substantially decreased flexural strength. Indeed, the flexural strength developed was slightly lower at all ages than that of normal LMC.

Incorporating silica fume while reducing latex content provided essentially no further change in flexural strength. Thus it appears that reducing the latex content, while ?? beneficial in terms of compressive strength, is somewhat deleterious with respect to flexural strength.

7.5.4 Effects on Dynamic Modulus of Elasticity

Reducing the latex content by half in a heavily superplasticized system produced a small reduction (about 3%) in E_d values at all ages as

compared to those of corresponding concrete with full latex content. This reduction in E_d may be associated with the much higher porosity (Figure 6.1-6) shown for reduced latex content paste. Apparently the expected increase in E_d due to reduced latex content was not large enough to compensate for the reduction in E_d caused by higher paste porosity. The E_d values were about the same as those of reference LMC at 7 days and beyond.

Adding silica fume to such reduced latex content concrete increased the dynamic elastic modulus at all ages, the E_d values approaching those of normal LMC at 7 days and beyond.

7.5.5 Effects on Durability-Related Properties

Chloride Permeability Reducing the latex content by half in a heavily superplasticized concrete had surprisingly little effect on the chloride permeability. there was a slight increase at 3 months and a slight reduction at 6 months.

In contrast, adding 10% silica fume to such a mix had a very favorable effect on chloride permeability, reducing it to "negligible" value in as little as 3 months.

Pore Structure Reducing the latex content by half in a heavily superplasticized separately-batched LMC paste had a profound effect on the mercury pore size distribution results, more than doubling the intruded volume. The response also involved a significant coarsening of the size distribution, significant pore volume in sizes coarser than $0.2 \mu\text{m}$ ($2000 \text{ \AA}$) being present, for the first time in any LMC paste examined.

Adding 10% silica fume significantly reduced the volume of these coarser pores, especially at later ages, but did not reduce the total intruded porosity significantly.

7.5.6 Summary of Effects of Reducing Latex Content in Heavily Superplasticized LMC

Radically modifying the normal LMC formulation by heavily superplasticizing the mix and at the same time reducing the latex content by half produces a number of changes, as compared to simply superplasticizing the mix. The behavior of the fresh concrete is similar in terms of workability to normal LMC, but the compressive strength is significantly higher. However, the flexural strength is somewhat less than that obtained with a superplasticized concrete at normal latex content, and surprisingly, the modulus of elasticity is a bit lower. The chloride permeability is favorably affected, even though the paste porosity is increased and the size distribution somewhat coarsened. The sum of these effects is rather less pronounced than might have been expected.

Further modifying the system by adding 10% silica fume to the heavily superplasticized, reduced latex content mix modifies these effects somewhat. The mix becomes sticky and somewhat difficult to consolidate, but it retains reasonable workability. The compressive strength, already very high, is improved substantially, and the 28-day strength exceeds 10,000 psi. There is no effect on the flexural strength, and an increase in modulus of elasticity. The chloride permeability is quickly reduced to negligible values, and the pore size distribution is shifted to finer sizes, but the total intruded pore volume is not changed appreciably.

7.6 General Discussion of Microstructure of LMC and Modifiers

The SEM examination on the selected pastes suggested that all LMC pastes examined had a less porous microtexture than seen for the reference OPC paste.

The results of SEM observation on the HCl-leached LMC pastes showed that latex admixture formed a continuous sponge-like network in the cement pastes. It is this network that embraces unhydrated cement particles and cement hydration products to form a co-matrix surrounding sand and coarse aggregate grains in the concrete. This co-matrix imparts the superior physical and chemical properties to LMC. The incorporation of fly ash made the latex film system apparently denser and less porous. It was observed that fly ash particles were firmly embedded in the latex network, even after HCl treatment. There was no evidence for any kind of reaction on the fly ash particles or in the sockets observed with SEM.

8. FINDINGS AND CONCLUSIONS

The first section of this chapter contains the specific findings of this investigation. Based on these findings, a set of conclusions is presented in the second section of this chapter.

8.1 Findings

Based on the information previously presented, the individual findings of this investigation are given as follows:

1. All the latex-modified concretes used in this study showed a reasonably good workability over a period of 20 to 25 minutes during the laboratory concrete preparation, even when the w:c ratio required for the designated slump was very low (0.20 to 0.29).
2. The compressive strengths of all latex-modified concretes were significantly higher than that of the reference plain concrete at all ages. The higher compressive strengths of latex-modified concretes may be mainly due to the lower w:c or w:cm ratio needed with the various latex-modified concretes.
3. All of the latex-modified concretes used in this study showed substantially higher flexural strengths than the reference plain concrete, especially after 7 days of curing. It is believed that the flexural strength improvement is provided

by the continuous latex film network formed in latex-modified concretes.

4. The dynamic modulus of elasticity for latex-modified concretes of all types was initially slightly higher than that of the reference portland cement concrete, but after 7 days it was generally lower. Lower values are expected, since the polymer is less stiff than cement paste.
5. Chloride permeability measured at up to 1 year was very much lower for all latex-modified concretes than for the reference portland cement concrete.
6. In general, at early ages the total pore volume of pastes intruded by mercury porosimetry was substantially less for all latex modified pastes than for the reference portland cement paste. At later ages this continued to be true for most latex modified cement pastes studied, but not for all.
7. Freeze thaw durability tests carried out according to ASTM C 666 Procedure A indicated that properly air entrained latex-modified concrete was resistant to freezing damage.
8. Latex modified cement paste has a significantly higher contact angle to mercury than does ordinary portland cement paste, obviously due to the influence of the latex films.
9. The incorporation of fly ash (four types at two replacement levels) into latex-modified concrete reduced the water content required to produce a 4-6 inch slump. There was no additional difficulty in placing or finishing.

10. Fly ash did not significantly reduce the compressive strength of latex-modified concrete, and in a few cases it increased it slightly.
11. Flexural strength was not significantly affected by incorporating fly ash into latex-modified concrete.
12. Incorporating fly ash into latex-modified concrete reduced the early dynamic modulus of elasticity, but the difference disappeared after 3 days.
13. The incorporation of fly ash into latex-modified concrete reduced the chloride permeability substantially. The different fly ash types and replacement levels gave almost the same results.
14. Properly air entrained latex-modified concretes containing fly ash also exhibited very good durability according to ASTM C 666. The indicated durability factors at 302 cycles were all over 90 percent.
15. Incorporation of fly ash somewhat reduced the total pore volume intruded by mercury porosimetry in latex modified cement pastes at all ages.
16. Incorporation of fly ash into latex modified cement paste resulted in some changes in measured contact angle to mercury, but these changes were not considered significant with respect to interpretation of mercury porosimetry results.
17. Indirect flexural bond strengths were slightly increased by incorporating fly ash into latex-modified concretes.

18. All of the fly ashes used and both replacement levels (15% and 25%) produced generally similar effects on the properties of latex-modified concretes examined.
19. Incorporating superplasticizer into latex-modified concrete substantially reduced the w:c ratio required to obtain the designated 4-6 in. slump; doubling the normal dose level further reduced the water demand. There was little effect on the placing and finishing characteristics of the fresh concrete.
20. Incorporating superplasticizer at normal dosage significantly increased the compressive strength of the latex-modified concrete, especially at later ages. But using higher than normal dosage of superplasticizer provided no significant further compressive strength improvement.
21. Incorporating a normal dosage of superplasticizer provided a small but consistent flexural strength increase at all ages. Doubling the dosage of superplasticizer made the increase slightly larger.
22. Incorporating superplasticizer at normal dosage into latex-modified concrete produced a small but consistent increase in dynamic modulus of elasticity at all ages, but doubling the dosage of superplasticizer produced no further increase.
23. Incorporating superplasticizer improved the good impermeability to chloride ions already characteristic of latex-modified concrete.

24. Incorporating superplasticizer (at a heavy dosage rate) into latex modified cement paste provided a paste with a very low intruded pore volume by mercury porosimetry; in fact that values were the lowest for any cement paste examined.
25. Incorporating 10% silica fume along with the superplasticizer did not result in further water reduction, but it made the fresh concrete somewhat sticky.
26. Incorporation of 10% silica fume with either normal or heavy dosage of superplasticizer also provided essentially no further compressive strength improvement to the latex-modified concrete.
27. Incorporation of 10% silica fume, while using either normal or heavy dosage of superplasticizer, provided only a very small flexural strength improvement (less than 100 psi) to the reference latex-modified concrete at all ages.
28. Flexural strength of latex-modified concrete was not significantly affected by incorporating silica fume along with superplasticizer.
29. Incorporating 10% silica fume with superplasticizer reduced the dynamic modulus of elasticity at all ages.
30. Incorporating silica fume with the superplasticizer provided the best chloride permeability results for any system studied; the chloride permeability values were rated as "negligible" as early as 3 months.
31. Incorporating 10% silica fume along with superplasticizer resulted in an unexpected and very substantially increase in

- pore volume intruded in paste by mercury porosimetry.
32. Reducing the latex content by half while using a heavy dosage of superplasticizer produced fresh concrete with workability similar to that of reference latex-modified concrete.
 33. Reducing latex content by half while using a heavy dosage of superplasticizer provided an obvious compressive strength improvement at all ages as compared to corresponding concrete with full latex content.
 34. For superplasticized latex-modified concrete, reducing the latex content to half of normal produced a significant flexural strength reduction, but the strengths were still comparable to that of normal latex-modified concrete.
 35. Reducing the latex content by half produced a small reduction in dynamic modulus of elasticity at all ages.
 36. Surprisingly, reducing the latex content by half in a heavily superplasticized latex-modified concrete actually improved the chloride permeability, at least at later ages. The permeability values were significantly better than normal latex-modified concrete without superplasticizer at all ages.
 37. Reducing the latex content of superplasticized latex modified paste by half resulted in a significantly increase in the pore volume intruded by mercury porosimetry.
 38. Incorporating silica fume while at the same time reducing the latex content of superplasticized latex modified concrete produced fresh concrete similar to the corresponding concrete with full latex content; the concrete was equally sticky.

39. Reducing the latex content of superplasticized latex-modified concrete by half provided a significant compressive strength improvement. Such concretes reached a compressive strength of 10,000 psi by 28 days and was the strongest of any formulations examined.
40. For superplasticized latex-modified concrete containing silica fume, reducing the latex content by half also reduced the flexural strength, but again the resulting values were comparable to those of normal latex-modified concrete.
41. For superplasticized latex-modified concrete with silica fume, reducing the latex content by half increased the dynamic modulus of elasticity at all ages.
42. For superplasticized latex-modified concrete with silica fume, reducing the latex content by half did not change its excellent chloride permeability characteristics.
43. For superplasticized latex modified cement paste with silica fume, reducing the latex content by half produced a large increase in the pore volume intruded by mercury porosimetry. The resulting paste had the largest intruded pore volume of all latex modified cement pastes examined, and in addition, the pore size distribution was significantly shifted toward the coarser size range.

8.2 Conclusions

The first objective of this research was to provide needed information on the possible effects of incorporating fly ash as a partial

replacement of portland cement in conventional latex-modified concrete as used for bridge deck overlays.

the conclusions reached with respect to fly ash incorporation are as follows.

1. Incorporating fly ash into latex-modified concrete somewhat reduces the water requirement for a given slump without significantly changing the placing and finishing characteristics of such concrete.
2. Compressive strength are not significantly reduced, and in some cases are increased slightly, even when using as much as 25% fly ash replacement; flexural strength are reduced slightly at early ages, but subsequently the effect disappears.
3. Chloride permeability values are much reduced, even considering the already low chloride permeability of normal latex-modified concrete; the total pore volumes intruded in mercury porosimetry of pastes are also reduced somewhat.
4. Freezing resistance of properly air entrained latex-modified concrete is not affected.
5. Tests carried out by a non-standard procedure (the "break off" tester) indicate that bond strength is slightly improved.

The conclusions above were reached from studies involved four different fly ashes of varying quality, and of both Class F and Class C classification, at replacement levels of up to 25%. The differences in effects observed among the different fly ashes and replacement levels were comparatively small.

It is necessary to point out that these conclusions above were reached on the basis of test results on concretes mixed by standard laboratory pan mixing procedures, which produce more thorough mixing than the concrete mobile auger mixers conventionally used in placing latex-modified concrete bridge deck overlays.

A method of directly imaging the latex network in latex-modified concrete was developed and the following conclusions were drawn from SEM observations:

6. The latex films interpenetrates the inorganic part of the cement paste system to form a continuous, 3-dimensional porous network.
7. The presence of fly ash appears to modify the network by increasing its density and by directly bonding it to individual fly ash particles.

Studies on the effects of modifying the normal latex-modified concrete formulation by incorporating superplasticizer or superplasticizer plus silica fume led to the following conclusions:

8. Superplasticizer incorporation without otherwise changing the formulation:
 - (a) significantly reduces the water requirement;
 - (b) significantly improves compressive strength at later ages;
 - (c) slightly increases flexural strength;
 - (d) significantly reduces the already low chloride permeability;

- (e) very significantly reduces the pore volume of pastes intruded by mercury porosimetry.
9. Incorporating silica fume along with the superplasticizer:
- (a) makes the fresh concrete sticky, but does not otherwise change its behavior;
 - (b) does not affect compressive strength and only slightly increases flexural strength;
 - (c) reduces chloride permeability to very low values;
 - (d) unexpectedly increases the pore volume intruded in pastes by mercury porosimetry.
10. Reducing the latex content of superplasticized latex-modified concrete:
- (a) does not appreciably affect fresh concrete behavior;
 - (b) further improves compressive strength but reduces flexural strength to that of ordinary latex-modified concrete;
 - (c) actually reduces chloride permeability at later ages;
 - (d) significantly increases the pore volume of pastes intruded by mercury porosimetry.
11. Reducing the latex content of latex-modified concrete with superplasticizer and silica fume:
- (a) does not affect fresh concrete behavior, the fresh concrete remaining sticky;
 - (b) provides a great increase in compressive strength but reduces flexural strength slightly to normal latex-modified concrete levels;

- (c) does not affect chloride permeability which remains very low;
- (d) greatly increases the total pore volume of pastes intruded by mercury porosimetry.

Again it is necessary to point out that the conclusions above with respect to concrete were reached on the basis of test results on concretes mixed by standard laboratory pan mixing procedures, not by auger mixers conventionally used in placing bridge deck overlays.

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Appendix A -- Individual Strength Testing Results

This Appendix contains the individual strength testing results for all the concretes studied. The data with superscript asterisk (*) are treated as outlying points and rejected when calculating the average, based on the criterion described in Section 4.4.3.

Table A1 Individual Compressive Strength Testing Results

Mixes	Repli- cates	Compressive Strength (psi) at:						
		1 day	3 days	7 days	28 days	90 days	180 days	360 days
OPC	1	2264	3890	4810	6366	6437	6932	7286
	2	2051	3749	4881	5942	7286*	4010*	7144
	3	2264	3820	4739	6437	4810	6861	7993
	4	2122	3608	5022	5800	5164	4456*	7852
	5	2193	3466	4386	6366	5093	5730	5871
LMC1	1	2688*	4456	6578	7639	7639	8347	8630
	2	2476*	5164	6366	8064	7427	8913	8276
	3	3466	4810	5588	6720	7993	6861	8064
	4	3395	5447	6366	7710	8064	7993	7781
	5	3254	5305	6154	6791	8135	7356	8276
R15F00	1	2829	4103*	6437	7639	7356	7639	8842
	2	2900	5517*	6366	8135	7781	7569	8418
	3	2759	4951	6437	8064	8913	8135	8488
	4	2829	4810	6225	7710	8276	7852	8842
	5	2476	5093	6578	7781	8488	7215	8488
R25F00	1	3466*	5659	6649	7569	8347	7922	8630
	2	3395	4810	6225	8205	7710	7852	8771
	3	2759	5164	-	8135	8559	7003	7993
	4	2829	5093	-	7639	7922	7781	8559
	5	2412*	4881	-	6508	8347	6437	8347
A15F00	1	2829	5164	6154	7356	7356	6649*	8418
	2	2688	5588	5942	7922	8276	7498	8700
	3	2334*	5376	6508	7498	7781	7569	8630
	4	2334*	5234	6154	7569	7710	7569	8418
	5	2914	5093	5659	7639	7852	7639	8559

Table A1, continued.

A25F00	1	2334	5447*	5871	7003	7356	7781	8205
	2	2476	4739	5942	7074	7569	7781	8842
	3	2575	4386	5093*	6720	7074	7144	7922
	4	2462	5234	6083	7498	7639	7144	8135
	5	1344*	3890*	6295	7427	7922	7639	8276
G15F00	1	2334*	4951	6083	7286	7639	7215	9054
	2	2971	5517	6437	7710	8418	8064*	8064
	3	2617	5093	6083	7710	8418	6578	9196
	4	2759	5164	6083	7215	8559	7144	8630
	5	2829	5093	5871	7498	7569	5730*	8630
G25F00	1	2617	5022	6437	7427	7852	6932	8913
	2	2688	4881	5305	7498	8488	7710	9337
	3	2917	5022	6508	6791	8205	8205	8630
	4	2617	5411	5871	7144	7639	7356	8913
	5	2193	4103	5517	7003	7852	6649	6366*
T15F00	1	2476*	4739	5659	6225	7852	6861	8488
	2	2405*	4739	5730	7144	7639	6791	8913
	3	2334	3961	5659	7144	7215	6932	7569
	4	2122	4173	5517	6649	7286	7710	7498
	5	1839	4456	4669*	6861	7356	7710	8347
T25F00	1	2900	3961	6013	6295	7922	7215	8064
	2	3042*	4456	6508	6932	7639	7781	8556
	3	2546	4598	6225	6366	7852	7215	8205
	4	2688	4456	5871	7144	7215	7074	8276
	5	2193*	4244	5942	6437	6791	7144	7993
LMC2	1	2740	-	4809	6791	-	6677	-
	2	2948	-	5185	6827	-	8161	-
	3	2821	-	5342	6955	-	8362	-
	4	3216	-	5284	7045	-	8437	-
	5	3046	-	3673*	7028	-	7453	-
N00F15	1	3252	-	5921	6677	-	8887	-
	2	3306	-	5891	7591	-	9102	-
	3	3176	-	5936	7628	-	9191	-
	4	3368	-	6270	7859	-	8903	-
	5	3649	-	6185	6527	-	9131	-
N00F30	1	2924	-	6334	7939	-	9613	-
	2	3670	-	6322	7963	-	9493	-
	3	3711	-	6194	7935	-	8903	-
	4	3518	-	6236	7969	-	9643	-
	5	3373	-	5158	7884	-	9739	-

Table A1, continued.

N00H30	1	5134	-	7852	9580	-	8512	-
	2	4994	-	7444	9737	-	8739	-
	3	5141	-	7122	9411	-	10823	-
	4	4207	-	6174	8584	-	9551	-
	5	3383*	-	6686	8736	-	10210	-
S10F23	1	3787	-	6431	8744	-	9822	-
	2	3791	-	6130	8584	-	8988	-
	3	3866	-	5638	8474	-	9395	-
	4	3248	-	5735	8399	-	9227	-
	5	3268	-	5236	7842	-	9330	-
S10F38	1	2927	-	4386*	6823	-	6915*	-
	2	3115	-	6106	5512*	-	6498*	-
	3	2571	-	6593	8309	-	9479	-
	4	3175	-	6652	8331	-	9237	-
	5	3176	-	6450	8713	-	9092	-
S10H38	1	4371	-	8204	9974	-	10912	-
	2	4039	-	8498	10105	-	11216	-
	3	3991	-	8210	10634	-	11028	-
	4	3165*	-	8200	10346	-	9150	-
	5	3704	-	8392	8852	-	8583	-

Table A2 Individual Flexural Strength Testing Results

Mixes	Repli- cates	Flexural Strength (psi) at:						
		1 day	3 days	7 days	28 days	90 days	180 days	360 days
OPC	1	511	767	840	996	978	982	1089
	2	540	684	911	938	1027	1093	996
	3	498	649	858	973	911	1138	1124
	4	529	738	829	947	1071	1142	1120
LMC1	1	773	1042	1091	1560	1756	1933	1853
	2	680	782*	880*	1364	1716	1671	1724
	3	711	1042	1029	1387	1680	1778	1680
	4	658	1022	1151	1560	1689	1627	1707
R15F00	1	680	996	1056	1367	1929	2018	1707
	2	576	978	869	1464	1747	1942	1676
	3	573	956	1002	1378	1960	1804	1778
	4	651	907	964	1393	1644	1676	1849

Table A2, continued.

R25F00	1	713	1020	1311	1556	1479*	1693	1920
	2	716	1020	1138	1333	1844	1729	1938
	3	800	864	1100	1511	1871	1969	1782
	4	702	895	1158	1356	1867	1804	1627
A15F00	1	552	849	882	1424	1413	1809	1644
	2	569	889	1084	1549	1578	1689	1911
	3	602	813	938	1313	1400	1520	1693
	4	602	902	958	1242	1467	1818	1724
A25F00	1	556	840	982	1253	1640	1938	1756
	2	542	925	953	1524	1684	1831	-
	3	520	827	893	1384	1372*	1698	1951
	4	556	831	964	1320	1724	1893	1907
G15F00	1	516	976	1253*	1133*	1369	2022	1827
	2	604	864	1009	1244	1769	1773	1884
	3	536	953	844*	1549*	1622	1822	1439*
	4	576	809	1022	1400	1516	1836	1871
G25F00	1	542	871	1031	1613*	1636	1742	2018
	2	587	818	880	1127*	1889	1667	1693
	3	569	807	973	1220	1391*	1658	1738
	4	567	851	920	1302	1613	1756	1742
T15F00	1	547*	789	913	1300	1449	1804	1600
	2	473	871	887	1462	1538	1898	1560
	3	473	924	898	1564	1658	1747	1791
	4	418	800	918	1258	1458	1636	1813
T25F00	1	680	787	902	1153	1684	1520	1858
	2	596	709	942	1044*	1522	1796	2000
	3	569	789	960	1304	1444	1640	-
	4	631	747	831	1373	1556	1698	1689
LMC2	1	697	-	1052	1235	-	1591	-
	2	716	-	1015	1055	-	1346	-
	3	769	-	1144	1171	-	1557	-
	4	781	-	1012	1178	-	1406	-
N00F15	1	682	-	1064	1380	-	1723	-
	2	750	-	1048	1191	-	1675	-
	3	778	-	1045	1273	-	1895	-
	4	803	-	1195	1356	-	1758	-
N00F30	1	793	-	1113	960*	-	1845	-
	2	802	-	1369	1192	-	1876	-
	3	799	-	1037	1329	-	2111	-
	4	740	-	1277	1148	-	2100	-

Table A2, continued.

N00H30	1	760	-	1104	1170	-	1306	-
	2	745	-	850*	1202	-	1230	-
	3	617	-	1074	991	-	1315	-
	4	685	-	1021	861*	-	1342	-
S10F23	1	765	-	973	1149	-	1421	-
	2	697	-	944	1253	-	1681	-
	3	626	-	995	1192	-	1533	-
	4	579	-	724*	967*	-	1188*	-
S10F38	1	524	-	957	1247	-	1648	-
	2	608	-	953	1363	-	1424	-
	3	601	-	1078	1232	-	1547	-
	4	662	-	946	1270	-	1568	-
S10H38	1	761	-	911	1102	-	1341	-
	2	720	-	988	1234	-	1208	-
	3	666	-	930	1144	-	1416	-
	4	609	-	981	1239	-	1349	-

Appendix B -- Individual Dynamic Modulus of Elasticity Testing Results

This Appendix contains individual dynamic modulus of elasticity measurement results for all the concretes studied. In the following table, the double asterisk (**) indicates no individual measurement result available since the individual density at this specific age is not available.

Table B1 Individual Dynamic Modulus of Elasticity Measurement Results

Mixes	Repli- cates	Dynamic Modulus of Elasticity (ksi) at:						
		1 day	3 days	7 days	28 days	90 days	180 days	360 days
OPC	1	5662	6279	6883	7770	8259	6697	8677
	2	5550	6628	6968	7571	7937	6936	8547
	3	5550	6136	6946	7457	8108	6934	8452
	4	5676	6150	6858	7644	7833	6902	8554
LMC1	1	6349	6886	7094	7391	7842	7807	7643
	2	5861	6877	6763	7129	7760	6852	7179
	3	5869	6713	6748	6935	7462	6841	7033
	4	6110	6242	6587	6952	7162	7049	7323
R15F00	1	5896	6715	6804	7271	7283	7371	7722
	2	5463	6505	6809	7380	7609	6087	7596
	3	5684	6567	6628	7251	7407	5202	7504
	4	5666	6617	6780	7330	7471	6796	7520
R25F00	1	6142	6786	7344	7490	7577	8627	7874
	2	5949	6750	6919	7407	7721	7592	7520
	3	5593	6603	6793	7254	7608	8021	7090
	4	5779	6530	6939	7291	7358	6386	7332
A15F00	1	6010	6675	6755	7470	7348	6442	7432
	2	5449	6693	6724	7196	7439	7675	6986
	3	5523	6541	6747	7395	7339	6752	7481
	4	5574	6611	6813	7298	7319	6473	7428
A25F00	1	5793	6518	6875	7179	7342	6773	7522
	2	5325	6746	6600	7069	7427	6126	7245
	3	5485	6462	6591	7312	7337	5772	7468
	4	5458	6452	6664	7268	7374	7126	7279

Table B1, continued.

G15F00	1	5821	6847	7158	7432	7668	**	7788
	2	5356	6775	6723	7383	7439	**	7592
	3	5219	6738	6865	7113	7549	**	7259
	4	5230	6312	6487	6873	7150	**	7211
G25F00	1	5843	6805	6942	7404	7752	7522	7755
	2	5819	6849	6844	7353	7643	7001	7419
	3	5320	6622	6785	7243	7522	6250	7310
	4	5421	6540	6800	7060	7485	6202	7309
T15F00	1	5458	6583	7168	7188	7420	**	7503
	2	4949	6514	6611	6850	7579	**	7281
	3	4795	6371	6547	6868	6979	**	7290
	4	4684	6273	6788	7002	6987	**	7296
T25F00	1	5920	6344	6922	7385	6745	8445	7470
	2	5616	6488	7077	7234	6671	8258	7295
	3	5588	6363	7096	7132	6665	6714	7404
	4	5705	6157	6747	7117	6645	5914	7195
LMC2	1	5719	-	6727	7299	-	7362	-
	2	5740	-	6859	7185	-	7264	-
	3	5979	-	6823	7197	-	7246	-
	4	5916	-	6858	7222	-	7359	-
N00F15	1	6140	-	7010	7372	-	7641	-
	2	6287	-	7050	7295	-	7553	-
	3	6295	-	7180	7346	-	7359	-
	4	6282	-	7136	7348	-	7503	-
N00F30	1	6214	-	7191	7275	-	7274	-
	2	6234	-	6994	7343	-	7502	-
	3	6231	-	7096	7380	-	7602	-
	4	6264	-	7331	7570	-	7520	-
N00H30	1	6394	-	7397	7316	-	7561	-
	2	6472	-	6974	7268	-	7303	-
	3	5503	-	6736	7070	-	6964	-
	4	5966	-	6456	6984	-	7027	-
S10F23	1	5999	-	6551	6599	-	7166	-
	2	5956	-	6751	7064	-	6997	-
	3	5467	-	6391	6853	-	6651	-
	4	5316	-	5829	6492	-	6436	-
S10F38	1	5476	-	6351	6843	-	7074	-
	2	5431	-	6507	6644	-	7032	-
	3	5496	-	6633	6973	-	6909	-
	4	5525	-	6555	6630	-	6905	-

Table B1, continued.

S10H38	1	5434	-	6933	7275	-	7327	-
	2	5494	-	7040	7206	-	7061	-
	3	5494	-	6957	6912	-	7245	-
	4	5463	-	6841	7142	-	7253	-

Appendix C -- Individual Chloride Permeability Measurement Results

This Appendix contains individual measurement results of chloride permeability test for all the concretes studied.

Table C1 Individual Chloride Permeability Measurement Results

Total Charge Passed (coulombs) at:				
Mixes	Replicates	3 months	6 months	12 months
OPC	1	2947	1941	1824
	2	3137	1983	1525
	3	2626	1758	1617
LMC1	1	557	182	132
	2	576	198	121
R15F00	1	458	144	109
	2	392	148	88
R25F00	1	338	98	101
	2	353	114	78
A15F00	1	439	123	132
	2	514	133	70
A25F00	1	399	111	60
	2	349	95	51
G15F00	1	375	116	180
	2	356	-	132
G25F00	1	380	88	92
	2	280	92	66
T15F00	1	608	136	99
	2	421	154	79
T25F00	1	457	101	77
	2	370	119	63
LMC2	1	652	-	335
	2	482	-	271

Table C1, continued.

N00F15	1	349	-	169
	2	373	-	206
N00F30	1	269	-	163
	2	241	-	165
N00H30	1	-	-	150
	2	296	-	137
S10F23	1	80	-	72
	2	-	-	64
S10F38	1	77	-	62
	2	59	-	56
S10H38	1	63	-	57
	2	71	-	77

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