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Use of polymers in highway concrete, September 1975

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USE OF POLYMERS IN HIGHWAY CONCRETE

Prepared for

National Cooperative Highway Research Program
Transportation Research Board
National Research Council

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Bethlehem, Pennsylvania

September 1975

National Cooperative Highway Research Program

Project 18-2

USE OF POLYMERS IN HIGHWAY CONCRETE

Final Report Draft

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

ABSTRACT

The deterioration of concrete bridge decks due to corrosion of reinforcing steel by deicing salts is universally recognized as a major maintenance item facing highway agencies today. The development of polymer-impregnated concrete and the demonstration of its remarkable mechanical and physical properties and, in particular, its durability presented a potential solution to the bridge deck deterioration problem. To develop this potential solution, this research project was investigated with the following goals: (1) to select an appropriate monomer system, (2) to develop suitable field techniques and apparatus for impregnation of concrete bridge decks, (3) to evaluate the effectiveness of the techniques, (4) to demonstrate the techniques in the field, and (5) to prepare a procedural manual for routine polymer impregnation of concrete bridge decks.

Using gas-fired infrared heaters for drying the concrete and moderate pressure impregnation followed by hot-water polymerization, it was demonstrated that deep (up to 4 in. [10 cm]) polymer impregnation could be achieved under field conditions. Demonstration projects were carried out on two bridge decks, both structurally sound and one severely salt contaminated. The equipment and techniques developed for and used in these demonstrations are suitable for scale-up for commercial applications.

A field manual describing the techniques and including safety precautions and acceptance criteria was developed and is included in the final report on the project.

The properties of typical bridge deck concrete impregnated with poly (methyl methacrylate), using the techniques and equipment developed in this research, were found to agree with the remarkable qualities attributed to polymer-impregnated concrete in general.

SUMMARY OF FINDINGS

GENERAL

The major research finding described in this report is that the field impregnation of structurally sound, salt-contaminated concrete bridge decks with polymer to a depth of 4 in. (10 cm) is technically feasible. Following preliminary small-scale field trials in two different locations using two drying methods and two impregnation methods, the most promising combination was selected and demonstrated in three larger-scale trials. The techniques and principles used are applicable to commercial-scale application, and although the equipment used was smaller than that proposed for commercial-scale applications, it can be scaled-up readily. The specific findings for the various research areas are detailed below.

MONOMER SELECTION

All field trials used a 90:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture containing 0.5 percent azobisiobutyronitrile initiator. Despite the flammability and vapor pressure of this monomer mixture, it was handled safely without hazard in the field trials. It is likely that any other monomer system produced by future research can also be handled safely, provided its physical, chemical, fire hazard, and health hazard properties are known.

DRYING METHODS AND CRITERIA

Concrete can be impregnated with monomer to any desired depth provided it is dried to that depth. The time required for drying depends on the heating rate and surface temperature attained.

In order to achieve impregnation to the specified depth, the concrete must be heated until the temperature at the specified depth is 230°F (110°C), assuming the deck can withstand the associated thermal stresses. The application of heat to the surface of the concrete must not permit surface temperatures to exceed 500°F (260°C) during the first hour and, at any time, 675°F (357°C). Gas-fired infrared heaters were found to be the most efficient means of drying the concrete, although torches may also be used.

IMPREGNATION METHODS AND CRITERIA

Field impregnations of dried concrete substrates have been carried out at atmospheric and greater-than-atmospheric (30 psig [207 kPa]) pressure. Since the time required for impregnation varies directly with the square of the desired depth of impregnation and inversely with the square of the applied pressure, pressure impregnations are preferred for field use. A pressure-impregnation chamber covering a 3x12 ft (0.91x3.66 m) area was developed and used for the field impregnations.

POLYMERIZATION

The 90:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture containing 0.5 percent azobisiobutyronitrile was polymerized in situ to high conversions (as indicated by lack of monomer odor) at 158-185°F (70-85°C). The heating was accomplished by pumping hot water through the pressure impregnation chamber.

EFFECT OF ROADWAY SURFACE CONTAMINANTS

Salt contamination in the concrete substrate was found to decrease the drying rate, impregnation rate, and overall monomer

loading, but not to such an extent that the feasibility of the method was affected. Polymer impregnation immobilizes the salt in the concrete matrix and thus lessens its corrosive effects. Organic surface contaminants are removed by high temperature drying procedures. Polymerization is retarded by surface contaminants at polymerization temperatures of 131°F (55°)C or below, but not at polymerization temperatures above 158°F (70°C).

MECHANICAL PROPERTIES AND DURABILITY

Polymer impregnation of typical bridge deck concrete from the traffic surface using the foregoing monomer mixture gave a three-fold increase in compressive strength and a two-fold increase in split-tensile strength; impregnation of similar concretes and mortars gave a six-fold decrease in the rate of salt penetration, and a seven-fold decrease in water absorption and loss by abrasion. Moreover, impregnation of structurally sound, salt-contaminated concrete with the same monomer mixture arrested the corrosion of the reinforcing steel, virtually eliminated freeze-thaw damage, and dramatically increased resistance to chemical attack (etching with hydrochloric acid). The mechanical properties of polymer-impregnated concrete can be varied systematically by the choice of the monomer, e.g., from a ductile material of strength only slightly greater than that of the control (butyl acrylate) to a very strong, hard, brittle material (methyl methacrylate). Copolymerization of methyl methacrylate-butyl acrylate gives an optimum combination of properties. Finally, preliminary tests of skid resistance after 13 months of service indicated no significant effect of impregnation (see p. E-43).

ECONOMICS OF POLYMER-IMPREGNATION OF BRIDGE DECKS

Polymer-impregnated concrete offers an economical solution to the deterioration of concrete highways and bridge decks because of its longer service life and reduced maintenance costs.

PART I

CHAPTER ONE

INTRODUCTION AND RESEARCH APPROACH

INTRODUCTION

Corrosion of the reinforcing steel and the resulting deterioration of the concrete bridge decks is universally recognized as a critical maintenance problem facing highway agencies today. Highway departments in the United States now spend $70 million each year on bridge deck repairs, and this amount is expected to "skyrocket" in the future (1). Moreover, the traffic obstruction from reconstruction and repair of deteriorated bridge decks causes inconvenience and expense to highway users. The deterioration is the result of a complex interaction between freezing and thawing, differential expansion and contraction, corrosion of reinforcing steel, chemical attack, high traffic loads, and wear. But the deterioration of bridge decks is not the only problem confronting highway agencies; the concrete itself has deficiencies such as high permeability to water and salt solutions, low strength, high wear rate, and a pronounced tendency to crack and spall. There is a need for concrete with better mechanical properties and corrosion resistance.

Impregnation of concrete with polymers gives promise of improving the mechanical properties and corrosion resistance of the highways and bridge decks already in service. This concept was first demonstrated in the laboratory by the Brookhaven National Laboratory in conjunction with the U.S. Bureau of Reclamation and the Federal Highway Administration (2-7), and later was developed and extended by the University of Texas (8), the present authors (9-12), and others.

1

The original laboratory technique comprised impregnation of previously cured concrete by evacuation to remove air and moisture, infusion with monomer, and polymerization with γ rays from Co60 or free-radical initiators. Extension of this technique to field use by substituting surface drying methods for the evacuation gave only shallow penetrations of monomer (1 in. [2.5 cm] or less). The purpose of the work reported here was to develop the concept of polymer-impregnated concrete for application in the field, where the desired depth of impregnation (4 in. [10 cm]) is sufficient to envelop the top layer of reinforcing steel.

OBJECTIVES

The overall objective of this research was to develop material systems and application techniques for the practical application of polymer-impregnated concrete to highway bridge decks. Specific technical objectives included:

1. Selection of the monomer system, e.g., a 90:10 methyl methacrylate trimethylolpropane trimethacrylate mixture containing 0.5 percent azobisisobutyronitrile initiator.

2. Development of field techniques and apparatus for surface impregnation of the concrete using the selected monomer system, with the apparatus of appropriate size for field use on bridge decks, but not necessarily as large as would be used in commercial-scale impregnations.

3. Evaluation of the effectiveness of the impregnation techniques in terms of (a) properties and condition of the concrete substrate; (b) preparation of the concrete substrate for impregnation; and (c) properties of the polymer-impregnated

2

concrete (especially durability, skid resistance, abrasion
resistance, strength, permeability, etc.).

4. Field demonstration of the impregnation techniques on one
   or more bridge decks, followed by evaluation tests (see 3c
   above), with the goal of 4-in. (10 cm) impregnation of a
   structurally sound, salt-contaminated bridge deck.

RESEARCH APPROACH

The research was carried out by an interdisciplinary team
comprised of faculty members of Lehigh University and The Pennsylvania
State University, with supplemental support from the Pennsylvania
Science and Engineering Foundation (PSEF) and the cooperation and
assistance of the Pennsylvania Department of Transportation (PennDOT).

The research approach was based on an interdisciplinary team
effort in which the backgrounds and expertise of the team members were
brought to bear on the various phases of the problem. These backgrounds
included surface chemistry, polymer chemistry, materials science, and
civil engineering, all of importance to the solution of the problem.
Despite the fact that the work was carried out at two locations 200 mi
(322 km) apart, duplication of effort was minimized and the efficient
use of the team members' expertise was maximized. Close liaison was
maintained, not only between the two collaborating groups, but also
with government laboratories and agencies, universities, and companies
working in the same field.

The above-mentioned research objectives were pursued in four
phases:

1. A comprehensive literature search on polymer-modified concrete was carried out to produce a state-of-the-art review, which has been updated and included in this report as an annotated bibliography (Appendix A).

2. Laboratory investigations were carried out on the selection of the monomer system, drying of the concrete, impregnation of the dried concrete, polymerization of the monomer in situ, and determination of mechanical properties of the composite, particularly with relation to field application (Appendices B-G).

3. Field trials based on the laboratory investigations were carried out to demonstrate the feasibility of polymer impregnation of highway bridge decks (Appendix H).

4. A field manual for polymer impregnation of bridge decks was prepared, based on the successful field trials (Appendix I).

A detailed description of the Research Approach is given in Appendix J, "Project Statement and Amplified Research Plan".

4

CHAPTER TWO

RESEARCH FINDINGS

LITERATURE SEARCH

The search of the literature and consultation with other
investigators yielded much information on the preparation and evalua-
tion of polymer-impregnated concrete in the laboratory, but little if
any on the impregnation to a depth of 4 in. (10 cm) in the field.

The literature described the laboratory impregnation of
concrete with various monomers and the remarkable improvement in such
properties as tensile and compressive strengths, Young's modulus, and
resistance to sulfate and chloride ions, according to the composition
and concentration of the monomer. The only field work described was
that done by the Brookhaven National Laboratory on badly deteriorated
bridge decks, in which the penetration of monomer into the very porous
substrates presents few problems, and the University of Texas on new
bridge decks, in which the goal was a shallow penetration of only about
1 in. (2.5 cm).

Specifically, the literature contained little reference to:
(1) the one-sided drying of concrete slabs at temperatures high enough
to complete the drying within a reasonable time; (2) the rate of pene-
tration of fluid monomers and prepolymers into the concrete substrate;
(3) the laboratory or field impregnation of structurally sound concrete
to a depth greater than 1 in. (2.5 cm) without the use of vacuum for
moisture removal; and (4) the ability of the polymer to immobilize the
salt already in the concrete and thus retard the corrosion of the
reinforcing steel.

5

MONOMER SELECTION

The properties that determine the effectiveness of a monomer in polymer-impregnated concrete are its viscosity, surface tension, and ease of polymerization _in situ_ to a high molecular weight conversion. Earlier work used methyl methacrylate and, to a lesser extent, styrene, styrene-polyester, and styrene-acrylonitrile mixtures, either alone or in combination with crosslinking monomers.

The advantages of methyl methacrylate are its very low viscosity and its tendency to undergo rapid autoaccelerating polymerization in bulk. This autoaccelerating polymerization, which is enhanced by the presence of crosslinking monomers, gives high conversions in a short time, once the polymerization is initiated and an adequate heat flux is maintained by heating from one surface.

The disadvantages of methyl methacrylate are its flammability, low flash point, high vapor pressure, relatively high cost, slight toxicity and slightly irritating character.

In the present work, many laboratory experiments and all field trials used a 90:10 or 100:10 methyl methacrylate-trimethlolpropane trimethacrylate mixture containing 0.5 percent azobisisobutyronitrile initiator. This mixture penetrated into the concrete without complication and polymerized rapidly to high conversions at 167-185°F (70-85°C). When broken open, the polymer-impregnated concrete specimens showed no detectable monomer odor, as well as high tensile and compressive strengths, excellent freeze-thaw resistance, and greatly decreased permeability to water and salt solutions. Safe handling procedures

were developed to cope with all the hazards and disadvantages (except high cost).

The present work also showed that the properties of polymer-impregnated concrete can be altered systematically by varying the composition of the monomer mixture. For example, methyl methacrylate, which polymerizes to a hard, brittle polymer, especially when cross-linked, gives polymer-impregnated concrete of much greater strength and higher modulus than the unmodified concrete, but shows no ductility--it fractures without warning (unacceptable to engineers as a material of construction). In comparison, butyl acrylate, which polymerizes to a soft, rubbery, elastic-type polymer, gives polymer-impregnated concrete of strength and modulus only slightly greater than unmodified concrete, but shows great ductility before fracture. Copolymerization of methyl methacrylate (MMA)-butyl acrylate (BA) mixtures gives polymer-modified concrete that combines high strength with adequate ductility.

Although it has been demonstrated that the properties of polymer-impregnated concrete can be varied systematically, it has not been determined what properties are needed for durability and minimum cost in the highway application, which requires improvements in durability rather than strength. It is speculated that continual freezing and thawing would eventually damage the adhesive bond between the polymer and cement paste phases, leading to penetration by water and salt and eventual deterioration. This polymer-cement bond would be expected to be more durable if the polymer were rubbery and elastic rather than hard and brittle. However, there are no long-term freeze-thaw or durability date to resolve this point; preliminary studies with mortar

7

indicate that the hard polymer PMMA confers greater resistance to salt penetration than the soft polymer PBA.

The cost of the monomer cannot be disregarded; the material costs of bridge-deck impregnation are estimated to be greater than the labor costs for pressure impregnation, but less for ponding. There are several liquid vinyl monomers--styrene, vinyl acetate, vinyltoluene, acrylonitrile, vinylidene chloride--that are lower in cost than methyl methacrylate, and several acrylate esters of about the same cost. All of these can be polymerized in bulk at reasonable polymerization rates, especially in combination with cross-linking monomers.

DRYING STUDIES

General

Drying the concrete is one of the most important and difficult steps in the impregnation process. The monomer cannot penetrate into concrete pores that are filled with water. The concrete in highways and bridge decks must be considered as saturated with water. Earlier work (13) showed that, even after a long period of dry weather, the water content of concrete at a depth greater than 1 in. (2.5 cm) is 60-70 percent of the saturation value, and under ordinary conditions, it is 90-100 percent of the saturation value. This means that the drying must be exhaustive to achieve a 4-in. (10-cm) impregnation, but need be only cursory for an impregnation of 1 in. (2.5 cm) or less.

Various Drying Methods

Several drying methods were studied in the laboratory, and two of these were tested in the field to determine their effectiveness and economy. The methods studied in the laboratory included kerosene-fired and electrically-heated blowers, infrared and microwave radiation, direct flame heating, and electro-osmotic and electrical-resistance drying.

The electro-osmotic method, which does not increase the temperature of the concrete significantly, did not remove the water from the pores completely because the conductive current path was lost after only part of the water was removed. Electrical-resistance drying failed for the same reason. The hot-air drying methods did not dry the concrete to a depth sufficient for 4-in. (10-cm) impregnation because they failed to produce sufficiently high surface temperatures.

Only the propane gas-fired torch, gas-fired infrared, microwave radiation, and hot-air oven drying methods were effective in drying the concrete to the desired depth. Microwave radiation proved to be the fastest method; however, its large power requirement, the unavailability of units large enough for field applications, and its inherent safety hazards precluded its serious consideration for this program. Similarly, hot-air oven-drying, although a useful laboratory method, is not practical for field applications. Therefore, the gas-fired torch and gas-fired infrared methods offered the most promise of successful application in the field.

Drying Criteria

Gas-fired torch and gas-fired infrared drying methods were tested in the laboratory to establish the criteria for drying. These

9

studies used 72-in. x 72-in. x 6-in. (1.83-m x 1.83-m x 0.15-m) or 72-in. x 72-in. x 8-in. (1.83-m x 1.83-m x 0.20-m) reinforced concrete slabs with embedded thermocouples and moisture gauges to measure the temperature and humidity at various positions and depths. It was found that surface temperatures of 600°F (316°C) or higher were required to dry the concrete to a depth of 4-6 in. (10-15 cm) within a reasonable time (4-6 hr). These high surface temperatures produced temperature gradients that cracked some of the unrestrained laboratory slabs. However, severe cracking did not occur on bridge decks. This cracking was somewhat avoided in the laboratory by spreading a 1-in. (2.5 -cm) layer of sand on the concrete surface and keeping the rate of temperature increase below 100°F (38°C)/hr until the surface temperature reached 600°F (316°C). A temperature of 230°F (110°C) at 4-in. (10-cm) depth was taken as the criterion for complete drying. This temperature was reached after 4-6 hr at surface temperatures of 600°F (316°C) or greater, and was adopted as the drying criterion in the field trials.

Later work with slabs indicates that moisture is lost, not only during the heating cycle, but also after the heating is stopped and the concrete is cooling to ambient temperature. Thus, the moisture may be removed more efficiently by heating the concrete to a surface temperature of 600-700°F (316-371°C), allowing it to cool, and then reheating before the surface temperature drops below 100°F (38°C). This heating-and-cooling sequence would allow the drying of a larger area at the same time.

Field Drying

The drying tests in the field (PSU Test Track) gave results consistent with laboratory experience. The concrete bridge deck surfaces were veined with microcracks and macrocracks, which opened up when the surface was heated to high temperatures, but closed when the surface was cooled. The impregnation healed all but the largest of the macrocracks. One deep crack was observed in one field trial. In the large-scale trials (3x12-ft areas) using infrared heating, which did not use the sand layer, only shallow surface crazing was observed, with no evidence of delamination of the concrete from the reinforcing steel. The high temperature drying methods were effective in removing oil and grease contamination from the deck surface.

IMPREGNATION STUDIES

General

Several basic and applied studies were carried out to develop impregnation methods. The basic studies determined the variation of the rate of penetration with time and pressure, as well as the variation of the depth of impregnation with drying conditions. The applied studies comprised the development and testing of procedures and equipment to impregnate concrete slabs in the laboratory and, finally, bridge decks in the field.

Rate of Impregnation

The rate of penetration of monomer into dried concrete substrates followed in part the Rideal-Washburn equation (14), which predicts that the depth of penetration should vary directly with the

product $(\gamma t/\eta)^{\frac{1}{2}} \Delta P^{\frac{1}{2}}$, where γ and η are the surface tension and viscosity, respectively, of the monomer, t the time, and $\Delta \underline{P}$ the pressure differential. In this work, however, the rate varied with ΔP, not $\Delta P^{\frac{1}{2}}$ (11). Therefore, for a given depth of impregnation, doubling the pressure reduces the time four-fold, and, for a given pressure differential, doubling the desired depth of impregnation quadruples the time required. Thus, significant reductions in impregnation time can be achieved by (1) relatively small increases in ΔP, and (2) relatively small decreases in the desired depth of impregnation.

Drying Requirements for Impregnation

Concrete mortar specimens with various moisture concentrations were impregnated with the 90:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture containing 0.5 percent azobisiobutyronitrile initiator. Monomer loadings up to 90 percent of that achievable in completely dried specimens were obtained with moisture contents as high as 20 percent of the saturation value. Therefore, acceptable monomer loadings can be obtained without drying the concrete completely. This is believed due to the fact that some of the water removed is "interlayer" water in the calcium-aluminum silicates forming the cement paste. Because of the larger molecular sizes and nonpolar nature of the monomer molecules, the monomer does not enter the interlayer regions to an appreciable extent.

Atmospheric-Pressure Impregnation

The simplest impregnation method is atmospheric-pressure impregnation or "ponding". While this method requires a much longer time than pressure impregnation to achieve a given depth of impregnation,

12

the size of the area that can be impregnated at one time is virtually unlimited. It is necessary only to provide a suitable container and a vapor-tight cover for the monomer. The time required to impregnate to a given depth is up to four times longer using "ponding" than using pressure impregnation at 15 psig (103 kPa); however, it is possible (in principle) to "pond" an area more than four times greater at one time. The monomer loading is usually slightly less with "ponding" than with pressure impregnation.

Pressure Impregnation

The impregnation times can be reduced sharply by application of modest pressures, e.g., in the first small-scale field trial, impregnation with the methyl methacrylate monomer mixture to a 4-in. (10-cm) depth can be achieved in about 8 hr using 15 psig (103 kPa) pressure. Such pressure impregnations are easily accomplished in the laboratory, but this method presents serious problems in field applications, especially in commercial-scale operations. First, it is difficult to seal the edges of the pressure-impregnation device to the bridge deck surface because of its rough surface finish, wear in the wheel paths, and surface deterioration. Second, even modest pressures applied over areas large enough to be considered commercial scale result in the application of very large forces, and it is not possible to hold down even small impregnation units with weights, e.g., an impregnation unit covering a 10-ft x 12-ft.(3.0-m x 3.7-m) area at 15 psig (103 kPa) would require a hold-down force greater than 130 tons (1160 kN), which would exceed the load-carrying capacity of the bridge superstructure. Therefore, bolt-down impregnation units were developed and built, the

first covering a 16-in. (41-cm) diameter circular area and the second, a 3-ft x 12-ft (0.9-m x 3.7-m) area. Both worked very well, the smaller unit in the laboratory and the first field trial, and the larger in the last two field trials. Moreover, the larger unit is amenable to scaling-up to commercial size. However, because of the strengthening and stiffening requirements, the weight of such an impregnation unit would increase sharply with increasing size (area covered) and pressure. In addition, it would require holes drilled in the deck for installing tie-down bolts.

From the standpoint of simplicity, low cost, and ease of application, a pressure-mat impregnation unit offers more promise than the bolt-down impregnation units. Pressure-mat impregnation units were designed, built, and used to impregnate 24-in. x 24-in. x 6-in. (61-cm x 61-cm x 15-cm) concrete slabs in the laboratory. This unit comprises a flexible rubber mat with a cellular pattern on the side facing the concrete; pressure is applied to the top of the mat rhythmically, using a roller or hydraulic loading mechanism, so that each cell becomes, in effect, a small pressure impregnation chamber. The unit worked very well in the laboratory, but requires more development before use in field applications.

Choice of Impregnation Method

Both the "ponding" and pressure-impregnation methods have been demonstrated to be feasible in field applications. The "ponding" method was used successfully in the first field trial and the two different pressure-impregnation units in all three field trials. The "ponding" method requires a much longer time for impregnation to a

14

given depth, but can, in principle, be used over a large area. The pressure-impregnation method requires shorter times, but the area that can be impregnated at one time is limited by the weight of the unit and the tie-down mechanism. A detailed cost analysis is needed to decide which of the two methods is better for a given case.

MECHANICAL PROPERTIES AND DURABILITY

General

Concrete slabs (non-air-entrained type) were impregnated from one side with the 90:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture. The mechanical properties and durability of core specimens from these slabs were compared with those of typical high-quality concrete used in bridge decks. The properties measured were those of significance to the bridge-deck deterioration problem, i.e., tensile and compressive strengths, permeability to water and salt solutions, freeze-thaw resistance, protection of reinforcing steel against corrosion, resistance to chemical attack, abrasion resistance, and skid resistance.

Strength

The core specimens from the slabs showed two-fold greater split-tensile and three-fold greater compressive strengths than the unmodified control specimens. Young's modulus was not determined for these specimens, but comparable polymer-impregnated concrete cylinders showed a 70-100 percent increase in the value of E. Stress-strain curves of the core specimens showed a higher modulus than the control and brittle fracture without warning. The laboratory cylinders showed

that this brittle fracture could be avoided by addition of butyl acrylate to the monomer mixture, which gave ductile fracture at the expense of only a modest decrease in ultimate strength.

Permeability to Water and Salt Solutions

Mortar specimens showed a 76-92 percent reduction in water absorption relative to the unmodified control specimens. After one month's exposure to 8 percent aqueous calcium chloride BA- and MMA-impregnated mortar solution, specimens showed only traces (0.1 percent) of total chloride ion at a depth of 0.25 in. (0.64 cm) and none at all below 0.50 in. in comparison with the 1.6 percent and 0.5 percent found for the unmodified control specimens at 0.25 (0.64 cm) and 1.50 in. (3.81 cm), respectively. After one year's exposure, the MMA-impregnated specimen showed 0.3 percent total chloride ion at the 0.25-in. (0.64-cm) depth, about 0.1 percent at a depth of 0.5 in. (1.27 cm), and undetectable amounts at lower depths, in comparison to 5.5 percent and 0.6 percent at 0.25 in. (0.64 cm) and 1.50 in. (3.81 cm), respectively, for the control specimens and 1.8 percent and 0.1 percent at 0.25 in. (0.64 cm) and 1.50 in. (3.81 cm), respectively, for the BA-impregnated specimens. This reduction in water and salt solution permeability should retard corrosion of the reinforcing steel, which is the major cause of deterioration in concrete bridge decks.

Freeze-Thaw Resistance

Freeze-thaw tests (ASTM Designation C671) were carried out on core specimens from salt-contaminated and uncontaminated non-air-entrained concrete slabs. All of the core specimens from the polymer-impregnated slabs, salt-contaminated and uncontaminated, showed exceptional resistance

to freezing and thawing (they were undamaged after 10 cycles), while all of the unmodified control specimens failed quickly, the salt-contaminated ones in the first cycle, and the uncontaminated ones in the third cycle.

Protection of Reinforcing Steel Against Corrosion

Scanning electron micrographs of the reinforcing steel rods in core specimens from salt-contaminated, polymer-impregnated concrete slabs showed no signs of corrosion after freeze-thaw cycling, while the reinforcing steel rods from salt-contaminated, unmodified control specimens showed significant etching. Polymer impregnation apparently immobilizes the salt in the concrete matrix and thus lessens its corrosive effects.

Resistance to Chemical Attack (Acid Etching)

Core specimens from polymer-impregnated slabs, soaked for two hours in 18.5 percent or 37 percent (concentrated) hydrochloric acid, showed no damage to the cementitious matrix, although the limestone aggregate particles were eaten away. Unmodified control specimens disintegrated so thoroughly and rapidly that this acid-etching test can be used as a measure of the depth of impregnation in core specimens from field trials.

Abrasion and Skid Resistance

The abrasion resistance was measured by the weight loss in an abrasion test instrument constructed specially for this purpose. This loss in weight may be a measure of skid resistance, if wear exposes a surface less resistant than the original.

Core specimens from the polymer-impregnated slabs showed 80-90 percent smaller weight losses in the abrasion test than the unmodified control specimens.

The skid resistance of these polymer-impregnated specimens was not measured, but others (8) have found it to be the same or slightly greater than that of unmodified concrete (see also p. 23).

EFFECTS OF CONTAMINANTS
General

Concrete bridge decks are contaminated with substances that may affect the drying, impregnation, and polymerization processes, e.g., deicer salts, grease, oil, asphalt cement, and rubber. The effects of these contaminants were determined by experiment.

Drying

Salt-contaminated concrete requires longer drying times at a given temperature than uncontaminated concrete to remove the moisture. For example, 3 percent sodium chloride in the concrete decreased the moisture removed under the same drying conditions to only 87 percent of that removed from uncontaminated concrete.

High-temperature drying burns off all organic contaminants-- grease, oil, asphalt cement, rubber--from the concrete surface.

Rate of Impregnation and Monomer Loading

Salt-contaminated concrete shows slower rates of impregnation and lower monomer loadings than the corresponding uncontaminated concrete. For example, the time required to impregnate concrete infused

with 0.3 percent sodium chloride to a 6-in. (15. -cm) depth using

methyl methacrylate at 60 psig (413 kPa) pressure (after 1.5 hours

28 in. [95 kPa] Hg vacuum to remove the moisture) was 30 percent longer

than for the uncontaminated concrete, and the polymer loading (after

polymerization) was 10 percent less.

Surface-ponding impregnation of core specimens from a 7-year-

old bridge deck showed statistically significant correlations (95

percent confidence level) between the chloride ion content 0.25 in.

(0.64 cm) below the surface and the rate of monomer impregnation and

monomer loading. The higher the salt content, the slower was the rate

of impregnation and the lower the monomer loading.

Removal of surface contaminants by various cleaning processes,

e.g., scrubbing with detergent or lye and grit blasting, does not

affect the monomer loading.

Polymerization

Laboratory polymerization studies were carried out to determine

the effect of various contaminants, e.g., deicer salts, linseed oil,

motor oil and grease, and asphalt cement, on the rate of polymerization

of methyl methacrylate. At $131^{\circ}F$ ($55^{\circ}C$), all of these contaminants

except sodium chloride retarded the polymerization rate significantly;

at $149^{\circ}F$ ($65^{\circ}C$), only asphalt cement exerted a retarding effect; at

$167^{\circ}F$ ($75^{\circ}C$), none of the contaminants retarded the polymerization.

Mechanical Properties

The increase in split-tensile strength and Young's modulus

achieved by polymer impregnation was reduced by 15 percent and 40

percent, respectively, by the infusion of 1 percent sodium chloride into the concrete prior to impregnation. However, the impregnated specimens still retained a several-fold advantage over nonimpregnated specimens. The compressive strength was unaffected by the presence of 1 percent sodium chloride.

Freeze-Thaw Resistance

Salt contamination reduced the freeze-thaw resistance of non-air-entrained unmodified concrete (from 3 to 1 cycles), but had no effect on the polymer-impregnated concrete (which was undamaged after 10 cycles).

FIELD TRIALS

General

Four field trials were carried out: (1) two (1.4-1.8 sq ft [0.13-0.17 m^2]) impregnations on the PSU test track bridge using gas-fired torch drying with pressure-chamber impregnation and steam polymerization and gas-fired infrared torch drying with "ponding" impregnation with hot water polymerization (March 1974); (2) a commercial-scale (72 sq. ft. [6.7 m^2]) impregnation on the PSU test track bridge, using gas-fired infrared drying, pressure-chamber impregnation, and hot-water polymerization (August 1974); and (3) one commercial-scale (36 sq ft [3.3 m^2]) impregnation on the northbound traffic lane of the Pennsylvania Route 378 highway bridge over Union Boulevard in Bethlehem using gas-fired infrared drying, pressure-chamber impregnation, and hot-water polymerization (March 1975).

<u>All field impregnations achieved the goal of a 4-in. (10-cm)</u>
<u>impregnation of a structurally sound, salt-contaminated concrete bridge</u>
<u>deck</u>. Further details are given below.

PSU Test Track--March 1974

In March 1974, two impregnations were carried out on the PSU test track bridge, one using gas-fired torch drying and pressure-chamber impregnation and the other, gas-fired infrared drying and "ponding" impregnation.

In one test, the bridge deck was dried for 10 hr using the gas-fired torch drying until the temperature at a depth of 4-5 in. (10-12 cm) reached $250^{\circ}F$ ($121^{\circ}C$) and the surface temperature was $700^{\circ}F$ ($371^{\circ}C$). The deck was allowed to cool for 8 hr, and holes were drilled and inserts installed for bolting-down the circular 16-in. (41-cm) diameter impregnation pressure chamber. The deck was impregnated with the 90:10 methyl methacrylate (MMA)-trimethylolpropane trimethacrylate (TMPTMA) mixture containing 0.5 percent azobisisobutyronitrile (AZO) initiator for 8 hr at 15-20 psig (103-137 kPa) pressure. The monomer was polymerized by feeding 10-13 psig (68-89 kPa) steam from a pressure cooker through the pressure chamber and over the deck for 10 hr.

Core specimens from the polymer-impregnated region showed a dense impregnation to a depth of 5 in. (12 cm) with complete impregnation throughout the 7.5-in. (19-cm) depth in some regions.

For the second, the bridge deck was dried for 10 hr using the gas-fired infrared dryer until the temperature at a depth of 4 in.

(10 cm) was 230°F (110°C) and the surface temperature was 675°F (357°C). The deck was allowed to cool for 8 hr, and a 30-in. x 18-in. (76-cm x 46-cm) "ponding" chamber was sealed to the deck using Silastic rubber. The monomer mixture (100:10 MMA-TMPTMA mixture with 0.5 parts AZO) was allowed to stand in the chamber (which was covered to prevent evaporative losses) for 4 days 10 hr. Then the excess monomer was removed, and 203°F (95°C) bath water was circulated for 10 hr through the chamber to polymerize the monomer. Core specimens from the polymer-impregnated region showed a dense impregnation to a depth of 4.5 in. (11 cm).

These first two field impregnations demonstrated that the goal of this project had been achieved, i.e., the field impregnation of structurally sound, salt-contaminated concrete to a depth of 4 in. (10 cm) is technically feasible.

PSU Test Track Bridge--August 1974

In August 1974, two adjacent 3-ft x 12-ft (0.9-m x 3.7-m) areas on the PSU test track bridge were impregnated using gas-fired infrared drying, pressure-chamber impregnation, and hot-water polymerization. The overall 6-ft x 12-ft (2-m x 3.7-m) area was dried in three stages using the gas-fired infrared heaters. Each stage required about 4 hr for the temperature at a 4-in. (10-cm) depth to reach 230°F (110°C). The deck was allowed to cool for about 12 hr, and holes were drilled and inserts installed for bolting-down the impregnation pressure chamber. The first impregnation was begun at 15 psig (103 kPa) pressure, but leaks around the gasket made it necessary to decrease the pressure; it was impregnated for 7.5 hr at 5 psig

22

(35 kPa) pressure. The second section was impregnated for 3 hr at

15 psig (103 kPa) pressure, followed by 4 hr at atmospheric pressure

and 5 hr at 5 psig (35 kPa) pressure. Both sections were polymerized

by circulating 170-180°F (77-82°C) water through the impregnation

pressure chamber for 12 hr.

Core specimens showed a dense impregnation to a depth of 3.5-

4.0 in. (8.9-10-cm) and a less dense impregnation extending 1 in.

(2.5 cm) or more downwards. The chloride ion concentration in these

core specimens ranged from 0.67 to 1.38 lb/cu yd (0.40-0.82 kg/m^3) at

0.5-in. (1.27-cm) depth to 0.02 to 0.04 lb/cu yd (0.01-0.02 kg/m^3) at

2 in. (5 cm).

These field impregnations confirmed the results of the earlier

field impregnations and demonstrated that two adjacent areas could be

impregnated in sequence. Tests also showed no significant effect of

impregnation on skid resistance.

PennDOT Route 378 Bridge in Bethlehem--March 1975

In March 1975, the northbound traffic land of the Pennsylvania

Route 378 (Bethlehem Spur Route) bridge over Union Boulevard was closed

to traffic, and a 3-ft x 12-ft (0.9-m x 3.7-m) area was impregnated

using gas-fired infrared drying, pressure-chamber impregnation, and

hot-water polymerization. The bridge deck was structurally sound,

but the slag aggregate was worn and porous at the surface; the deck

was contaminated with a high concentration of deicer salts (chloride

ion concentrations up to 4.8 lb/cu yd [285 g/m^2]). A 4-ft x 12-ft

(1.2-m x 3.7-m) area was dried in two 4-ft x 6-ft (1.2-m x 1.8-m)

stages using the gas-fired infrared dryer. The drying time to reach

230°F (110°C) at a 4-in. (10-cm) depth was about 6 hr, for a total time of 13 hr, including time for changing the position of the dryer. During the drying, water oozed out of the top surface of the deck at an expansion joint and on the underside at one location at the end of the permanent steel forms. The precise location of moisture exit on the bottom side could not be determined because of the forms. The deck was allowed to cool for 8 hr, and holes were drilled and inserts installed for bolting-down the impregnation pressure chamber (same as used for the August 1974 field trial at PSU test track bridge). New holes had to be drilled in the pressure chamber flange to avoid piercing the reinforcing steel rods while drilling to insert holes. The pressure chamber was evacuated for 30 min at 27 in. (91 kPa) Hg pressure and then pressurized at the 100:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture containing 0.5 percent azobisisobutyronitrile initiator for 75 min. at 5 psig (34 kPa), 7.25 hr at 2 psig (14 kPa), 1 hr at 3 psig (21 kPa), and 30 min at 8 psig (55 kPa) pressure. The periodic adjustments in pressure were necessitated by monomer leaking through the deck. Here again, the precise location of exit was obscured by the permanent steel deck forms. The polymerization was carried out by circulating 165-170°F (74-77°C) water through the impregnation pressure chamber for 12 hr. The chamber was covered with glass-fiber insulation and plastic film so that there was no noticeable monomer odor in the vicinity.

Seven core specimens were taken from the polymer-impregnated and unmodified areas of the deck, and laboratory tests were carried out to determine the depth of impregnation and the properties of the polymer-

impregnated regions. The core specimens from the polymer-impregnated regions showed a dense impregnation to a depth of at least 3 in. (8 cm) with a less dense impregnation extending to 4 in. (10-cm) in most regions. The split-tensile strength of one core specimen from a polymer-impregnated region was 606 psi (4.18 MN/m^2).

This last field impregnation in the NCHRP 18-2 program on a PennDOT bridge confirmed the feasibility of polymer impregnation of a structurally sound, salt-contaminated bridge deck to a depth of 4 in. (10 cm).

FIELD MANUAL

General

A field manual for the polymer impregnation of concrete bridge decks has been developed for the guidance of contractors and highway department engineers, based on the experience gained from laboratory studies and the firld impregnations. This field manual includes basic guidelines, data, procedural instructions, acceptance criteria, and safety requirements. The complete field manual is included in this report as Appendix I.

Materials and Methods

The manual prescribes techniques and materials used by the authors to achieve 4-in. (10-cm) field impregnations of concrete bridge decks. The monomer system specified is the 90:10 or 100:10 methyl methacrylate (MMA)-trimethylolpropane trimethacrylate (TMPTMA) mixture containing 0.5 percent azobisiobutyrontrile initiator. Recommendations

are included for preparing, handling, and storing the monomer mixture, as well as for estimating the quantity required for a given job.

The manual also prescribes the drying requirements to achieve a specified depth of impregnation and the means for monitoring the drying process. The recommended drying system is the gas-fired infrared heaters. In addition, the manual describes the cooling of the deck prior to impregnation and the protection of the dried areas from the weather.

The equipment, procedures, and monitoring criteria are specified for monomer impregnation at pressures ranging from atmospheric to 15 psig (100 kPa). Procedures and criteria for the hot-water polymerization are also included.

Acceptance Criteria

An attribute sampling plan and acceptance criteria are specified for quality assurance as to the depth of impregnation and completeness of polymerization. It is not yet possible to estimate the producer's and consumer's risks associated with this sampling plan because of the lack of sufficient data to provide estimates of variance for polymer-impregnation of concrete. Therefore, it may be necessary to modify the sampling plan and acceptance criteria as more experience is gained.

Safety Conditions

The manual also discusses the safety and fire hazards associated with the monomer mixture and the precautions to be taken with the high-temperature drying, in all operations of the impregnation process.

CHAPTER THREE

INTERPRETATION, APPRAISAL, APPLICATION

MONOMER SYSTEMS

The field trials used the 90:10 or 100:10 methyl methacrylate-
trimethylolpropane trimethacrylate monomer mixture containing 0.5
percent azobisisobutyronitrile initiator. This mixture, which was
derived from earlier experiments with methyl methacrylate, functioned
well in all of the tests carried out in this program. It had a
suitably low viscosity [0.6 cp ($6x10^{-4}$ Pa.s)] and penetrated well into the
dried concrete substrate. The addition of the crosslinking monomer
increased the viscosity of the mixture somewhat, but the improvement
in properties it gave outweighed the increase in viscosity and decrease
in penetration rate. Moreover, once inside the concrete, this monomer
mixture polymerized readily at temperatures of about $176^{\circ}F$ ($80^{\circ}C$).
The polymerization is autoaccelerating, which helps it reach high
conversion in a short time. Usually there is no odor of monomer when
the specimens are broken open.

The properties of concrete impregnated with this monomer
mixture are generally very good (three-fold increases in tensile and
compressive strengths; greatly decreased permeability to water and salt
solutions; increased resistance to freezing and thawing; increased
resistance to abrasion; and no change in skid resistance). Such polymer-
impregnated systems are, therefore, well suited to application in high-
way bridge decks.

The present program, however, did not treat the subject of
monomer cost broadly. The cost analysis (see Appendix H) showed that

much of the cost of impregnating a concrete bridge deck is for labor.

However, for deep impregnation, the estimated monomer cost is about

equal to the direct labor costs (not including traffic control) for

ponding, and 1.5 times labor costs for pressure impregnation. In

any case, the total amount of monomer required for a large expanse of a

bridge deck would be very great. Therefore, it is still worthwhile

over the long range to consider other less-expensive impregnants and

monomer systems, and investigation, of the long-term durability of

various monomer systems would be useful in optimizing selection.

DRYING METHODS AND CRITERIA

Methods

Of the various drying methods investigated, gas-fired infrared

radiant heating is the most practical and efficient. Propane-fired

flame heating can also be used to achieve effective drying, for impreg-

nation to 4 in. (10 cm), but it is less efficient than the gas-fired

infrared (IR) and probably more susceptible to variations caused by

wind. Furthermore, the gas-fired IR heaters are commercially available

and can be obtained in units large enough to be considered practicle for

bridge deck work. For practucal use, units should have a heat output

of at least 9,000 BTU/hr/sq ft. (102 MJ/hr/m^2).

Drying Criteria

The concrete should be heated to a temperature of 230°F

(110°C) at the depth to which impregnation is to occur. For a speci-

fied impregnation depth of 4 in. (10-cm) this results in surface

temperatures above 600°F (316°C). To prevent excessively steep thermal

gradients, in order to minimize cracking problems, surface temperatures

one hour after starting the drying process should not exceed 500°F (260°C) and they should never exceed 675°F (357°C). It was found that when the rate of increase in surface temperature dropped below 10°F 5.5°C)/hr for surface temperatures over 600°F (316°C), a satisfactory degree of drying was effected to a depth of at least 4 in. (10-cm).

IMPREGNATION METHODS

General

If concrete is sufficiently dried, impregnation with MMA monomer can be achieved to any desired depth utilizing any of a variety of combinations of pressure and time. In general, for a given impregnation depth, the time required varies inversely with the square of the applied pressure.

Methods

The most rapid rates and highest polymer loadings may be achieved by impregnation under pressure. With this method, the size, weight, and complexity of equipment needed for economic commercial-scale application must be balanced against the reduction in time requirements through the use of pressure. Further, if the pressure-mat principle demonstrated in this program can be developed to a commercial scale, it certainly would provide a most convenient impregnation procedure in terms of time reduction and ease of handling. Ponding should also be considered as a viable alternative. Although more time is necessary to achieve impregnation to a given depth at a given location, ponding units which are many times larger than those practical for impregnating with pressure chambers can be built.

29

Obviously, more work is needed to evaluate the relative economics involved for a given case based on the practical size limitations inherent with the methods. The purpose of this research was to establish the technical feasibility of the methods, and this has been shown.

POLYMERIZATION METHODS

The only polymerization method tried in this research--thermal-catalytic using hot water ponding or steam--was found to work very well in pracitcal field applications.

MECHANICAL PROPERTIES AND DURABILITY

The mechanical properties and durability of concrete impregnated with methyl methacrylate using techniques applicable to field impregnation, were found to improve significantly in comparison with nonimpregnated concrete. Compressive strengths were tripled, tensile strengths doubled, chloride penetration reduced to less than one-sixth, moisture absorption reduced by an average of 85 percent, reinforcement corrosion in salt-contaminated concrete arrested, resistance to chemical attack dramatically increased, freeze-thaw damage eliminated, and resistance to abrasion increased by an average of 85 percent. These results are comparable to the findings of other researchers. It was also shown that the stress strain behavior of the concrete can be varied by use of combination of monomers.

FIELD PROCEDURES

The practicality of transferring the techniques developed in the laboratory for deep polymer impregnation of concrete bridge decks to the field was clearly demonstrated. While the equipment employed was small in scale, it was designed to permit ready scale-up for commercial field applications. Based on the research carried out in this project, the estimated unit costs for polymer impregnation of concrete bridge decks to depths of 1, 2, 3, or 4 in. (2.5-cm, 5.1-cm, 7.6-cm, 10-cm) using either ponding or pressure impregnation at 15 psig (103 kPa) are presented in Table 1. These costs are based on equipment scale-up to commercially feasible size units capable of covering areas 12-ft x 40-ft (37-m x 12-m), but do not include amortization of capital equipment, maintenance, weather delays, or traffic control. The computations for the data contained in Table 1 are presented in Appendix H.

Procedures that were found in this research to provide successful deep (up to 4 in. [10 cm]) impregnation of concrete bridge decks are presented in a field manual (Appendix I). The report also presents technical data which support the feasibility of applying the principles demonstrated to commercial-scale operations. Of course, with additional experience in the field, revision of detailed procedures may be necessary. Similarly, the procedures for assurance of specification compliance, as presented in the field manual, may require revision with experience. Since there has been no commercial experience to date with the process on bridge decks, the magnitudes of variance of penetration depth and, consequently, the producer's and consumer's risks associated with the proposed compliance standards are not known.

31

Table 1. Cost Estimates for Commercial-Scale Polymer Impregnation

of Concrete Bridge Decks

Impregnation Depth, in.	Impregnation Pressure, psig	Total Time hr/sq ft	Material & Fuel Costs, $/sq ft	Total Cost, $/sq ft
1	0	0.022	0.86	1.30
2	0	0.055	1.82	2.92
3	0	0.102	2.88	4.92
4	0	0.163	4.06	7.32
1	15	0.016	0.86	1.18
2	15	0.034	1.82	2.51
3	15	0.060	2.88	4.09
4	15	0.096	4.06	5.98

Unit Conversion: $1 \text{ ft}^2 = 0.0929 \text{ m}^2$.

CHAPTER FOUR
CONCLUSIONS AND SUGGESTED RESEARCH

CONCLUSIONS

The deep (up to 4 in. [10 cm]) polymer impregnation of bridge deck concrete in the field has been demonstrated using concrete which is salt contaminated but structurally sound. To achieve this goal, a process consisting of a combination of infrared drying, pressure impregnation and hot-water polymerization was developed. Commercially available propane-fired infrared heaters may be used for drying; a special pressure impregnation unit was designed, and a prototype, capable of scale-up, was constructed. While the costs are high, so are the costs of alternate repair methods. With current costs for repair of bridge decks running in the order of $6 per sq ft (0.09 m^2) for repairs that may be expected to last only 3 to 5 years, the estimated costs for polymer impregnation of $6 per sq ft (0.09 m^2) plus the costs of amortizing and traffic control should be economically feasible in view of anticipated greater lifetime.

SUGGESTED RESEARCH

The magnitude of the problem area represented by this research and the myriad possibilities and variables that exist for each of the several phases of the problem required concentration of effort in certain areas, with emphasis on the demonstration of technical feasibility of a combination of process and equipment. Thus less attention could be devoted to other areas which were less central to the project goal, but which should be worth additional study. Also, as in any research endeavor, unanticipated items that should be studied further turned up.

In terms of field applicability of the polymer impregnation of concrete, the pressure-mat concept is particularly attractive, and should merit further research. Parallel research should be done to evaluate the relative economies of the various means of impregnation (pressure chamber, pressure mat, and ponding) and to quantify more precisely the relationships between time, differential pressure, depth, and concrete pore characteristics.

Since the cost of impregnation increases exponentially with the depth of impregnation specified, research should be carried out to provide a rational basis for specifying the impregnation depths and loadings required for adequate corrosion protection.

With regard to the drying operation, research should be carried out to refine the drying criterion and to develop criteria for concretes containing all types of common aggregates. Most aggregates encountered in this research were carbonates. Conceivably, concretes containing other aggregates, especially siliceous materials, might not be able to tolerate the high temperature differentials used in this research without spalling or otherwise damaging the concrete. The question of potential structural damage due to the high temperatures used requires attention.

It is also proposed to screen various monomer systems in comparison with the 90:10 or 100:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture used in this work. Chapter Three describes the results that can be obtained by copolymerization and points out that there are several monomers that might be used in place of methyl

methacrylate at lower cost. Some of these monomers, e.g., styrene, confer about the same mechanical properties as the polymethyl methacrylate, yet their costs are lower. In addition, a rapid screening test should be developed to distinguish between different types of polymer-impregnated concrete, rather than to emphasize the difference between polymer-impregnated concrete and the unmodified controls. Such tests would comprise many different compositions tested for ultimate durability using freeze-thaw as well as abrasion resistance methods. Other nonmonomeric impregnants should also be examined, e.g., tar and sulfur.

The efficiency of the various impregnants with respect to the resistance to salt penetration and to immobilization of pre-existent salt needs to be demonstrated in long-term laboratory and field tests, with emphasis on the ability to prevent or delay corrosion of the steel.

Finally, the acceptance criteria put forth in this research should be evaluated and adjusted as necessary, first by determining the magnitude of the variance that might be expected in impregnation depth, and second by developing a well-defined method of measuring impregnation depth.

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PART II

APPENDIX A
LITERATURE REVIEW

INTRODUCTION

This report is based on a state-of-the-art survey covering major aspects of polymer-impregnated concrete (PIC) as applied to highway bridge decks. The report covers the literature up to March 1975; abstract cards for the references are on file at each institution. As indicated in the Table of Contents, the topics generally conform to the major phases of the research. It should be noted that the search was selective; only the most pertinent references were included. Additional references, including those to papers based on this program, will be found in the remaining appendices.

IMPREGNATION

General Considerations

Concrete displays a wide variation of porosities, i.e., in the number, size, shape, and configuration (e.g., connecting vs. nonconnecting) of the pores. In new concrete, the porosity depends on the proportions of ingredients used in the mix and the conditions of cure; with ageing, however, the porosity may decrease as a result of further hydration. The rate of penetration of a given monomer system into concrete depends on the porosity of the concrete. Thus, the penetration could generally be enhanced by formulating the concrete so as to increase its porosity; however, this approach could be self-defeating because the improvement in physical properties derived from polymer modification depends on the properties of the unmodified concrete, i.e., the properties of a polymer-modified "weak" (very porous).

concrete might be only slightly better than those of an unmodified "strong" concrete. Moreover, even if it were possible to use more porous concrete in highways and bridge decks, there are many already existing structures which could benefit from polymer modification. Therefore, it is necessary to develop permeation techniques which are applicable to a wide range of porosities in concrete. The factors which affect this permeation are discussed in the following sections.

Theoretical Aspects

The basic formula for fluid flow through porous media is Darcy's equation ($\underline{1}$):

$$q = Q/t = \rho_o \, A\Delta P/L$$

where q is the rate of flow through the sectional area A; Q the volume of flow; $\underline{t}$ the time; ΔP the pressure drop through the porous media of depth L; and ρ_o a constant (Darcy's permeability, units $M^{-1}L^3T$) which depends on the fluid, temperature, and characteristics of the porous media.

Buckingham ($\underline{2}$) showed that if the particles comprising the media are not wetted by the fluid, ΔP is proportional to the 7th power of the porosity ν:

$$q = \rho_o \, \nu^7 \Delta P/L.$$

Darcy's equation may also be expressed as:

$$v = (\rho/\eta) \, (dP/dx)$$

where v is velocity of fluid flow in the x-direction; and ρ is the absolute permeability (units L^3) defined as the volume of fluid of unit viscosity passing through a unit cross section under unit pressure in unit time. The quantities v and P are statistical averages applicable to the body of the porous media rather than to the smallest elements, and v is not a velocity

in the usual sense, but rather the quantity of flow per unit area of the media.

Assuming that dP/dx is constant throughout the porous media, the permeability is defined as:

$$\rho = \eta q L/A\Delta P.$$

The application of these principles to the penetration of a given monomer system into concrete shows that the penetration can be enhanced by: (1) increasing the porosity of the concrete; (2) decreasing the viscosity of the monomer system; and (3) increasing the pressure gradient of application.

Poiseuille's equation (3), which was developed independently from classical hydrodynamics about the same time as Darcy's, describes the rate of flow in terms of the average diameter D_c of the pores:

$$q = \pi D_c{}^4 P/128\eta L = (\rho A/\eta) \ (P/L).$$

This equation has been modified and extended by many workers, particularly Kozeny (4), who showed the relationship to the particle-size parameters of the system according to:

$$q = (kAv_w{}^3/\eta S_w{}^2) \ (\Delta P/L)$$

where S_w is the specific surface of the media with v_w voids per unit-length (which is related to the surface per unit-volume S_v by $S_w = [1 - v_w] S_v$). For the case in which the fluid flows through the porous media under its own head h:

$$q = (\rho_c A/\eta) \ (h/L)$$
$$\text{and} \quad \rho_c = (kg\rho/S_v{}^2) \ \{\eta_w{}^3/ \ (1-\eta_w)^2\}$$

where ρ is the density of the fluid; g the gravitational constant; and ρ_c the capillary permeability (units MT^{-2}).

Fair and Hatch [5] obtained an equation of the form of Kozeny's using dimensional analysis:

$$h/L = (k/g) \ (\eta/\rho)^{2-n} \ v^n \ D_c^{n-3}$$

where n is an exponent ranging from 1.0 for streamline flow to 2.0 for turbulent flow. Substituting for D_c, the hydraulic radius defined as the void volume/surface area, or (volume of solids/surface area) $\cdot$ $\{v/(1 - v)\}$, the expression for streamline flow (n = 1) becomes:

$$h/L = (k/g) \ (\eta/\rho)v' \ S_v^2 \ \{(1 - v)^2/v^3\}$$

where v' is the approach velocity defined as νv.

The application of these principles to the penetration of monomer into concrete adds to the previously developed relationships (i.e., with porosity of the concrete, viscosity of the monomer, and pressure gradient of application) the possibility of correlating the rate of penetration with the experimentally measurable particle-size parameters of the concrete, e.g., the surface area determined by gas adsorption.

Poiseuille's equation and its variations assume the porous media to be a system of cylindrical capillaries, but does not take into account the capillary-rise phenomenon. The curvature of a liquid surface in a cylindrical capillary of radius r gives rise to a capillary pressure of $2\gamma\cos\theta/r$, where γ is the surface tension of the liquid and θ, its contact angle on the capillary surface. The height of rise h of a liquid ascending in porous media is given by the Rideal-Washburn equation [6]:

$$h^2 = \gamma r \ t \ \cos \ \theta/2\eta$$

which rearranges to:

$$r \cos \ \theta = 2\eta h^2/\gamma t.$$

This latter form is often used in studies of liquid absorption into porous substrates (e.g., paper) because the experimentally measurable quantity $h(\eta/\gamma t)^{\frac{1}{2}}$ is approximately constant for a given substrate and dependent only on the pore size and contact angle.

The application of this principle indicates that the penetration can be enhanced by formulating the monomer system (e.g., with the appropriate surface-active agents) so that it wets the concrete substrate well ($\Theta = 0$) and by using concrete of large capillary pore size. However, this latter point is obviated according to Tollenaar (7) if the substrate consists of interconnected capillaries with a distribution of capillary sizes—if the liquid wets the substrate, it will be forced from the wide capillaries into the narrow capillaries so that the height of capillary rise depends on the distribution of capillary sizes.

The foregoing theoretical treatments are applicable to only one phase of the infusion of concrete with monomer. In practice, a measured amount of monomer is applied to the concrete surface (e.g., by brush, roller, or spray) and penetrates into the substrate in accordance with the foregoing parameters; however, the penetration proceeds only until it is counter-balanced by the evaporation of monomer from the surface after capillary rise. This point may not be obvious, but it has been noted by Steinberg et al. in studies on highway applications of MMA-impregnated concrete (8).

Theoretical treatments of the concurrent penetration-into-capillaries and caillary-rise-and-evaporation are generally lacking; however, Corman and Walmet (9) have recently presented a theoretical treatment of evaporation from capillary wick surfaces. According to their analysis, liquid is "pumped" to the surface by the capillary pressure and evaporates; this

"pumping" is counterbalanced by the liquid flow pressure drop produced by penetration into the porous structure. Evaporation of liquid at the surface causes the process to continue until the requirement for liquid flow to the surface causes the flow pressure drop to exceed the maximum capillary pressure head, and the surface dries out. Equations are given for the maximum capillary supply pressure and the total liquid flow pressure.

The application of this theory to monomer-infused concrete indicates that the monomer volatility and weather conditions during application and curing can be taken into account, as well as the porosity of the concrete and the viscosity and wetting properties of the monomer. The analog in monomer-infused concrete to the assumed heat input is the temperature gradient resulting from surface cooling by evaporation.

Interestingly, there has been little explicit confirmation of the theoretical predictions. However, recently Vanderhoff et al. (10) and Mehta et al. (11) showed that the penetration of water and monomers into portland cement mortar and concrete exhibit a linear dependence of rate on (time)$^{\frac{1}{2}}$. This finding was confirmed independently by Heins (12), Weyers (13), Godard et al. (14), and Paul (15). The latter authors critically analyzed the various theories of penetration.

The effect of pressure is not well understood. Theory (6) predicts that h should vary with $\Delta P^{\frac{1}{2}}$ as well as $t^{\frac{1}{2}}$. However, experimental work to date seems to suggest a linear dependence (11, 16, 17).

Experimental Techniques

Several parameters are important in processes used to impregnate concrete and other porous media (8, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27). Some of these parameters are listed below.

Monomer or Prepolymer. Viscosity and surface tension characteristics of the monomer are important in the ability of the monomer to wet and penetrate the void volumes. For concrete, the monomer must be capable of being polymerized in the alkaline matrix and the resulting polymer must resist permeation of water and salts (especially sodium and calcium chloride). Also, the polymer should contribute to the strength and toughness of the resulting composite system.

Concrete Porosity. The number, size, shape, and configuration of the pores are a prime concern for any impregnation. The rate of penetration of any monomer system will depend on the porosity.

Drying. The maximum amount of monomer can only be impregnated into concrete if the void volume of the material is not occupied by water, etc. Water can be removed from concrete by heating, or by using a laboratory method of vacuum drying (17).

Vacuum. It has been shown that if monomer is introduced while a concrete specimen is placed under vacuum, it will produce an almost fully impregnated (depends on monomer viscosity) concrete specimen faster than just soaking nonevacuated specimens (17, 28). Vacuum is generally a controllable parameter for laboratory experiments. It was reported that vacuum and a monomer viscosity of 9 centipoises (cp) (9×10^{-3} Pa·s) or less is required to fully impregnate a 6-in. diameter x 12-in. long (15.2 cm x 30.4 cm) concrete specimen (17).

Pressure. After the specimen has been covered with the monomer, pressure can be applied to increase the rate of penetration of the monomer into concrete. It was reported that pressures had been used up to 75 psig (517 kPa). Findings at PSU demonstrate that concrete can be impregnated with

epoxy using various pressures and times of pressure application (28). For example, there is a difference in the loading of concrete and other porous material with high viscosity monomers for pressures of 100 psig (690 kPa) as compared to 200 psig (1380 kPa) for 3 hr of application. It seems reasonable that similar loadings can be acquired for pressures below 100 psig (690 kPa) for long periods of time and for pressures above 100 psig (690 kPa) for shorter periods of time.

Many methods have been developed for the impregnation of porous materials (17, 29). In the impregnation of a porous material, such as concrete, the impregnation method used depends on the monomer and material properties. Listed below are some of the methods that have been used in the impregnation of concrete and other porous material (17, 28, 29, 30, 31, 32, 33, 34, 35, 36).

Soak. In this method the concrete is usually dried and slowly lowered into the monomer, usually of low viscosity, and soaked for various periods of time.

Vacuum Soak. Here the concrete is evacuated to various vacuums and the monomer is then permitted to cover the specimens while the specimens are still under vacuum.

Vacuum. The porous medium is immersed in the monomer while vacuum is maintained on one section of the material. Here the monomer is pulled into and through the material.

Pressure. The monomer is forced into the porous medium through the application of pressure.

Vacuum-Pressure. The material is placed under vacuum, the monomer is is introduced, and the system is then pressurized.

Solvent Exchange. The porous medium is first saturated with a solvent through a sorption process. Next a resin or other monomer is dissolved into the solvent. The saturated specimen is placed into the monomer-solvent solution. Because of a concentration difference between the saturated specimen and the solution, the monomer diffuses into the material. After sufficient time has elapsed, the solution is changed to one which contains a higher concentration of the monomer. This process is continued until the final solution contains about 95 percent monomer and 5 percent solvent. The monomer is then polymerized in situ. This method is presently being investigated as a possible means for impregnating high viscosity monomers into concrete (28). Methods like this have also been used successfully for impregnating wood products (29) and stone statuary (33).

In addition to the above laboratory techniques for impregnating porous media, some methods have been developed for impregnating roads and bridge decks. These methods can be generally classified as soak, pressure injection, vacuum-soak, and vibration. Using MMA and a 9 to 1 mixture of MMA and TMPTMA, a penetration depth of up to 1-3/4 in. (4.4 cm) on bridge deck material has been achieved using a ponding or soak technique (36, 37, 38, 39, 40). A modification to soaking is to pond the monomer in over-dried, lightweight fine aggregate on top of the concrete (38). The fine aggregate acts like a wick and helps to minimize evaporation of low viscosity monomers, permitting a deeper penetration of the monomer into the concrete. A vacuum-soak technique using MMA and a 9 to 1 mixture of MMA and TMPTMA resulted in a penetration of about 1/4 in. (6.3 cm). This method is being investigated in more detail (39). In the application of ultrasonic vibration to a ponded monomer, a penetration depth of 1-1/4 in. (3.2 cm)

was obtained in a short period of time (39). Pressure injection of epoxy

into bridge decks has been used and it was found to be another promising technique

(41, 42, 43).   The techniques discussed and other techniques are present-

ly being investigated.

Table A-1 lists some of the various monomers that have been used to

impregnate concrete and mortars. Also listed are the various impregnation

methods that were used for each monomer and some brief remarks concerning

the results.

Table A-1. Experimental Techniques for Polymer-Impregnated Concrete and Mortars

	Polymer	Impregnation Technique	Remarks	Typical Reference
1.	Methyl Methacrylate	Soak	Preliminary investigation--impregnated mortar bars, 5.7% loading (weight).	17
2.	Methyl Methacrylate	Soak	Fiber-reinforced mortar bars. No vac. or press.--just soak. Bars were vac.-dried at 85°C (24 hr). 7.4% wt for mortar 9.1% wt for steel-reinforced mortar 10.7% wt for glass-reinforced mortar.	32
3.	Methyl Methacrylate	Vacuum-Soak	Preliminary investigation--impregnated mortar bars, 5.4% weight loading	17

Table A-1.   Experimental Techniques for Polymer-Impregnated Concrete and Mortars (Continued)

	Polymer	Impregnation Technique	Remarks	Typical Reference
4.	Styrene	Soak	Preliminary investigation-- impregnated mortar bars, 5.8% weight loading.	17
5.	Styrene	Vacuum-Soak	Preliminary investigation-- impregnated mortar bars, 6.6% weight loading.	17
6.	Ethylene (Gas)	Soak	Preliminary investigation-- impregnated mortar bars, 1.0% weight loading.	17
7.	Ethylene in liquid SO_2	Soak	Preliminary investigation-- impregnated mortar bars, 3.2% weight loading.	17
8.	Vinyl acetate	Vacuum-Soak	Preliminary investigation-- impregnated mortar bars, 5.7% weight loading.	17

Table A-1. Experimental Techniques for Polymer-Impregnated Concrete and Mortars (Continued)

Polymer	Impregnation Technique	Remarks	Typical Reference
9. MMA	Evacuation	Mortar over-dried at 105°C	34
88% MMA - 10% TMPTMA	Soaking	and paste over-dried in	
Styrene, 87%Styrene-10%DVB	Coat with prepolymer	vacuum at 50°C.	
10. MMA	Soak	Best loadings with dry	17
	Vac-Soak	specimens in vac.-soak or	30
	Vac-Press (5 psig)	vac.-press. method.	31
		Greatest improvement in	
		durability properties.	
11. Styrene-Epoxy-Acrylate	Soak-Vac-Press (5 psig)	Viscosity 22 to 24 cp at RT, penetration of 1/4 to 1/2 in. Epocryl U-16 (Shell	17
12. Styrene-Polyester	Vac-Soak	Viscosity 800 to 1 cp at RT. Various percentages of each monomer. High compressive and tensile strength, over-dried Plaskon 941 and Hetron 197.	17, 41

Table A-1. Experimental Techniques for Polymer-Impregnated Concrete and Mortars (Continued)

Polymer	Impregnation Technique	Remarks	Typical Reference
13. a. 90% MMA and 10% TMPTMA* b. 70% MMA and 30% TMPTMA	Vac-Soak, Press (5 psig)	High temperature studies, highest compressive strength 70-30 good resistance in brine at 177°C.	17
14. Styrene 60% and Acrylonitrile 40%	Vac-Soak	-----	17
15. Styrene	Vac-Soak	Specimens are subject to cracking.	17
16. Acrylonitrile	Vac-Soak	High temperature studies, Least improvement in durability properties. Over-dried at 105°C and undried (undried gave low loading).	17

Table A-1. Experimental Techniques for Polymer-Impregnated Concrete and Mortars (Continued)

Polymer	Impregnation Techniques	Remarks	Typical Reference
17. 60% Styrene and 40% TMPTMA	Vac-Soak	High temperature studies, greatest strength for high temp. applications and smallest decrease in strength at elevated temperature--over-dried at 150°C.	17
18. 90% Diallyl phthalate 10% MMA	Vac-Soak	High temperature study, over-dried at 150°C, found to be unsatisfactory for high temperature applications.	17
19. Vinyl chloride	Vac-Soak, Pressure (40 psi during polymerization)	Gaseous, difficult to handle, erratic results, low polymer loading, over-dried (150°C).	17

Table A-1. Experimental Techniques for Polymer-Impregnated Concrete and Mortars (Continued)

Polymer	Impregnation Technique	Remarks	Typical Reference
20. Vinylidene chloride	Vac-Soak	Over-dried (150°C), low polymer loading.	17
21. Chlorostyrene	Vac-Soak	-----	17
22. Tert-butyl styrene	Vac-Soak	High compressive and tensile strength, over-dried (150°C).	17
23. Diallyl phthalate		High temperature studies	17
24. Epoxy-styrene	Vac-Soak	weight, % vis (cp)	17
		65E +35S 250	
		60E +40S 125 Over-dried (150°C)	
		58E +42S 90 Irradiation polymerized	
25. MMA	Vac-Soak,Press	Polymer-impregnated concrete pipe.	27
26. Epoxy	Soak	Concrete surface, depth of 10mm.	36

Table A-1. Experimental Techniques for Polymer-Impregnated Concrete and Mortars (Continued)

Polymer	Impregnation Techniques	Remarks	Typical Reference
27. Diallyl isophthalate	Vac-Soak	High temperature studies, smallest weight change in brine and in vapor at 143°C.	17
28. 50% MMA 50% Ethyl-Glycol dimethacrylate (EGDm)	Vac-Soak	High temperature studies. Good resistance in brine at 177°C.	17
29. MMA-isobornyl methacrylate (IBOMA)	Vac-Soak	High temperature studies.	17
30. Styrene-triallyl isocyanurate (TAIC)	Vac-Soak	High temperature studies.	17
31. IBOMA - TMPTMA	Vac-Soak	High temperature studies.	17

Table A-1. Experimental Techniques for Polymer-Impregnated Concrete and Mortars (Continued)

Polymer	Impregnation Techniques	Remarks	Typical Reference
32. MMA, 1% BP, 10% TMPTMA	Soak	Applied to bridge decks,	37
Isodecylmethacrylate (IDMA)		covered deck with 1/4 in.	38
1% BP, 10% TMPTMA		oven-dried fine aggregate	
Isobutylmethacrylate (IBMA)		(served as "wick" and helped	
1% BP, 10% TMPTMA		slow down evaporation).	
		Impregnation up 3/4 in.	
33. MMA and Polyester	Vac-Soak	Polyester-Dion synthetic	41
		marble polyester resin.	
		Up to 1.5 in. penetration.	

Unit Conversions: 1 in. = 2.54 cm

$1 \text{ cp} = 10^{-3} \text{ Pa's}$

$°F = (\frac{9}{5}) °C + 32.$

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PHYSICAL AND MECHANICAL PROPERTIES

General

A wide range of concrete polymer composites is under investigation at present. Concrete has been used in one form or another since Roman times. It is easy to see why concrete has become so important to the economy. It is made from readily available, very inexpensive materials, and it can be molded into almost any shape desired. However, some of the major deficiencies of the concrete presently used are the lack of sealing qualities, strength and wearing ability, and susceptibility to cracking and spalling. The old technology of concrete is combined with the new technology of polymers to give the most dramatic improvement in all the properties of concrete and to overcome the deficiencies, thus producing an excellent structural material.

Polymers in Concrete

The development in this field can be divided into three distinct types (1, 2, 3, 4):

1. Polymer-cement concrete (PCC), a premixed material in which a monomer is added to a water-portland cement-aggregate mix and subsequently polymerized in place.

2. Polymer concrete (PC), a generally resin concrete or a composite material formed by polymerizing a monomer and aggregate mixture. This is potentially a most promising material for cast-in-place applications.

3. Polymer-impregnated concrete (PIC), a precast portland cement concrete impregnated by a monomer system which is subsequently polymerized in situ. This is the more developed of the

composites and exhibits the highest degree of strength and
durability.

Polymer Cement Concrete (PCC)

The introduction of various organic materials to a concrete mix has
been tried numerous times in the past by researchers all over the world.
The results obtained in terms of improvements of strength and dura-
bility are either disappointing or relatively modest (4). In many cases,
materials poorer than concrete are obtained. Under the best conditions,
compressive strength improvement over conventional concrete of ~ 50 per-
cent are obtained with relatively high polymer concentrations of ~ 30
percent. Polyester styrene, epoxy styrene, furans, and vinylidene
chloride have been used in PCC with limited success. These concretes,
grouped under "resin concretes," have been investigated by some who
found that by carefully controlling the particle size of the aggregates
and by using special blending techniques, a strong cohesive mix can be
obtained using approximately one-tenth the usual amount of resin.

The use of plastics to improve the properties of conventional con-
crete construction material was discussed with 16 references by Zonsyeld
(5). The use of surface coatings as well as bulk addition to the con-
crete were described. Barnes (6) described stress-strain diagrams for
longitudinal, transverse, and volumetric strains, and change in Poisson's
ratio of variously composed resin-concretes. A graphic representation of
their interrelation with the mix composition and with the Poisson
strengths reveals uniform behavior for all types of resin concrete.
Kamaitis et al. (7) showed that use of PCC based on compositions of
indene-coumarone resin copolymers improves the properties of concrete,

especially the abrasion resistance. Satalkin et al. (8) in the RILEM symposium in 1967 stated that injection of water soluble resins into concretes and mortar helps to increase the physical properties such as impermeability, lowering of creep, and shrinkage without any decrease in compressive and tensile strength. Vazareiskoya et al. (9) showed that a 0.1 to 1.5 percent addition of polymer preparation K-6 (partially hydrolyzed polyacrylonitrile) to cement mix decreases the adsorption of water and electrolyte solution from soil by the concrete, thus reducing the amounts of the hydroscopic salts and gypsum depositions in the capillaries and increasing concrete durability. Hickey (10) prepared a comparison of concrete and epoxy materials. The results of this comparison showed that: "tests indicate good structural compatibility of physical properties except for thermal expansion and other volume changes. ... All physical properties tested and compared indicate that epoxy mixes using small amounts of resin are more compatible with portland cement concrete than mixes containing large amounts."

A research program was undertaken by Bull (11) to test concretes with varying amounts of epoxy resin added to the normal portland cement concrete. The concretes were tested under four different curing conditions: air curing (with no artificial control on temperature or humidity), fog room curing under standard control conditions, curing under water, and steam curing. The epoxy resin was added in 5 percent, 10 percent, and 15 percent amounts of the weight of portland cement used. The results were disappointing in that the increase of strength was only marginal, and thus there does not appear to be any economic case for the use of epoxy under these conditions. Increases of strength due to the

addition of epoxy resins were greatest in the steam-cured specimens.

A book published by Solomatov in Moscow in 1967 (12), translated from the original Russian by the Computer Branch of the U. S. Atomic Energy Commission, was the first attempt at generalization and systematization of theoretical and practical knowledge of the technology and use of polymer-cement concretes and polymer concretes--the new high-strength, stable materials whose properties can be changed at will within wide limits. Their high static and dynamic strengths and their resistance to wear and chemicals permit their wide use for chemical-resistant equipment, storage vessels, and pipelines for corrosive or biologically active liquids, chemical-resistant floors, sewage systems, and many other purposes. The book was written for construction engineers and for industrial workers who use construction materials. This book with 250 references is a very thorough attempt at summarizing the theoretical, experimental, and practical studies and applications of polymer-cement concretes and polymer concretes.

The very little success with PCC is generally explained by the fact that the organic materials are incompatible with aqueous systems and, in many cases, interfere with the alkaline cement hydration process.

Polymer Latex Modified PCC

Another material which can be classified under polymer-cement concrete material is formed by the use of polymer latex to modify mortars and concrete. The first work in this area began in the 1930s and involved the use of natural rubber latexes to modify cement mortars. These latexes produced extremely flexible mortar systems. The first use of synthetic latexes was in the 1940s, resulting from the development of

polyvinyl acetate latexes. These materials produced a modified mortar with very good bond strength to concrete and had improved compressive and tensile properties. Since these latexes were sensitive to water, the use of styrene-butadene latexes in portland cement systems, which had excellent water resistant properties, began in the 1950s. The acrylic latexes were introduced to the industries in the late 1950s and early 1960s. These showed slightly better properties than styrene-butadiene latexes. Saran latexes are the latest to be used in industry and have been found to produce significantly higher strength properties than any of the four types mentioned above. They produce a truly structural material with excellent durability and water-resisting properties and the ability to bond well to a substrate, usually concrete, by virtue of which it has found extensive use in floors, underlayments over concrete, and resurfacing of badly deteriorated bridge decks and brick masonry structural systems. Typical mechanical properties are given in Table A-2 (13). There is also a dramatic improvement of 200 to 500 percent in abrasion resistance over concrete.

Latex-modified concrete (LMC) is also being produced and has shown similar improvements in the physical and mechanical properties. These improvements can be attributed to the most significant fundamental improvements in the morphology of LMC concrete of almost complete absence of microcracking in the paste phase of the composite. Higher strength, low density concretes have been obtained by latex modification. Examples have been cited of use of bloated clay aggregate of low density of 72 pcf (1200 kg/m^3) to obtain 4,500 psi (32 MPa) concrete. In conclusion, latex modification does indeed improve the properties of portland

Table A-2. Typical Mechanical Properties of Mortars (19)

Property	Control psi	Styrene-Butadiene psi	Saran psi
Shear Bond[1]	50-200	>650	>650
Compressive	4,480	5,500	8,430
Tensile	350	740	870
Modulus of Rupture	820	1,620	1,820
Elastic Modulus	3.4×10^6	1.92×10^6	2.52×10^6

Unit Conversion: 1 psi = 6.89 kN/m^2. = 6.89 kPa

1. Dow method to obtain a more reliable correlation between laboratory and field results.

cement concrete. More importantly, this is achieved without any radical
departure from existing concrete construction methods. And the economics
of these in-place systems are favorable. Although these concepts are yet
in the research stage, the results thus far indicate that latex modifica-
tion will find a definite place in the construction industry.

Polymer Concrete (PC)

Considerable progress has been made in the development of PC. This
material can be cast and formed in the field.

Resin Concretes. One class of material forms by grading the aggre-
gate mass and using resins as binders. Cement is sometimes used as a
filler material. These types of concretes are known as resin polymer
concretes (14).

Dennard (14), in a summary of the literature on resin concretes,
states that there are only limited publications available.

Michaels (15) investigated the possibility of reducing the cost of
resin concrete by reducing the resin content using aqueous dispersion
techniques. By increasing the grain size (for narrow size distribution
sand) and adding some very small, particle-size sand, he obtained a com-
position having 1100-psi (7.58 MPa) tensile strength using 3.5 percent
resin by weight instead of the normal 40-50 percent resin by weight.

Bares (16) used furan resin and mineral aggregate to form a resin
concrete which he named Berol. Berol pipes with portland cement concrete
casings were found to be 25 percent cheaper than stoneware pipe and 15
percent cheaper than masonry sewer, and thus excellent for piping for
aggressive effluents from factories.

Mlodecki (17) investigated the use of isobutoxysiloxane resins. He

found that the addition of this silicone resin to epoxy and polyester

resins does not essentially reduce the strengths of these resins in con-

crete and should (due to the properties of the silicone resin) decrease

creeping and increase durability, frost and heat resistance, and elec-

troinsulating properties of the resin concrete.

Warren (18) altered Michael's (15) method for reducing resin content

by using less mixing water and no xylene in the dispersing agent. In-

corporating these changes, he found that the resin concrete could be

optimized by controlling aggregate size and gradation. Bares (16) dis-

puted this method--feeling that the mix is actually optimized by con-

trolling the volume of the voids, and further that the other variables

in a mix are: properties of the binder, proportion (by volume) of binder,

mechanical interaction between binder and aggregate, and mechanical inter-

action between the concrete and the environment.

Breckenridge (19) discussed the state-of-art of reinforced plastics

as load-carrying members in structures. Hickey (10) found that resin

concretes (with relatively low resin content) are compatible with port-

land cement concretes, the main differences being creep (at varying

temperatures), shrinkage, and thermal expansion.

Geymayer (20) reported on increasing the strength (either rigid or

flexural), cracking resistance, impermeability, and chemical resistance

of beams by composite construction using a resin concrete layer in the

tensile zone.

Knab (21) studied the effect of load rate on polyester concrete.

He found that a polyester concrete system will withstand both slow and

fast static loading in tension or compression. And Bull (11) added small

amounts of epoxy to portland cement concrete under four different curing

conditions. There resulted only marginal increases in strength.

Some test results indicating strengths of epoxide/cements

composites with sand mortars have been obtained [22]. Bloss (23) investigated

the maximum compressive strength that can be obtained with various mixes

of resin concrete. He found that the maximum compressive strength is

limited to about 15,000 psi (100 MPa) using conventional aggregates.

One mix (using type III portland cement as a mineral filler) reached

20,000 psi (140 MPa) compressive strength.

Solomatov (12) authored the only publication found that summarized

the existing knowledge (theoretical and practical) on resin concretes.

Other Types. Another class of polymer concrete is processed by

minimizing void volume in the aggregate mass so as to reduce the quantity

of the relatively expensive polymer needed for binding the aggregate

(2, 3, 4). After grading and mixing the aggregate, monomer is diffused

up through the mixed aggregates and the polymerization is initiated by

either radiation or chemical means. PC compressive strengths as high as

PIC (20,000 psi [140 MPa]) have been obtained (Table A-5 [24]). A

silane coupling agent is added to the monomer to improve the bond

strength between the polymer and the aggregate.

In conclusion, the authors generally agreed on the major advantages

and disadvantages of polymer concretes:

    1. Advantages

        High strength (both compressive and tensile)

        High static and dynamic resistance

        High bonding strength

Highly hydrophobic

Impermeability

Durability

High early strength (adjustable time of set)

Impact resistance

Low shrinkage

Creep resistance

Cracking resistance

Adjustable flexibility

Adjustable to suit particular needs

Resistance to wear, chemicals, abrasives, oils, salts,

  caustic and frost penetration.

2. Disadvantages

High cost of materials

High cost of handling (special equipment, etc.)

Short pot life (requires small batches)

Reduction in strength with temperature increase

Shrinkage in large pours

Difficult handling and placement (due to toxic effects and

  bonding characteristics).

Though epoxy resin concretes tend to give better results than other resins, they are difficult to manipulate whereas polyester and furanic resins cost much less than epoxy resins and are easy to cure. The silicone resins have generally the same characteristics as the polyester and furanic resins but exhibit much greater durability and water resistance than the epoxy resins. Although more research and experience are

A-33

required with PC for cost benefit analysis and to make it a relatively
acceptable material for construction, the authors generally agree that
polymer concretes are not a replacement for portland cement concretes
in the construction industry but are another construction material that
may be used to complement portland cement concrete structures.

Polymer-Impregnated Concrete (PIC)

General. Extensive studies conducted by the Brookhaven National
Laboratory (BNL) and the United States Bureau of Reclamation (USBR), and
confirmed by studies at Lehigh and other institutions all over the world,
demonstrate remarkable three- to four-fold improvements in the physical
and mechanical properties of concrete by impregnation with a monomer such
as methyl methacrylate followed by in situ polymerization. Much informa-
tion on the structural and durability properties of PIC have been accumu-
lated over the past 4 years in the United States (1, 2, 3, 4). Typical
reproducible improvements are summarized in Table A-3 (25), comparison
of strength due to different polymers is made in Table A-4 (3), and
strength and cost benefit index with other types of concrete are shown
in Table A-5 (24). Much of the information presented has appeared in BNL
annual reports (1, 2, 3, 4), internal reports, and research articles
which have been appearing more and more frequently in scientific and en-
gineering journals.

In general, all the composite systems showed significant improvement
in strength and durability. The MMA and MMA-TMPTMA impregnated concretes
have given the best results. The improvement in strength appears to be a
function of polymer loading. Improvement in durability appears to be
mainly a function of the polymer loading and the degree of success in

Table A-3. Concrete Polymer Materials—Summary of Properties of

Methyl-Methacrylate Impregnated Concrete[1] (65)

Property	Control	Treated	Difference percent[2]
Compressive strength, psi	5,267	20,255	285
Modulus of elasticity, 10^6 psi	3.5	6.3	80
Tensile strength, psi	416	1,627	291
Modulus of rupture, psi	739	2,637	256
Flexural modulus of elasticity, 10^6 psi	4.3	6.2	44
Water absorption, percent	5.3[a]	0.29[a]	-95
	6.4	1.08	-83
Abrasion, in.	0.0497	0.0163	-67
(g)	14	4	-71
Cavitation, in.	0.32	0,064	-80
Water permeability, 10^{-4} ft per year	6.2[a]	0[a]	-100
	5.3	0.8	-85
Thermal conductivity 73°F (23°C) btu/ft-hr-F	1.332	1.306	-2
Diffusivity at 73°F (23°C), ft^2/hr	0.0387	0.0409	6
Coefficient of expansion, in./in.°F	4.02×10^{-4}	5.36×10^{-6}	33
Creep for 800 psi load after 90 days, 10^6 in./in.	-95[b]	+34	Negative creep

Table A-3. Concrete Polymer Materials--Summary of Properties of

Methyl-Methacrylate Impregnated Concrete[1](65)(Continued)

Property	Control	Treated	Difference percent[2]
Freeze-thaw durability, cycles, percent weight loss	590;26.5[a] 490;25.0	2,420;0.5[a] 750;4.0	>310 >53
Hardness impact ("L" hammer)	32.0	55.3	73
Resistance to sulfate attack, 300-day exposure, percent expansion	0.144[a]	0[a]	-100
Acid corrosion in 15 percent HCl, 84-day exposure, percent weight loss	10.4	3.64	-65
Corrosion by distilled H_2O 120-day exposure at 206°F (97°C)	Severe attack	No attack	-100

Unit Conversions: 1 psi = 6.89 kN/m^2 1 in. = 2.54 cm

1 ft = 0.305 m   1 ft^2 = .0929 m^2

°F = $(\frac{9}{5})$ °C + 32   1 BTU/h ft$^2\cdot$°F/ft = 1.162 W/m·°C

Table A-3. Concrete Polymer Materials--Summary of Properties of

Methyl-Methacrylate Impregnated Concrete[1](65)(Continued)

1. Dried concrete specimen containing 4.6 to 6.7 weight percent MMA.

2. Difference percent = $\dfrac{\text{radiation-control}}{\text{control}}$ (100).

a. From survey series: all other data from CP-1 test series. Results based on average of 1 to 3 test measurements for each property.

b. Control creep data are for 30 days in test.

Table A-4. Compressive Strengths of Polymer-Impregnated Concretes (43)

Polymer	Wt. Loading, %	Compressive Strength, psi	
	Range	Thermal Cure	Radiation Cure
MMA	4.2-6.7	18,200	20,300
Styrene	4.2-6.0	8,800	14,100
MMA + 10% TMPTMA[1]	5.5-7.6	19,000	21,600
Acrylonitrile	3.2-6.0	10,750	14,410
Chlorostyrene	4.9-6.9	14,400	16,100

Unit Conversion: 1 psi = 6.89 kN/m^2

1. TMPTMA = Trimethylolpropane trimethacrylate.

Table A-5. Classification of Concrete-Polymer Materials (64)

Type	Polymer Loading wt% PMMA	Density lb/ft^3	Compressive Strength lb/in.^{2}	Strength Weight Ratio	Durability	Benefit Cost Index
1. Conventional Concrete Control	0.0	150	5,000	33	Poor	1.0
2. Surface Coating (SC) Paint or Overlay	0.0	150	5,000	33	Limited	1.1
3. Coating in Depth (CID)	1.0	150	6,000	40	Good	1.3
4. Polymer Cement Concrete (PCC) Premix	35.0	130	7,500	58	Fair	0.4
5. Polymer-Impregnated Concrete (PIC) Standard Aggregate						
a. Undried-Dipped	2.0	153	10,000	49	Fair	1.4
b. Dried-Evac.-Filled	6.0	159	20,000	126	Very Good	2.0
c. Hi-Silica Steam Cured	8.0	159	38,000	240	Very Good	3.0

Table A-5. Classification of Concrete-Polymer Materials (64)(Continued)

Type	Polymer Loading wt% PMMA	Density lb/ft^3	Compressive Strength lb/in.^{2}	Strength Weight Ratio	Durability	Benefit Cost Index
Lightweight Aggregate						
a. Struct. Lt. Wt. Concr.	15.0	130	25,000	193	Very Good	2.5
b. Insul. Lt. Wt. Concr.	65.0	60	5,000	84	Very Good	2.5
6. Polymer Concrete (PC)	6.0	150	20,000	133	Excellent	4.0
Cementless						

Unit Conversions: 1 psi = 6.89 kN/m^2

1 lb/ft^3 = 16.02 kg/m^3

sealing the surface of the concrete. A number of preparation variables

(1, 2, 3) were investigated including concrete composition, drying temp-

erature, curing time, and the age of the test. The age of concrete at

impregnation or its initial strength does not appear to affect the final

strength significantly.

Three encapsulation methods (4) for reducing monomer evaporation and

drainage losses from concrete specimens prior to polymerization have been

evaluated. The methods are (1) encapsulation of the specimen in a form

during impregnation and polymerization; (2) polymerization with the mono-

mer-saturated specimens in contact with water; and (3) impregnation with

monomer followed by a prepolymer dip, rapping, and rotation during poly-

merization. Polymerization under water yields good results and appears

to be most practical. Test data indicates (4, 26, 27, 28) that it has

no detrimental effects on the properties, and may even produce beneficial

effects of increasing the monomer content and thus increasing the

strength and durability properties. The use of heated water as a means

of initiating the thermal-catalytic polymerization has been tested in the

laboratory (4) and in field impregnation of bridge decks (26) where it

appeared to be a most successful means of polymerization.

A series of 10 different concrete mixes (4) were produced to inves-

tigate the effect of concrete mix design on the compressive strength and

polymer loading of PIC. The controls averaged between 4,220 psi and

7,280 psi (29.1 MPa   and 50.2 MPa   ) in compression while the PIC

specimens exhibited essentially the same strength 21,000 psi $\pm$ 1800 psi

(145 MPa $\pm$ 12 MPa   ). This work is currently being expanded to in-

clude a wide range of mix variables to optimize product quality and

process technology. The impregnation of high pressure, steam-cured concrete with MMA has produced PIC specimens with the highest compressive strengths of up to 27,000 psi (190 MPa). Similar improvements in tensile strength and modulus of elasticity are obtained.

Temperature Effects (4). Compressive strength, Poisson's ratio, and modulus of elasticity measurements have been made at 10.4°F and -4°F (-12°C and -20°C) on samples impregnated with MMA and (10-90) polyester styrene. No significant effect due to temperature was observed. Compressive strength measurements for two monomer systems, (60-40) styrene-TMPTMA and (90-10) diallyl Phthalate (DAP)-MMA, have been evaluated to determine the high temperature structural properties and durability for application such as would be encountered in desalting plants. Preliminary design values for compressive strength, tensile strength, Poisson's ratio, and modulus of elasticity have been established for operating temperatures of 70°F, 250°F, and 290°F (21°C, 121°C, and 143°C), respectively. Data have also been obtained for steel-reinforced PIC. A high reduction in compressive strength of OSW-type concrete impregnated with (90-10) DAP-MMA was observed when compared with initial compressive strength at 289.4°F (143°C) due to chemical attack by hot brine and distilled water at temperatures up to 350°F (177°C) and decomposition of polymer by hot water. Styrene-TMPTMA appears to be a more stable system. Effects of elevated temperature are, however, observed in uncrosslinked systems; see Appendix E.

Bond Strength. There is a significant increase in bond strength due to polymer impregnation. Increase in bond strength was determined from pull out tests for No. 11 deformed reinforcement steel embedded in CP-type concrete impregnated with the two monomer systems. The average increases in bond strength at 10.4°F and -4°F (-12°C and -20°C) were 200

and 220 percent for concrete impregnated with MMA and 255 and 245 percent for (10-90) polyester-styrene impregnated concrete.

Creep in PIC (1, 2, 3, 28, 29, 30, 31). Long-term creep tests of PIC have shown that the creep of PIC is usually 5 to 10 times lower than creep under the same load for unimpregnated concrete, a property which will have a significant bearing on design of concrete structures. Even some samples prepared with MMA have indicated a "negative creep," that is, a net change in length in the direction opposite that of the load. These samples in compression get longer and samples under tension get shorter. This phenomenon has only been observed under compressive loads of 800 psi (5.512 MPa) and tensile loads of 178 psi (1.23 MPa) and 345 psi (2.38 MPa). At compressive loads greater than 800 psi (5.512MPa), creep becomes positive. Also, negative creep has not been observed for all samples. Recent work at BNL confirms the negative creep at 800-psi (5000 MPa) compressive load. The negative creep has persisted after 3 years of load. Also, low positive creep was obtained with specimens impregnated with chlorostyrene acrylomtrite and MMA-TMPTMA. High stress creep tests on MMA and chlorostyrene-impregnated specimens show low positive creep after 261 days under sustained compressive loading of 690 psi (4.8 MPa), 2313 psi (16 MPa), and 7000 psi (48 MPa). Unit deformation was found to be essentially the same in all three cases and was approximately one-tenth that of the unimpregnated controls. The same results were obtained when high temperature compressive creep tests on OSW-type concrete, used in desalting plants, were made at 7000 psi (48 MPa).

The origin of negative creep is not clearly understood. Some

speculation on a negative creep mechanism has been made by Auskern (32).
In conclusion, it was stated that experiments designed to demonstrate
negative creep have not been completely successful and only careful ex-
periments can verify the creep model and resolve apparent discrepancies.

Abrasion Tests on PIC. The improvement of abrasion resistance of
concrete by addition of polymer is not new in construction industry. Use
of polyvinyl acetate emulsions and other latexes has been shown by many
authors to increase the abrasion resistance significantly (13, 33, 34).
Use of Saran latexes in bridge decks (13) has shown an increase in abra-
sion resistance of 200 to 500 percent. In earlier work at BNL (1),
abrasion resistance was measured by the shot blast test with use of the
Ruemelin abrasion machine. Two methods were used for evaluating resis-
tance to abrasion. They consisted of measuring the total weight loss of
the specimen and average abrasion depth in inches per 35.2 oz (1000 g) of
grit. Each method yielded different degrees of improvement. Test data
indicated that a 5.5 percent methyl-methacrylate specimen is 50 to 80
percent more resistant to abrasion than the controls. Lesser improvement
was obtained with styrene specimens. Also, unimpregnated specimens that
were irradiated and heated showed improvements (28 to 57 percent). Recent
work in PIC surface treatment for highway bridge decks by Fowler et al.
(26), using the standard test procedure, showed that the abrasive resis-
tance of the treated slabs has been quite good when compared to control
specimens, showing an average improvement of 20 to 50 percent. An inter-
esting point at hand was that the greatest abraded depths were obtained in
treated slabs with little or no polymer loading in the upper portion of
the surface due to monomer evaporation. For details of work on this
program, see Appendix E.

Properties of Wire-Reinforced PIC. Little research has been done

in this field. The combination of two structural systems, PIC and wire-

or fiber-reinforced concrete, result in the most desirable material. Both

materials tend to compensate for the disadvantages when mixed together.

Some interesting results have recently been published on PIC fiber-rein-

forced mortars (35). These results show for a mortar with 2 per-

cent by volume of 3/4 in. (1.9 cm) by 0.015 in. (0.04 cm) diameter steel

fibers, an increase by about five times in maximum load and deflection

for the steel fiber-reinforced mortar over the plain mortar. When poly-

mer is added to the fiber reinforcement, another factor of five increase

results, and the failure mode changes. Now the steel fibers themselves

break, so that the presence of the polymer permits the full utilization

of the strength of the steel. Failure is no longer sudden, as in PIC

mortar; the material behaves in a plastic manner, and can absorb 50 times

as much energy at failure as the polymer-filled mortar. Recent work in

Norway (36, 37) shows similar improvements.

Work at BNL (4) using polymer-impregnated ferro-cement was under-

taken to determine the effect of polymerization on the flexural, tensile,

and durability of composite. From the limited test data it appears that

for the controls, the slabs containing the greater amount of steel have

somewhat greater flexural strength. However, after polymer impregnation,

there appears to be little difference in flexural strength, even though

one set of slabs has more than twice the wire content.

The agricultural research service, U. S. Department of Agriculture,

studying the feasibility of using wire-reinforced PIC for precast

panels in low-cost housing, stated in their second topical report (38)

that four- to five-fold increases in flexural and compressive strength have been attained with 2 to 8 percent steel fiber reinforcement and monomer impregnation. In conclusion, the authors generally agree that wire-reinforced PIC can result in a cementitious composite material which is strong, flexible, tough, impermeable and corrosion resistant.

Partially Impregnated Concrete (Surface Treatment) (4, 26). Experiments to partially impregnate concrete with selected monomer systems have been successful and indicate potential uses for improving the durability and skid and abrasion resistance. Also, evaluation of surface treatments, performed on 6-in. x 10-in. x 10-in. (15.24-cm x 25.4-cm x 25.4-cm) lab specimens and 6-in. x 12-in. x 12-in. (15.24-cm x 30.48-cm x 30.48-cm) specimens cut from field-treated slabs showed that differential expansion due to expansion of PIC being greater than ordinary concrete up to 25 percent did not cause any spalling of the top surface. Sopler et al. (28) undertook an experimental program to study the preparation and properties of partially impregnated PIC. Significant findings were:

1. Variations in the original concrete quality and its treatment prior to soaking did not radically affect the compressive strengths obtained for the polymer-impregnated specimens, but did influence the speed of the drying and soaking stages of production, as well as the total monomer loading.

2. A controlled, uniform depth of polymer penetration was obtained by varying the duration of soaking.

3. The stress-strain curve for the partially impregnated polymerized specimens was essentially linear up to from 70 to 75 percent of failure and deviated from linearity by only 10 to

15 percent at failure.

4. No significant shrinkage or creep was measured on PIC or on corresponding dried and sealed concrete specimens.

5. For the lowest polymer loading, corresponding to a 5-min duration of soaking, both the compressive and splitting strengths of the PIC specimens were less than those obtained for the dried concrete specimens. This result indicates that the polymer-impregnated shell and the inner core did not function as a unit at failure. Spalling of the outer shell, however, was not observed during testing.

6. The limiting sustained load capacity for PIC prisms was between 70 and 75 percent of their ultimate short-term strength.

Polymer-Impregnated Lightweight Materials (30, 39). Lightweight concrete is prepared by using porous rather than dense aggregates in the concrete mix. Some typical lightweight aggregates are prepared by expanding clay, shale, slate diatonaceous shale, perlite, obsidian, and vermiculite through the application of heat. Others occur naturally as pumice, volcanic cinders, and diatonite; some are prepared from industrial cinders. The strength of lightweight concretes generally varies as the density. The strength of concretes made from expanded shale and clay is relatively high and compares favorably with that of ordinary concrete. Perlite and vermiculite concretes are very weak, typically 50-500 psi $(344.5 - 3445 \text{ kN/m}^2)$.

Strength of Polymer-Impregnated Lightweight Concrete. The very lightweight concretes have been considered for applications such as housing panels and highway signs and lamp posts. They are at present

too weak for these applications. However, on polymer impregnation, the strength is improved to an acceptable level and potentially useful material results. Fine, very lightweight concretes have been impregnated and tested in BNL under the auspices of the U. S. Atomic Energy Commission (30, 39). All the material contains considerable polymer, ranging from 31 volume percent for a foamed glass concrete to 49 volume percent for a perlite concrete. Normal concretes contain 12-15 volume percent polymer. The strengths of all the impregnated concrete increased over the unimpregnated materials. In general, the unloaded samples had compressive strengths less than 1000 psi (7 MPa) and for one perlite concrete around 100 psi (690 kPa). Most strengths of loaded specimens were in the range of 3000-5000 psi (21-34 MPa), with one perlite sample showing a strength of 8000 psi (55 MPa) and a glass aggregate sample and the mearlcrete sample achieving 1000 psi (7 MPa). A model for the strength of polymer-impregnated lightweight concrete which is different from ordinary concrete has been developed (39) since the strength of the former can be seriously underestimated by using a simple porous solid model for perlite concretes. The possible reason for this serious discrepancy may be due to aggregate-polymer interaction resulting in a strong aggregate, and a system to which the simple porous solid model no longer applied. In conclusion then, it appears that the improvement in strength of lightweight concrete depends to a large extent on the polymer-aggregate interaction.

Discussion on Mechanicsl Properties of PIC. Perhaps the most dramatic demonstration that a fundamental change in the nature of concrete after polymer impregnation takes place is to observe a PIC specimen

fail in compression ($\underline{1}$, $\underline{2}$, $\underline{3}$, $\underline{31}$). The normal concrete on failure exhibits a few cracks but essentially remains in one piece. However, PIC completely shatters on fracture. What is most significant about the fracture is that the cracks pass through, not around, the large aggregates. This suggests that the role of the polymer must be, at least in part, to strengthen significantly the bond between mortar and aggregate.

Further evidence of the change in the nature of PIC is the stress-strain relationship ($\underline{31}$). The normal concrete shows typical nonlinear stress-strain behavior from nearly the start of loading; at fracture, the stress-strain curve is nearly horizontal. The PIC sample behaves much differently. The stress-strain curve is linear until 75 percent of the fracture load and at fracture there is relatively little deviation from linearity. PIC thus behaves essentially elastically, which will have an important bearing on design criteria. The linearity of the stress-strain curve supports the suggestion that part of the role of polymer is to improve mortar-aggregate bond.

The approximate proportionality between the elastic modulus and the square root of compressive strength, known to exist for plain concrete, was also found to apply to polymer-impregnated concretes up to the maximum strength tested of 23,000 psi (160 MPa) ($\underline{27}$, $\underline{31}$).

Probably the most critical single factor affecting the compressive strength of PIC (at least PIC containing a glassy polymer) is the degree that the pores of the concrete are filled ($\underline{27}$). There is a very strong dependence of strength on polymer loading for any PIC system; the maximum strength is obtained with the maximum polymer loading. The effects of increasing polymer content on the stress-strain curve are:

1. To increase the linear portion of the stress-strain specimen

2. To increase the strain at failure

3. To increase the strain energy stored by the specimen.

These results confirm observations noted by Auskern and Horn (40) using specimens in compression and by Flagsman et al. (35) for the load deformation curve in flexure.

Probably the second most important factor affecting the strength of PIC is the concrete itself. Generally, unimpregnated compressive strengths of concrete range from 2500 psi (17 MPa) to 9500 psi (66 MPa). The final strength ranges close to 20,000 psi (140 MPa). However, it is independent of initial strength (1, 2, 3, 27, 41).

The greater the initial strength of concrete, the greater the PIC strength, although the relative increase is greater for weaker concretes (3, 27).

The change in elastic modulus may be explained by considering the composite to consist of two phases; an aggregate phase and a polymer-impregnated cement paste phase. The modulus of the polymer cement phase is determined by the porosity (27).

The polymer acts as if it were an equivalent volume of cement paste. The ability of the monomer to penetrate the microstructure of the concrete would therefore appear to be vitally important in producing a composite of minimum porosity. The properties of the polymer in the micropores could thus control the properties of the concrete polymer. The effect of the polymer on the microstructure may then account for the synergism in compressive strength and elastic modulus obtained through polymer impregnation (27).

Recent work on concretes cured by high pressure steam achieved compressive strengths greater than 30,000 psi (206.7 MN/m^2). Porosity measurements show that the average pore size of steam-cured cements is greater than that of water-cured cements although porosity was found to be the same in both cases, thus leading to more efficient polymer loading (4, 31).

The properties of concrete-polymer materials are also controlled by the particular polymer used (27). However, out of all polymers, MMA and MMA+10 percent TMPTMA produce the highest compressive strengths. The origin of all these polymer differences is not apparent. A number of possible mechanisms may be advanced to explain the role of the polymer in changing the properties of concrete. The extent of the changes may be determined by the ability of the polymer:

1. To act as a continuous, randomly oriented, reinforcing network

2. To increase the bond between the aggregate and the cement paste

3. To repair microcracking in the cement paste

4. To absorb energy during deformation of the composite system

5. To penetrate and reinforce the micropores of the cement paste

6. To bond with the hydrated or unhydrated cement.

The repair of microcracking at the aggregate-cement interface is taken to be included in the mechanisms (24) above. Auskern (39, 42) has suggested that the second explanation probably forms the dominant mechanism. Flagsman et al. (35) attributed the increase in strength of glass and steel fiber-reinforced mortars to improved filament to matrix bonding due to polymer impregnation.

The concentration of calcium hydroxide, as determined by DTA, is

lower in preformed PMMA cement pastes compared with the pure cement paste. This suggests that a chemical reaction between calcium hydroxide use and organic monomer or polymer is a possible cause of increase in strength (41).

No significant differences were apparent between the thermal-catalytically polymerized and the radiation polymerized samples (41).

At higher temperatures (over 212°F [100°C]), the polymer-treated mortar shows a small decrease in compression strength, probably because of thermal deterioration of the polymers. The resistance against higher temperatures depends on the monomer system employed. Thus MMA composites showed greater thermal stability than those formed with styrene. Cross-linking monomers therefore offer promise for higher temperature service (41).

Small samples of PIC have been tested at BNL (4) to evaluate in preliminary fashion the burning characteristics of different polymers. As expected, all samples ignited appeared to contribute fuel to the combustion and continued to burn for varying periods of time after removal of flame. On the basis of the previous experience in plastics industry, it would appear that concrete-polymer material containing fire retardants and meeting existing building specifications can be produced. However, if the strength of the PIC is to be taken into account, thorough evaluation of decrease in strength due to fire should be done before fabricating structural elements.

The modulus of rupture is strongly dependent on polymer loading, type, and cure. It is anticipated that the same factors that affect the compressive strength of PIC will affect the tensile strength and modulus of rupture (31).

Sopler at al. in their study of partially impregnated PIC (28) observed that although the strength of the PIC specimens is not influenced significantly by the original concrete quality, the preparation process is affected. The rates of drying and monomer pickup increased with decreasing concrete quality. In terms of the PIC preparation, the use of a lower quality concrete would be less expensive and would speed up production, but savings must be weighed against the added cost of monomer. They have also observed that even without vacuum treatment, the penetration depth was remarkably uniform and that the initial monomer pickup was very rapid to the extent that approximately 38 percent of the loading occurred within the first 5 min and only a small increase in loading occurred after 8 hr, with loading rate decreasing continuously. However, this small increase in loading occurring after longer periods of loading had a significant influence on the depth of impregnation and consequently resulted in high increase in the compressive and split-tensile strengths.

Work done by Tazawa and Kobayashi (43) shows:

1. Mechanical properties of PIC are influenced by self-stress
    generated in the material, possibly due to shrinkage caused by
    polymerization and the difference in thermal coefficients of
    expansion of polymer and concrete. Annealing and addition of
    a plasticizer are useful methods in reducing this self-stress.

2. Improvement of strength can be analyzed by Griffith theory
    and uniformity of PIC by Weibull's theory. Both of these
    analyses support impregnation as a reasonable method to
    improve mechanical properties of cementitious material.

3. In order to maintain a high quality in products, conditions of

drying, evacuating, impregnation, and polymerization should be
suitably selected and the mix proportion of the base material
should be optimized with reference to the most important prop-
erty required for its use.

Work done since 1969 at FCB, Technical University of Norway (44, 45),
confirmed the observations of different authors and may be summarized as
follows:

1. A poorer concrete quality will give:

    a. reduced necessary drying time

    b. shorter dipping time

    c. increased monomer loading with increased penetration.

2. There are very little differences in the final compressive
   strengths and modulus of elasticity of different quality con-
   cretes.

3. A reduced curing time will reduce necessary drying length,
   increase monomer loading and penetration at the expense of
   a little more monomer, but will not effect final strength.

4. A partial penetration treatment would give a marked increase
   in carrying capacity for sections up to 5.9-7.87 in. (15-20 cm)
   with a very high increase in surface strength as compared to
   fully penetrated PIC.

5. Drying of the specimen is very important. Small amounts of
   water left in the pores will give big reductions in the final
   strength of PIC.

6. Remarkable improvement in properties of concrete observed by
   polymer impregnation. Improvements are in the order of those

shown in Table A-3.

7. Temperature treatment of PIC confirms the results obtained at BNL (4). Further, specimens heated and then cooled down to ordinary room temperature lost no strength during this process if the heating temperature was less than 424°F (200°C). It appeared that the specimens gained strength from this heat treatment. For temperatures above 424°F (200°C), the polymerized monomer evaporated and the specimens attained about the same weight and strength as before dipping.

8. Treatment of lightweight concrete produced only double the strength of similar untreated specimens. This may be attributed to the failure of the treatment to influence the strength of the light aggregate used, thus reducing potential strength of lightweight PIC.

9. Testing of 12 treated ordinary reinforced concrete beams indicated at least a doubling of the failure load both in shear and moment.

10. A number of curbstones were tested in bending using a point load at the center of a 36-in. (90-cm) span. Test results indicated a significant increase in strength over the 28 days reference specimens.

Dahl-Jorgensen (46) working with MMA-impregnated concrete and latex (Sarabond) and diacetone diacrylamide modified PCC has found:

1. Even though full penetration was obtained for the specimens, full polymerization was not obtained due to the absorption of benzoyl peroxide in the outer layer of concrete. A possible reason

suggested is the great affinity of benzoylperoxide to concrete. This was also confirmed by Mattisson and Steinberg (4, 36, 37, 44).

2. By adding latex, 25 percent by weight of cement, an increase in strength of 50 percent resulted.

3. PCC with diacetone diacrylamide responded negatively to both heat treatment and moisture curing. The specimens lost all strength, crumbled, and fell apart. Possible reason cited is that hydration and polymerization are incompatible simultaneously.

Mattisson (36, 37) working with fibrous PIC found the all-round strength increment of five to six times the normal concrete strength. Significant findings included in the progress reports are:

1. Studying the PIC in a scanning-electron microscope, the space between the polymer and the cement could not be detected at a 26,000 times magnification, suggesting a good bond between polymer and cement.

2. Modulus of rupture and other properties decrease by 14 percent when tested at higher temperature of 167°F (75°C).

3. In x-ray investigation of specimens under zero and successively increasing loads, it was observed that the microcracks in the concrete were reinforced by polymer.

4. There was an uneven distribution of fibers and cracks developed in areas of low concentration of steel fibers.

5. Deterioration of glass fibers (E-type) in concrete could not be eliminated by styrene impregnation; however, the process was slowed down.

Auskern, discussing the application of models like Neilsen's

adhesion-no adhesion models for ideal particulate filled systems (25)

showed that the analysis of the modulus and the tensile and compressive

strengths of concrete and concrete polymer is, of course, limited by

the validity of the assumptions made, by the lack of extensive experi-

mental data, and by the limited theoretical treatments of compressive

strength of composite materials. In spite of this, the simple models

used gave fairly good agreement to the experimental results.

Some of the views of the participants in the ACI fall convention

in Florida (1972) have already been mentioned above. Additional views

relevant to properties of PIC are (47):

1. Manning stated that (a) porosity of concrete is important in

    properties of PIC; (b) failure stress and modulus of elasticity

    are maximum for specimens that are dried; (c) for PIC, failure

    stress is a function of polymer properties; and (d) if all the

    monomer is not polymerized, destructive reaction may occur at a

    later time causing deterioration and reduction in strength of

    polymer concrete.

2. Tazawa stated that (a) maximum moisture content allowable prior

    to impregnation should be 0.5 percent for best results; and (b)

    by dissolving the PMMA of PIC, using methyl ethyl ketone, only

    60 to 70 percent of polymer could be removed, suggesting that

    there is a chemical or mechanical bonding between the cement

    matrix and the polymer causing the increase in strength.

3. Narayan Swamy stated that he investigated use of small quanti-

    ties of polymers in emulsified form in concrete mixture along

with fiber reinforcement. He claimed that be obtained (a) reduced porosity; (b) improved wet-dry stability; (c) reduced long-term deformation under load (creep); (d) resistance to impact increased by adding organic fibers and the tensile strength increased by steel fibers; (e) improved fire resistance and reduced temperature effects; (f) environmental conditions have strong influence on properties; and (g) curing conditions have profound effects on polymer-fiber concrete systems.

4. Albertsen, investigating PIC for underwater vessels, stated that (a) PIC was brittle but highly predictable under hydrostatic loading; (b) PIC behaves elastically and there is no permanent deformation in cyclic loading; and (c) creep is much less than for ordinary concrete.

5. Sopler said that modulus of elasticity was greater for ordinary concrete and independent of properties of original concrete. Also, the amount of curing of concrete has little effect on strength of PIC.

Investigations to develop reliable methods for quality control of concrete-polymer products are being continued (4); to date, no single, simple, convenient, nondestructive technique has been identified which meets the unique requirements of concrete-polymer materials. Promising methods under test include acoustic impact, dielectric constant and electrical resistivity measurement, sonic velocity, and the impact hammer.

Conclusions and Recommendations

The authors generally agree that the work to date has indicated that

remarkable improvements in the structural and durability properties of concrete can be obtained by monomer impregnation and in situ polymerization by either radiation or thermal-catalytic means. However, it is quite likely that at present time the ultimate strength for PIC has not been reached. One reason for this is that a complete understanding of the interrelations between concrete, porosity, and polymer has not been achieved. Hence, the following recommendations are generally made for any future program:

1. Investigation should be made to obtain a better understanding of the major factors controlling the physical and mechanical properties of concrete-polymer materials. Important parameters include the effect of variation of concrete composition, aggregate type and size, method of curing, and polymer loading.

2. Experiments should be performed to determine the effects produced by the addition of additives to monomer prior to impregnation. Additives to be tested should include fire retardants, wetting agents, coupling agents, plasticizers, and thixotropic materials.

3. Further work should be done on evaluating PC and PCC and on the use of both radiation and thermal catalytic techniques of polymerization. In addition, comprehensive strength data should be obtained on all concrete-polymer systems to yield data on maximum and minimum strength curves for a given monomer.

4. Fundamental studies on the basic nature of concrete-polymer materials should be continued to determine areas for further improvement.

5. Investigations should be continued to develop reliable methods for the quality control of concrete-polymer products.

6. Design code requirements and preliminary process and product designs should be formulated using data for prototype and full-scale units to obtain systems for yielding optimum product quality and process technology at minimum cost.

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FIELD APPLICATIONS

General

Field applications of polymer-modified concretes, as described
in the literature, are briefly reviewed below. Unfortunately, there
has been only one trial field application of polymer impregnation of
a bridge deck to our knowledge, and that has not yet been described
in the literature (Sag Harbor Bridge---Brookhaven National Laboratory
and Federal Highway Administration project). Therefore, the applications
cited below do not relate strictly to the problem at hand, but do
serve to illustrate the breadth of problem areas in which polymer-
modified concretes have found application.

Some Field Applications

Fields of application of plastic concretes containing poly-
vinyl acetate and propionate, and butadiene-styrene copolymer were
investigated in 1965 by Guden in Germany (1).

Various uses of polymer-cement concrete and polymer-concrete
were proposed by Solomatov (U.S.S.R.) in 1967. They are summarized
below (2):

Polymer-cement concrete:	Seamless floor coverings
	Surfaces for roads, airfields, etc.
Polymer-concrete[*]:	Coating or covering of concrete building
	structures and inner surfaces of concrete
	pipes against water penetration and chemi-
	cal corrosion.

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[*]In which organic polymer is the only binder.

A-66

Steel-polymer-concrete supports for

underground tunnels.

Underground conduits.

Mine shaft reinforcement.

The use of plastic concrete with furan resins for protecting mountain water intake structures from bottom drifts was studied by Elshin (3), and practiced in Russia as early as 1962. Dam surfaces, 2368 ft^2 (220 m^2), was coated with this material and showed improvements. Plastic concrete was also used for protecting a steel reservoir for holding NH_4Cl solution. There was no decay of the plastic concrete caused by chemical corrosion after 10 months (3).

Shakhtakhtinskaya, Zemskova, and Mirzoev (U.S.S.R.) found that concrete containing ED-6 resin and igneous pyrites was a suitable construction material for marine oil drilling operation (4).

Design and construction of structures applying polymer concretes in highly corrosive environments were described by Moshchanskii and Paturoev of the U.S.S.R. (5).

A plastic-concrete mixture consisting of polymeric binders, mineral components, and 5-12 percent (of mineral materials) atactic polypropylene was found to be suitable for road surfacing in Russia by Gokhman, Gezentsvei, Petrova, and Frantsuzova (6).

A number of potential applications of polymer-contained concretes have been developed in the United States in recent years. Recommended applications have been seen in the society publications, private patents, and reports of government joint programs. They are summarized below.

Investigations were performed in a joint program carried out by the Brookhaven National Laboratory and U. S. Bureau of Reclamation with the support of the Division of Isotopes Development of the U. S. Atomic Energy Commission, the Office of Saline Water, and the U. S. Bureau of Reclamation. The following investigations on concrete-polymer applications have been made.

Pipe Applications

Due to the improved structural properties, durability, especially against water corrosion, the concrete-polymer pipes are more advantageous than ordinary ones (7, 8).

The impregnated asbestos cement pipes were found to be much stronger and more water-resistant (54 percent greater load capacity and 86 percent reduction of water absorption as compared with controls) than those not impregnated (9).

Polymer-impregnated concrete (PIC) draintiles have been under laboratory and field tests. PIC sewer pipe has been installed in the city of San Diego sewer system (10).

Housing Applications

Concrete-polymer materials are useable for a number of housing applications. These include (8, 9, 10, 11):

Columns and beams

Walls

Light-weight aggregate concrete products

Floor panels

Building blocks.

Marine Applications

The greatly improved structural properties, and negligible water absorption and permeability make PIC an excellent material for underwater applications. In Port Hueneme, California, a series of 16-in. (40.64-cm) outside diameter by 1-in. (2.54-cm) wall hemispheres are being impregnated and evaluated. Low vapor pressure monomers have been found to be mostly suitable for sphere impregnation (8, 9, 10).

Highway Applications

As a result of large improvements in freeze-thaw durability and abrasion resistance, applications for bridge decks, curbing, bridge approaches, and highway intersections have been suggested. If techniques for field applications are economically feasible, presumably, impregnation of highways would result in large improvements in strength and reduction in maintenance costs (12, 8, 9).

Antifragmentation Applications

Based on the results of ballistic limit tests, concrete-polymer materials suggested several potential applications. Protection barricades and storage bunkers for explosives and chemicals could be made smaller or capable of withstanding greater forces. Military applications in field fortifications would also be feasible if field-operated equipment can be developed (8, 9).

Desalination Plant Applications

For sea water desalination plants, ordinary concrete is subjected to severe corrosion even with protective coatings. An impregnation of polymer deep into the surface of the concrete to form a concrete-

polymer coating could possibly provide adequate corrosion resistance with the necessary strong bonding between the protective polymer material and the concrete base (13, 8).

Other Applications (8)

Other applications include prestressed concrete pressure vessels, and aesthetic applications such as color dyeing of floor surfaces.

Hop and Miodynski reported that polymer-mineral mixtures with synthetic resin as the binding medium were applicable for building construction (14).

Polymers and some other organic materials have been used in conjunction with cement, mortar, and concrete in the form as protective coatings for quite a long time in the United States as well as in other countries (15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30).

Resins

Application of a polymer cement composite consisting of polyester resin and portland cement was studied in England by Nutt (31).

Resins were used as adhesion for repair and protection of concrete bridges and dams; application was also brought to nuclear reactors and masonry structures. Techniques involving impregnation and injection were tried (32).

Synthetic resins were also applied to building construction and maintenance (33).

Davydov, Solomatov, and Shuidko (U.S.S.R.) (34) found that epoxy polymer concrete is useful for rewaterproofing of the joints in the reinforced concrete structures. In hydraulic-engineering

structures, epoxy polymer concrete could be used for "integrating" high-

duty joints; for ensuring watertightness of tunnels, galleries,

pipes, and underwater structures; for protecting structures in

aggressive media, etc.

Hahamovic and Knezevic of France made their "artificial stone"

by applying asbestos waste as the filler and polyester resin as the

binder (35).

The Polish engineer, Pierzchala, recommended polyvinyl acetate

cement pastes and mortars for various building construction uses

including shotcreting, injecting, dilation joint, inner plastering,

and plastering of concrete and reinforced concrete prefabricated

elements (36).

Nutt found that cost restricts a widespread use of polymer

cement materials to thin coatings of concrete, particularly for

industrial floors. He also suggested some other uses of polymer

cement mortars such as adhesive component in composite wall panels,

bonding agent and protective surface for wood-wool slabs, sealing

grout for leaking iron gas mains, setting agent of thick section

stained glass into framed windows, etc. (28).

In 1965 Okada reported (37) that epoxy resin had been widely used

in Japan as admixture of mortar and concrete or as a protective

coating of concrete structure surfaces. It had also been used as

concrete gluing agents. Polyvinyl acetate, polyvinyl

chloride , polyester, and various synthetic rubbers had also been

tested and applied in conjunction with cement, mortar, and concrete

in Japan, among them polyvinyl acetate was found to be effective

in increasing the workability and waterproofness of concrete;

polyester was useful for repairing cracks in concrete structures by

injection.

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DRYING AND PREPARATION

General

Paraphrasing the description presented by Harmathy (1), the
drying of a concrete slab by the application of heat proceeds as follows:
During the initial phase of drying a slab having a high moisture
content, the average moisture content will decrease at a constant,
but rapid, rate (the "constant rate" period). The rate of water loss
during that period will be approximately the same as the rate of
evaporation from a free water surface under the same environmental
conditions. The temperature of the slab will also remain constant
during the constant rate period, and if the drying takes place in
a rapid air stream, it is equal to the ambient wet bulb temperature.
Moisture concentrations will be only slightly higher in the center
of the slab than at the drying faces during this period. The prin-
cipal means of moisture migration during the constant rate period is
convection (capillary flow), with evaporation taking place entirely
at the slab faces. Continuous, liquid water threads must exist in
the capillaries to maintain convective flow. As the water threads
begin to break up, the so-called "critical point" is reached. From
this point on, the rate of moisture loss decreases with time ("falling-
rate" period). At the critical point, the central cores of the
capillaries are occupied by the gaseous phase and an increasing per-
centage of the liquid phase around the perimeters in being held by
adsorption on pore surfaces. Thus the liquid phase is nearly immobile
and most of the moisture migration takes place in the gaseous phase,
partly by diffusion, but mainly by a complex convection mechanism

induced by pressure gradients due to alternate evaporation and condensation. During the falling rate period, the temperature of the slab increases and the moisture content declines to the levels of the drying environment, both at declining rates.

Pihlajavaara has presented a comprehensive review of the fundamentals of drying of concrete (2) and a tentative semi-quantitative prediction of the drying of concrete with forecasts of the equilibrium and initial moisture contents (3).

Swenson and Sereda (4) developed an equation for the coefficient of moisture transfer for the flow of water in concrete under the influence of a constant temperature gradient.

Drying Preparation Relative to Polymer-Impregnated Concrete

Epoxy resin with a viscosity of about 1200 cp at normal temperature was used to impregnate the surface layer of concrete by lowering the viscosity by heating to approximately 40-60 cp (40 x 10^{-3} - 60 x 10^{-3} Pa.s) (5). The concrete was also heated and dried to approximate the same temperature. The depth of impregnation was about 1 in. (2.5 cm).

Efforts were made by BNL and USBR researchers toward obtaining a maximum monomer loading in the concrete specimen. The most important factor to achieve this was found to be the removal of free water from the specimen. This was done by either vacuum drying or heat drying.

Vacuum Drying. Cylinders, 3 in. x 6 in. (7.6 cm x 15.2 cm), were evacuated in a small chamber to $\approx$ 3 in. Hg (10 kPa) at 68°F (20°C). The specimen was periodically removed from the vacuum chamber

and weighed; the weight loss (removal of free water) was recorded as a function of vacuum time. A sample containing 3.4 wt. percent of free water revealed a rate of weight loss over 96 hr of 0.007 percent per hour.

Thermal Drying. Thermal drying was found to be more practical than the vacuum method. A large capacity, forced-draft type oven was used. Weight loss was again a function of drying time. The data indicated that 100 hr were required to obtain equilibrium weight when drying at 221°F (105°C), while only 8 hr were needed when drying at 302°F (150°C).

Evacuation of the specimen was done after drying and before soaking the specimen in monomer. The monomer viscosity, its wetting properties, and the type of concrete influenced the degree of monomer penetration through concrete. Application of a constant pressure over the monomer during soaking period significantly increased the monomer loading in the evacuated specimens; however, the pressure had little effect for nonevacuated specimens. Maximum and complete monomer loading (with MMA) was achieved after 1-3 hr soak time with pressure and 5 hr without pressure.

There does not appear to be anything in the literature regarding surface preparation that would be pertinent to impregnation of concrete bridge decks. Considerable consideration will have to be given to this problem, especially in the case of old bridge decks. Obviously, grease, oil, road dust, and other foreign materials are going to have to be cleaned from the surface of a deck before impregnation can be attempted. Historically, the methods for cleaning concrete surfaces prior to applying surface coatings of

various types include lye wash to saponify oils and greases, acid

(muratic) washing, sand blasting, and detergent washing. Some of

these may be applicable for the case at hand.

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PORE SYSTEMS IN CONCRETE AND CEMENT PASTE

General

When water is mixed with portland cement, chemical reactions take place which produce complex calcium silicate and aluminate hydrates and calcium hydroxide. The predominant compound produced is the tricalcium disilicate hydrate called "tobermorite." This mineral occurs in the form of thin sheets separated by monomolecular layers of absorbed water. The sheets are usually crumpled or rolled into tight "scrolls." The internal surface area of the mineral is enormous (8.78×10^6 in.^{2}/oz [2×10^6 cm^2/g]), causing it to take on the properties of a solid colloidal dispersion or gel.

The "interlayer" or "gel" water, held in the cement gel by adsorption, is largely responsible for shrinkage or swelling of cement paste and concrete when subjected to drying or wetting and the creep properties of hardened concrete. It comprises about 25 percent of the gel volume. In spite of the fact that the gel water is only loosely bound by van der Waals forces and can be driven off by heating to 221°F (105°C), it is not capable of hydrating fresh dement grains. Gel pores are extremely small, averaging perhaps 7.8×10^{-6} in. (2×10^{-7} cm) in diameter.

The hydration of fresh portland cement grains takes place in water-filled cavities remaining after completion of the initial "bleeding" stage. As hydration continues, these cavities continually decrease in size until at the essential completion of hydration they reamin as a network of fine capillary pores. The sizes of the capillary pores and the extent of the capillary system depends

entirely on the water to cement ratio of the mix and the degree of hydration obtained. However, it is certain that the capillary pores are much larger than the gel pores, ranging from the upper limit of the gel pore sizes to 3.9×10^{-2} in. (9.9×10^{-2} cm). The capillary system in a completely hydrated paste may occupy 10 to 20 percent of the paste volume (3 to 6 percent of concrete volume).

Finally, most bridge deck concretes contain purposely entrained air void systems to reduce the vulnerability of the concrete to frost damage. These air void systems consist of spherical bubbles averaging 1.97 to 3.9×10^{-3} (5 to 10×10^{-3} cm) in diameter and constituting about 6 percent of the volume of the concrete.

All concrete mixtures also contain a small percentage of large "entrapped" air bubbles, and poorly compacted mixtures may contain large voids referred to as "honey-combing." However, for most concretes used in bridge decks this latter type of void constitutes a small percentage of the total void system.

Relation of Void System to Polymer Impregnation

In terms of polymer impregnation of concrete, the capillary pore system is probably the only one of consequence. The gel pores are probably too small to admit monomer molecules. The entrained and entrapped air voids are generally isolated cavities surrounded by gel, and, even when intersected by capillaries, they are too large to compete with them for wetting fluids. In the case of vacuum impregnation, air voids that intercept capillaries may be filled. However, whether or not the air voids become filled in the impregnation process will probably have no effect on properties of PIC, especially durability properties.

The void system of the aggregates used in the concrete mixture may have an effect on the polymer impregnation of the concrete. The porosity of common aggregate materials may vary from near zero to 10 percent or more. The capillaries or interconnected voids in aggregates will almost invariably be larger in diameter than those in the cement paste. Thus in capillary competition, the aggregates will usually lose to the cement paste, and the aggregates may, therefore, not become impregnated unless vacuum impregnation is employed. As in the case of the entrapped and entrained air voids, this is not considered to be a point of significant consequence, since with the capillaries in the cement paste filled with polymer, the aggregates are, in effect, encapsulated.

Solomatov (1) showed that the porosity of concrete has a significant effect on the degree of penetration of the monomer. He found that the depth of impregnation could be increased by changing the nature of the concrete porosity, i.e., by increasing the initial penetrability.

Manning and Hope (2) found that the compressive strength and elastic modulus of the polymer-impregnated concrete are a function of the total porosity of the concrete after polymer impregnation. Three concretes of different porosities were tested.

Gebauer and Coughlin (3) of Lehigh University examined the microscopic structure of polymer-impregnated mortar which revealed the presence of polymer in the voids. Pores partially and completely filled with polymer were seen by using light microscopy. The samples studied were mortars impregnated with either styrene or MMA and

polymerized either by heat or by radiation. A lower content of calcium hydroxide was detected in cement paste impregnated with MMA than in pure cement paste or styrene-impregnated paste.

At the beginning of the experimental work at BNL and USBR (4), mixes used did not contain sand passing through No. 200 sieve because of the intention of obtaining a concrete that is more porous and more amenable to a greater degree of impregnation by monomer. Subsequent tests of this concrete indicated that its absorption and permeability characteristics were not greater than those normally expected for similar concrete containing the minus No. 200 sieve-sized sand. In view of this, and in order to have test data on a concrete similar to that which would be produced commercially, the minus No. 200 sieve-sized sand fraction was included in later mixes.

Recent work at BNL (5) showed that a very dense cement paste (water/cement ratio = 0.35 by wt.) having a porosity of 26.6 percent when subjected to impregnation by MMA had a resultant porosity of 7.4 percent. In other words, 72 percent of the pore volume was filled with MMA.

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SKID RESISTANCE

General

The skid resistance of portland cement concrete pavement is
governed largely by the surface texture of the pavement and the
characteristics of the fine aggregate (1, 2, 3). Texturing
provides escape channels for the removal of water from under the
tire tread to prevent hydroplaning. The fine aggregate provides
an abrasive microtexture. To assure the presence of long-term
skid resistance, the texturing applied to the surface of the
pavement during construction must be durable. This requires strong
and abrasion-resistant concrete.

Relative to Polymer-Modified Concrete

Polymer impregnation should assist in the retention of skid
resistant properties by strengthening the concrete and thus reducing
loss of surface texture under traffic. However, it may reduce, somewhat,
the effectiveness of the microtexture.

The use of concrete-polymer material for highway applications
has been studied at BNL with the support of U.S. Department of
Transportation (4). Among many factors determining the concrete-
polymer materials' highway applicability, skid resistance is an
important one. When polymers are induced in the concrete, one
might expect a decrease of skid resistance because of the smooth
surface properties of the polymer along; however, this was not the
case according to the BNL progress report.

Skid resistance measurements were made with use of the
British Portable Tester according to ASTM Method E 303-69. Specimens

were 14-in. x 14-in. x 3-in. (35.6-cm x 35.6-cm x 7.6-cm) concrete

slabs, partially impregnated with 50-50 polyester-styrene mixture,

and thermally polymerized at 167°F (75°C). The top surface was

broomed with the grain in one direction. Test data parallel to the

grain showed slightly less resistance to skidding than the unimpreg-

nated controls, while the test data against the grain indicated

essentially no difference.

The depth of penetration had little effect on the resistance,

since this is essentially a surface property.

In Japan, experimental studies on the skid resistance of

concrete pavement by surface treatment using epoxy resins and

scattered siliceous sand were made by Okada. In this test the

epoxy resin treatment was done in cold weather of temperature

less than 35.6°F (2°C); however, no test results were disclosed (5).

Extensive, more recent studies by Fowler et. al. (6) show that the

impregnation of highway-type concrete with PMMA resulted in a significant

improvement in the skid resistance (as measured by the British portable

skid tester) of dry, unworn specimens, and in a slight (5 to 10 percent)

improvement (while wet) relative to unimpregnated controls after wear and

polishing had occurred.

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PERMEABILITY

General

For a given monomer system and impregnation method, the degree of impregnation achieved is a function of the permeability of the concrete. The total polymer loading achieved depends, in addition, on the accessible porosity of the concrete.

Porosity was discussed in an earlier section of this report. The permeability, or rate of flow of a fluid through a porous solid per unit of pressure differential and thickness, increases with increasing pore size and pore volume and decreasing tortuosity of the interconnected pore system. It also increases with decreasing viscosity of the permeating fluid. Permeability may be augmented by capillarity, which is dependent on pore size and the "wettability" characteristics (contact angle) of the solid by the permeating fluid (1, 2, 3). Capillary condensation, discussed earlier, can also play a part in permeation of a solid by a fluid. It is dependent on pore sizes, temperature, and the vapor pressure of the fluid.

Concrete is permeable to water and water vapor (4, 5, 6, 7, 8). However, the water permeability of concrete in which the cement is not completely hydrated will decrease with time from constriction of the capillaries due to further hydration of the cement by the permeating water. The major factors relative to the concrete mixture and placement that affect permeability are water/cement ratio, maximum size of the coarse aggregate, and length of wet curing period. The most important of these is water/cement ratio. Several techniques

have been developed for determining capillarity (9) and permeability (10, 11, 12, 13).

Regarding Polymer-Modified Concrete

In 1965, Guden of Germany found that plastic concretes made of polyvinyl acetate, polyvinyl propionate, and butadiene-styrene copolymer had higher water resistance than ordinary cement concrete (14).

Okada of Japan reported at the 1965 RILEM (Reunion Int. Lab. Essais Rech. Mater. Constr.) symposium that epoxy, polyvinyl acetate, polyester, PVC - polyvinylidene chloride copolymer, and NBR latex (acrylonitrile-butadiene copolymer) were used in Japan for binders, glues, and coatings of concrete. Permeability of various resin concretes were studied (15).

In Russia, Davydov, who viewed and recommended early in 1958 on the value of concretes with organic polymers as the only binders, disclosed his investigations of property changes of concrete and reinforced concrete by polymers in 1969. He indicated that property changes could be controlled to meet specific needs by properly determining the composition and quantity of concrete components including polymers. The concrete he made with polymer was reported to be less susceptible to cracking or surface deterioration than the conventional concretes. It is presumable that the permeability of Davydov's polymer concrete was reduced and thus contributed to the decrease of surface deterioration (16). Water resistance of epoxy polymer concrete was further studied by Davydov and Solomatov in the later years (17).

Solomatov found that the water absorption by concrete containing polyvinyl acetate was approximately the same as that by ordinary concrete, only its absorption rate in the first 2 to 3 hr was slower; if vinyl acetate-vinyl chloride copolymer was substituted by polyvinyl acetate, the concrete became more water resistant, but on the other hand, the elasticity decreased when wet (18).

According to Shvidko's (U.S.S.R.) investigation, the water vapor permeability and water absorption of concrete containing epoxy resin-coal tar compounds were lower than ordinary concretes (19).

For improving the water resistance of concrete, Fridman, Royak, Eselev, Tartakovskii, Shtein, Borodai, and Narusov of U.S.S.R. applied imidazoline as a hardener and plasticizer for mixing the polymeric concrete in 1970 (20).

Watertightness was increased by injecting water-soluble resins into concretes and mortars according to the 1967 RILEM symposium paper reported by other Soviet researchers, namely, Satalkin, Solntsev, and Popov (21).

Varzareiskaya, Knysh, Glekel, and Akhmedov of U.S.S.R. disclosed in 1970 that the addition of 0.1 to 5.0 percent of partially hydrolyzed polyacrylonitrile to cement mix decreased the absorption of water, resulted in the reduced amount of the hygroscropic salt and gypsum deposition in the concrete capillaries, and thus increased concrete durability (22).

Oil- and water-resistant concrete containing polymer-cement compounds was also produced in U.S.S.R. by Cherkinskii. The application was limited by its high cost (23).

Murata and Kobayaski of Tokyo Metropolitan University, Japan, achieved excellent watertightness of concrete subjected to high water pressure through the following method (24).

The surface layer of the concrete was first impregnated with a low-molecular-weight epoxy resin (350-400) to fill the minute exposed pores on the surface and the voids underneath the surface, and then 2-3 coats of epoxy resin were applied on the top of the impregnated surface.

Ohama of Japan observed that mortars with a polymer/cement ratio (calculated on the basis of polymer solids in the emulsion) of 0-20 percent with various ethylene-vinyl acetate emulsion polymerizates were of better water-proofing capacity than mortars modified with ethylene emulsions (25).

Ohama also found that water resistance as well as other properties of polymer-modified mortars were not always improved in proportion to the increase in the polymer-cement ratio, e.g., with mortar modified with PVA, water resistance decreased with an increased polymer-cement ratio (26).

From his study of cement mortars modified by SB (styrene-butadiene) latexes with variable bound styrene, Ohama noticed that the waterproofing property of SB latex-modified mortars depended on the rubber-cement ratio, regardless of the bound styrene content (27).

In Hungary, water absorption of polymer-modified mortars was studied by Perenyi, and was found to be about the same as that of cement mortars. Ten-twenty percent by weight of cement of both poly-

vinyl acetate Mowilith and vinyl copolymer vinitex were applied (28).

Guden of Germany employed polyvinyl acetate and propionate, and butadiene-styrene copolymer to make plastic concrete, which was reported to be of higher water resistance than ordinary cement concrete (14).

Beginning in 1968, investigations regarding water resistance of polymer-containing cement, mortar, and concrete have been made in the United States by governmental agencies as well as private industrial companies. They are illustrated as follows.

Water absorption and permeability were studied by Steinberg, Kukacka, Colombo, Kelsch, Manowitz of Brookhaven National Laboratory, and Dikeou, Backstrom, Rubenstein and Jones of U.S. Bureau of Reclamation as part of the joint program on development of concrete-polymer composites supported by the Division of Isotopes Development of the U.S. Atomic Energy Commission, the Office of Saline Water, and the U.S. Bureau of Reclamation. Water absorption was found to be decreased with increasing polymer content and not dependent on the method of initiating polymerization. A reduction of water absorption by 83-95 percent was observed in the experiments. Maximum reduction was obtained with a sample containing 5.9 percent polymethyl methacrylate. Permeability indicated by the rate of water percolation through concrete-polymer material was measured with various samples. Zero permeability was obtained for a 1.4 percent methyl methacrylate sample polymerized by radiation while 6.18×10^{-4} ft/yr (1.88×10^{-4} m/yr) was obtained for the control. Reductions in permeability by 72-85 percent were obtained in the test series. Samples containing

styrene showed great variation of permeability through different polymerization methods, namely 55 percent increase by radiation polymerization and 72 percent decrease by thermal polymerization (29, 30, 31, 32). Later work disclosed that 97 percent reduction of water absorption was obtained with concrete impregnated with methyl methacrylate containing 10 weight percent trimethylolpropane trimethacrylate (33, 34, 35, 36).

In 1969, King, Jr., Walles, and Giachino found that laminates of surface sulfonated polyethylene or polystyrene and portland cement, optionally containing SBR latex, had good water vapor impermeability (37).

Nutt stated that the rate of diffusion of water into polymer cement, as with any polymer coating, depended on the chemistry of the binder; was proportional to the concentration of water in contact with the polymer; and increased with temperature. Therefore, a certain minimum thickness of polymer cement surface on concrete was necessary to avoid water penetrating to the interface (38).

Epoxy resin improved the waterproofness of concretes by serving either as admixture or as protective coating, according to Okada (Japan). Fair to good water-proofness was also obtained by using a small amount of polyvinyl acetate in mortar or concrete (15). A .02 - .04-in. (.05 - 1 cm) thick epoxy resin film reduced the mortar's permeability coefficient to 0-1/15 of that of nonepoxy-coated material.

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DURABILITY (FREEZE-THAW AND DEICERS)

General

Federal and state highway agencies in the U.S. are facing a mounting crisis in maintenance and repair costs of concrete bridge decks. It has been reported that on the Interstate system alone, approximately $6 billion are needed for repair and replacement of bridges. The rapidly increasing costs of bridge maintenance are certainly due in large part to the boom in highway construction since 1955 and to inflation. However, maintenance costs have outstripped estimates based on these causes alone. A third cause of the accelerating rate of maintenance costs is the reduction in service life of bridge decks in recent years. A number of studies have been carried out at national and state levels to determine the reasons for the observed increase in the rate of deterioration of bridge decks. The more significant findings of some of those studies are discussed below.

One of the most frequently cited causes for the increasing rate of bridge deck deterioration is the rising rate of deicer usage precipitated by the "bare pavement" policy adopted by most highway departments. According to figures from the Salt Institute, the use of chloride salts in pavement deicing increased by nearly 400 percent during the decade of the 1960s. Several studies have found deicers to be the major cause of fracture planes and spalling (1, 2, 3, 4). One investigation found the chloride content of concrete in areas of fracture planes and spalls to be higher than in areas of sound pavement (5).

Environmental factors have been emphasized by some as the cause of deterioration. It was determined in Michigan (6) that the severity of spalling could be correlated with the number of freeze-thaw cycles experienced by the bridges. In Missouri (4), the areal extent of mortar deterioration was found to increase from south to north in the state. Attempts have been made to correlate climate with deterioration by means of the ASTM weathering index (7, 8). The lack of success of these correlations has been attributed to insufficient sample size. The primary role of moisture in environmentally caused deterioration, and as a carrier of deicers, is well recognized. Poorly drained decks have been observed to deteriorate more readily than those that are well drained (3).

A number of studies have suggested that shallow reinforcement is a major contributor to deterioration. Both longitudinal (3) and transverse (3, 6) cracks have been found to exactly follow the reinforcing steel. Spalls are usually aligned with, and frequently expose, reinforcement (2, 6),and most fracture planes occur just above the reinforcement mat (4). Corrosion of the reinforcement, by deicers gaining access to the steel through cracks or pores in the pavement, is considered by most researchers to be a major cause of fracture planes and spalls (9).

It is obvious that concrete quality bears a direct relationship to bridge deck deterioration. Low air content has frequently been associated with mortar deterioration (2, 3, 6,). Although specifications have been set in all states for such factors as air content and slump, it has been widely observed that uniform practice on the

part of contractors is the exception rather than the rule.

Clearly, the problem of concrete bridge deck deterioration is not a simple one. There are many causal factors and many forms of deterioration involved. However, it is quite evident that the accessibility of moisture to the interior of the concrete is prerequisite to all of the forms of deterioration whether it be deicer scaling, freeze-thaw deterioration, or corrosion of the reinforcement.

Freezing and Thawing

In 1955, Powers (10), drawing heavily on previously published work, proposed three complementary theories regarding the mechanism of destruction of concrete and aggregates by frost. For purposes of description, concrete may be considered to consist of two phases--paste and aggregate. The paste phase consists of hydrated cement gel, capillaries (which are remnants of originally water-filled spaces), and purposely or accidentally entrapped air bubbles. The hydrated gel is a granular substance possessing an inherent porosity of at least 25 percent. However, due to the smallness of the gel grains, the interstitial grain pores are exceedingly small, on the order of 20 to 40 A (20 to 40 x 10^{-4}m). The capillaries are much larger than the gel pores, but, in turn, are many fold smaller than the air bubbles. The void systems in hydrated cement paste were discussed in detail earlier in this report.

The voids systems of the aggregate particles were assumed by Powers to consist of cavities and interconnected capillaries. Capillaries in mineral aggregates are generally somewhat larger than those in the paste. The aggregate pore systems were theorized to

be the results of imperfectly joined crystals and capillaries in the cementing materials between the grains. Sufficient evidence exists, in the form of permeability tests, to support the presence of interconnected pore systems in essentially all mineral aggregate materials.

The destruction of concrete by frost action, as viewed by Powers, hinges on the ability of either the paste or the aggregate to attain a critical degree of saturation on contact with water. Water is readily drawn into concrete by capillary action. In the competition for moisture within the concrete, the smallest voids will become saturated first in accordance with the physical laws governing capillarity. Thus evaporable water will be held in the gel pores after all capillary water has been removed. Also, the capillaries in the paste will compete successfully with the capillaries in the aggregate, due to the generally smaller size of the capillaries inthe paste. The air bubbles and other macrovoids are saturated with difficulty because of their large size.

Expansion, or dilation, of concrete occurs when the capillary pores in either the aggregate or the paste contain an amount of water in excess of some critical value and the temperature is lowered below the freezing point of the water in the voids. Note that this implies that the gel pores are also saturated. However, the gel pores are too small to permit ice formation, and, therefore, the gel water plays no part in the source of the disruptive action described here. Theoretically, since water expands 9 percent upon freezing, the critical degree of saturation is 91.7 percent. However,

much lower critical values are possible (and have been observed) due
to lack of uniformity of water distribution and heterogeneity of
pore systems. The dilation that results in the event of freezing
in the presence of super-critical saturation evolves from hydraulic
pressure generated in the capillaries by the advancing ice front.
Therefore, the destructive pressure is a function of the porosity,
permeability, degree of saturation, strength, homogeneity of
the aggregate or the paste, and rate of freezing.

In addition to the "hydraulic pressure" theory just described,
Powers postulated that additional, less rapid dilations will occur
when critically saturated concrete is held at temperatures well
below the freezing point for extended periods of time. This he
termed "growth of ice bodies," and is the result of the attraction
of gel water to ice bodies in the capillaries and other larger
voids where it subsequently adds to the ice volume and increases the
hydraulic pressure. The movement of gel water to the capillary ice
results from the difference in free energy of the ice and the water,
where the free energies are taken to be the net effect of the respective
capillary tension and vapor pressure of each phase.

Powers suggested a third possible source of internal pressure
resulting from freezing of the capillary water. This results from
increasing concentrations of alkalies in the unfrozen water as
freezing progresses which produces osmotic pressure due to the
difference in concentrations between the unfrozen capillary water
and the gel water. This is thought to be a relatively minor component
of the dilating force.

Deicer Scaling

There is little question that the use of deicer chemicals is linked to the surface scaling of concrete. Concretes of widely varying proportions and entrained air characteristics have been shown to be more vulnerable to scaling when exposed to deicers under freeze-thaw conditions than when exposed to water alone under these conditions (11).

Most of the factors found to reduce the severity of deicer scaling involve the reduction of moisture in the concrete. This reduction in moisture is directly related to hydraulic pressure: with little or no moisture available, mechanisms based on hydraulic pressures would be ineffectual.

Powers (10) pointed out that deicer solutions lower the thawing temperature of the surface water, causing a disruption of the normal conditions. The surface ice, melting first, creates a reservoir of liquid which supplies the pores of the interior as it thaws. Successive cycles of freezing and thawing increase the degree of saturation of the concrete until critical saturation occurs. At this point, deterioration commences. In this way, the use of deicers contributes to the accelerated deterioration of concrete.

A variation of the hydraulic pressure mechanism was proposed by Snyder (12). This mechanism is based on the diffusion of the deicers into the concrete and their effect on the freezing point of the moisture within the capillaries. Snyder suggested that the presence of a deicer gradient near the surface of the concrete causes a change in the direction in which freezing normally takes place.

Instead of the concrete freezing from the surface inward, the deicer

gradients caused the freezing to begin in the interior and to progress

toward the surface. He proposed that this change in direction causes

pressures to be exerted toward the surface, lifting the surface

of the concrete and causing scaling. Experiments conducted by

Snyder were not entirely successful in proving this hypothesis.

The growth of crystals within the concrete has also been thought

of as a possible cause of scaling. Hansen (13) was the first to

attempt a detailed explanation of this mechanism. Deicer molecules

contained in a solution on the surface can migrate to the interior

by either diffusion in the water contained in the pores or by diffusion

through other crystals. The pressure caused by growth of crystals in

the larger pores below the surface of the concrete can cause surface

deterioration. Hansen pointed out that the formation of ice crystals

is also an expansive process which can cause excessive internal

pressures and result in surface scaling.

Hartmann (14) attributed deicer deterioration of concrete to

thermal shock. This mechanism is based on the endothermic reaction

of deicers when applied to frozen concrete. The melting of ice

requires heat which is drawn either from the environment or from the

concrete itself. The removal of heat from the concrete causes thermal

gradients, which are described by Hartmann as being detrimental.

Verbeck and Klieger (11) showed that a pessimum concentration

(approximately 3 percent) at which maximum scaling occurs exists

for a range of deicing chemicals. Work carried out at Penn State

(15) revealed that the reason for this phenomenon is that at the

pessimum concentration maximum absorption of the deicer solution
by the concrete occurs. Additionally, the Penn State work showed
that very strong solutions of calcium chloride chemically attack
concrete.

Applicability to Polymer-Modified Concrete

Solomatov of U.S.S.R. did his experiments of freeze-thaw
resistance of polymer-cement concretes (PCC) containing vinyl
acetate-dibutyl maleate copolymer by observing the variation of
dynamic moduli of elasticity of specimens subjected to increasing
numbers of freeze-thaw cycles. Solomatov noticed that, different
from the ordinary concrete, the properties of the polymer in
different phases had great influence on concrete's freeze-thaw
susceptibility, e.g., after 30 cycles, the modulus of dry-cured
PCC was only 60 percent or less than the original value; however,
this loss of modulus was recovered after prolonged cycles (20-
30 percent higher modulus was obtained after 100 cycles). This
indicated that the initial loss of modulus was due to the polymer
swelling in water rather than freeze-thaw attack. Solomatov
concluded that the effects of freezing action and of water along,
acting simultaneously on his PCC sample,were not equal--the
plasticizing effect of the water was stronger than the effect of
changing temperature; however, based on measurements of modulus,
strengths, weight loss, and length change, his overall results
showed that the PCC had a higher freeze-thaw resistance than does
ordinary concrete. Polymer concrete was found to be very resistant
to freezing. The polymer-concrete sample made of concrete and

furtural-acetone condensation did not lose its weight or strength after 100 and 200 freeze-thaw cycles (16).

According to Perenyi (Hungarian), polymer-modified mortars containing polyvinyl acetate and vinyl copolymer indicated a greater loss of bending-tensile and compressive strength than polymer-free specimens when 28-day cycles of freeze and thaw had been applied (17).

Researchers of BNL and USBR carried out a series of freeze-thaw tests on concrete-polymer materials as a portion of the government joint research program. Important findings are as follows (18, 19, 20, 21, 22).

The test sample containing 3.9 percent styrene failed after 1810 freeze-thaw cycles, while the control failed after 590 cycles.

Weight loss of a sample containing 6.7 percent methyl methacrylate (polymerized by radiation) after 7220 cycles was only 0.5 percent which indicated an improvement of about 900 percent over the control, and there was no observable increase of weight loss after 2420 cycles. The control specimens failed at 740 cycles (25 percent loss was the criterion used for failure).

With methyl methacrylate (MMA) the freeze-thaw durability improved with polymer loading, while for styrene the opposite effect was obtained.

A minimum improvement in freeze-thaw durability of 366 percent was obtained from MMA-impregnated specimens when compared with controls. The degree of improvement appeared to be a function of the polymer loading rather than the method of initiation.

Styrene-impregnated specimens indicated an improvement of freeze-thaw durability of 172 and 340 percent. A considerably lower rate of attack was observed in thermal-catalytically produced specimens.

Specimens impregnated with MMA+ 10 wt percent TMPTMA (tri-methylolpropane trimethacrylate) were also tested. The results showed that for radiation-produced specimens, the rate of attack was greater than for MMA and less than for styrene. The thermal-catalytically produced specimens showed very little weight loss (none after 1230 and 0.5 percent after 2560 cycles).

Acrylonitrile-impregnated samples polymerized by radiation showed the least improvement in freeze-thaw durability (108 and 149 percent), while the thermal-catalytically polymerized ones showed better results (173 percent) (18, 19, 20, 21, 22).

A general discussion was made in 1967 by Yamasaki on coatings to protect concrete against damage by deicer chemicals. Coatings reviewed included linseed oil, mineral oil, wax, coal tar, silicone oil, latex, and epoxy resins. It was stated that the performance of silicones had been conflicting and, in general, poor; epoxy paving cements had given good results, but were expensive; linseed oil was considered most effective and economical (23).

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APPENDIX B

MONOMER SYSTEM

MONOMER SELECTION

The monomer selected for the field trials was the 90:10 or 100:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture containing 0.5 percent azobisisobutyronitrile initiator. This monomer mixture was selected because: (1) methyl methacrylate was the monomer used in most earlier experiments by other laboratories so that there was a considerable background of experience with it (1); (2) methyl methacrylate undergoes a rapid autoaccelerating polymerization, which aids in achieving high conversions in short times in situ; (3) methyl methacrylate has a very low viscosity, one of the lowest viscosities of any monomer, which aids in the impregnation; and (4) concrete specimens impregnated with methyl methacrylate and polymerized showed high compressive and tensile strengths as well as other desirable properties.

Since the main thrust of this work was development rather than research, our objectives were to: (1) confirm the earlier results obtained with the methyl methacrylate system; (2) establish an appropriate initiator system, in this case azobisisobutyronitrile; and (3) establish an appropriate crosslinking monomer system, in this case trimethylolpropane trimethacrylate, to enhance the autoaccelerating polymerization and to give a crosslinked polymer of higher mechanical strength.

This monomer system performed well in all of the tests, and its selection was obviously a good choice. However, other monomers should

also be considered. For example, styrene-polyester and styrene-acrylonitrile mixtures were found to give even better properties in polymer-impregnated concrete than methyl methacrylate ([1]). The styrene-polyester mixture is higher in viscosity and, consequently, can be used only at the expense of penetration time. Styrene-acrylonitrile mixtures are sufficiently low in viscosity but have not been investigated in any detail. The same can be said for other monomer systems.

In March 1973, the prices of all monomers which were available in large volume and high purity (and therefore would be possible candidates for this application) were listed in order of increasing cost. This list is presented in Table B-1.

The monomers on this list that are gases at room temperature (ethylene, propylene, butadiene, and vinyl chloride) can be eliminated from consideration. This leaves several monomers--styrene, vinyl acetate, acrylonitrile, vinylidene chloride, vinyl toluene--which are lower in cost than methyl methacrylate, and several other monomers-- methyl acrylate, ethyl acrylate, butyl acrylate--which are competitive in cost with methyl methacrylate. It should be pointed out that monomers such as vinylidene chloride, whose polymers precipitate on polymerization, may pose problems in field applications. In particular, styrene has about the same mechanical properties as methyl methacrylate when polymerized, but at about one-third the cost. This list points out the work that can be done in this area to optimize the monomer selection with respect to cost.

Copolymerization is another approach to optimize the properties-cost relationship. From the list of monomers that are lower in cost than methyl methacrylate, it would be desirable to try styrene-acrylonitrile,

Table B-1. Typical Monomer Costs in Bulk[1] and as Impregnated[2]

Monomer	Cost/lb	Cost/sq ft
Ethylene	$0.0325	$ ---
Vinyl Chloride	0.050	---
Styrene	0.0675	0.111
Vinyl Acetate	0.0875	0.157
Butadiene	0.095	---
Acrylonitrile	0.130	0.239
Vinylidene Chloride	0.140	0.306 - 0.350
Propylene	0.145	---
Vinyltoluene	0.180	0.289
Methyl Methacrylate	0.185	0.346
Ethyl Acrylate	0.190	0.341
Methyl Acrylate	0.200	0.359
Butyl Acrylate	0.200	0.359
Isobutyl Acrylate	0.200	0.359
Ethylhexyl Acrylate	0.230	0.413
Butyl Methacrylate	0.290	0.543
Isobutyl Methacrylate	0.380	0.712
Ethyl Methacrylate	0.425	0.796

Unit Conversions: 1 lb = 0.454 kg

1 sq ft = 0.092 m^2.

1. Chemical Marketing Reporter, March 26, 1973.

2. Assuming impregnation of concrete of 15% porosity to a depth of

2 in. (5.08 cm).

styrene-methyl methacrylate, vinyl acetate-acrylonitrile, vinyl acetate-acrylate ester, and vinylidene chloride copolymers. It is of interest to note that in latex-modified concrete, the vinylidene chloride copolymer latexes are superior to all other types.

As yet, however, there is no standard of comparison for monomers other than measurement of mechanical and physical properties of the polymer-impregnated concrete in laboratory tests. No polymer-impregnated concrete specimens have been tested for ultimate durability in any test that is comparable to actual service life. Many accelerated laboratory tests for freezing and thawing, salt solution penetration, abrasion resistance, or other properties have been carried out. However, these tests tend to demonstrate the superiority of polymer-impregnated concrete over unmodified concrete, rather than to differentiate between different types of polymer-impregnated concrete. Polymer-impregnated concrete is too new and there are too few specimens out on exposure in the field to determine its ultimate durability.

Nevertheless, ultimate durability is the objective of all of the research and development work carried out on polymer-impregnated concrete. Therefore, it would be desirable to develop methods of testing to distinguish between different types of polymer-impregnated concrete. Not only are there different types of polymers available, but, as mentioned above, copolymerization can also be used to prepare a wide variety of compositions tailored to the specific application. One example is given in the present work: concrete impregnated with methyl methacrylate has high modulus and high ultimate strength, but undergoes brittle fracture, a property which is somewhat unacceptable to civil engineers;

concrete impregnated with butyl acrylate has a modulus and ultimate

strength only slightly greater than that of unmodified concrete, but

shows greater ductility before fracture than unmodified concrete;

concrete impregnated with 75:25 or 90:10 methyl methacrylate: butyl

acrylate mixtures have strengths almost as great as that of methyl

methacrylate alone, but show ductility before fracture (see Appendix

E). Similar relationships are expected for other monomer pairs.

Therefore, it is proposed to develop a laboratory test to distinguish

between different types of polymer-impregnated concrete and to confirm

these differences by tests in the field, with this program to run

concurrently with the testing of concrete impregnated with the methyl

methacrylate-trimethylolpropane trimethacrylate mixture. One possible

approach to such differentiation is the freeze-thaw test. The current

test (ASTM designation C671) is too time consuming for the large number

of specimens in the proposed study (probably 200-500). Such a large

number of specimens requires a simplified test procedure. Various

procedures have been discussed, e. g., circular discs of 2-3 in. (5.08-

7.62 cm) diameter and 0.125 - 0.250 in. (0.32 - 0.64 cm) thickness with

a 0.125-in. (0.32-cm) diameter hole near one edge could be hung on hooks

in a freezer chest, frozen, allowed to thaw, immersed in water, then

frozen again, until the mortar becomes so weak that it falls off of the

hook. Large numbers of these discs could be prepared and impregnated.

Daily recycling would allow 365 cycles per year. In this way, many

different monomer combinations, developed systematically from a basic

understanding of polymerization fundamentals, could be tested to determine

which offered the most promise. At the same time, the question could be

answered as to which would combine adequate properties in the field with lowest cost.

Some hint of this problem is found in the present work, in which concrete impregnated with various proportions of butyl acrylate and methyl methacrylate were tested by freezing and thawing. Beforehand, it was speculated that the hard, brittle, high-modulus polymethyl methacrylate, under the differential expansion and contraction of the freeze-thaw testing, would eventually separate from the cement paste phase, i. e., the polymer-cement adhesive bond would fail, but the soft, rubbery polybutyl acrylate would form a polymer-cement adhesive bond that would remain intact through many freeze-thaw cycles. However, some preliminary experiments showed that the best resistance to salt penetration was obtained with the polymethyl methacrylate rather than with the polybutyl acrylate specimens; the effect of freezing and thawing remains to be determined. Also, the abrasion resistance tests showed that the harder and more brittle the polymer, the better the abrasion resistance of the corresponding polymer-impregnated concrete, e. g., styrene was the best, followed by methyl methacrylate, isobutyl methacrylate, in that order. These results demonstrate why it is important to carry out this screening program.

MONOMER PENETRATION RATE STUDIES

Since no engineering or scientific data were available on the rate of impregnation of concrete by monomers at various pressures, it was necessary to obtain the data (2). Experiments were conducted on both mortared concrete and slabs. (See also Appendix D.)

Impregnation of Mortar Cylinders

Small 1-in. x 2-in. (2.5 -cm x 5.1 -cm) portland cement mortar cylinders were prepared and used in the first impregnation experiments. The organic liquids (acetone, styrene, methyl methacrylate, acrylic acid, trimethylol-propane trimethacrylate [TMPTMA]) were commercial grade and were used as received. Laboratory distilled water was used. The portland cement mortar cylinders were prepared using a 12:24:64 water-type 2 portland cement-Ottawa silica sand (ASTM C-109) mix and were cured for 28 days in water at room temperature.

The cylinder volume was determined by saturating it with water, measuring its weight in air and then in water, using Archimede's principle. For the liquid sorption experiments, the cylinders were dried to constant weight under an infrared lamp, weighed in air, then immersed in the liquid. The weight in the liquid was measured periodically after immersion until a constant weight was attained, usually in 60-120 min for the less-viscous liquids. The weight at zero time was calculated from the cylinder volume and specific gravity of the liquid, using Archimedes' principle.

To obtain reproducible liquid sorption curves, the cylinders must be dried thoroughly. Incompletely dried cylinders sorb less liquid, according to the residual volume of water. This residual water cannot be driven out by penetration of even water-miscible liquids. Since the same cylinder was used in a series of sorption experiments, it was necessary to remove the sorbed liquid before the next experiment. Volatile liquids such as acetone, methyl methacrylate, styrene, or water were removed by heating with the infrared lamp. Less-volatile liquids were removed by immersing

the cylinder for 24 hr in a series of acetone baths and finally removing

the acetone by heating. With these procedures, the same cylinder could

be used again and again, each time giving reproducible sorption values.

The sorption-time$^{1/2}$ variation for styrene (Figure B-1) is linear over

most of the time range up to the asymptotic approach to equilibrium.

Similar results were found for MMA. However, the corresponding curve

for the 90:10 styrene-acrylic acid mixture shows initially a smaller

linear slope up to an inflection point at about 55 percent of equilibrium,

followed by a second linear region of even smaller slope. Despite these

differences in slope, the equilibrium sorption values were the same,

suggesting a specific interaction between the acrylic acid and the

potential cement substrate to reduce the effective pore radius. The

curve for the much slower penetration of styrene into the salt-filled

cylinder (not shown) shows a single linear region over most of the time

range.

The curve for a 90:10 styrene -TMPTMA mixture was also linear and in good

agreement with that for styrene, an important observation because of the

common use of trimethylolpropane trimethacrylate as a crosslinking agent

in polymer-impregnated concrete and its very slow rate of penetration.

The slower penetration of styrene into the salt-filled cylinder

(3 percent NaCl by weight) can be explained by a reduced pore radius and

volume. At equilibrium, the sum of the salt and styrene volumes is

equal to the porosity (14.5 percent), consistent with a simple volume

additivity rule. This observation is also important because of the

practical requirement of impregnating bridge decks which are contaminated

with deicing salts (see Appendix F).

The rate of penetration of monomer into large slabs can be predicted from the laboratory experiments using these small cylinders. For example, the application of 2 lb (0.9 kg) styrene/sq ft (0.9 m^2) of surface should give penetration to a depth of 2.4 in. (6.7 cm) in 9.6 hr, in comparison with the 2-in. (5.1 -cm) value reported (3) for penetration of methyl methacrylate under rather similar conditions.

Impregnation of Concrete Slabs

Impregnation tests were carried out on 24-in. x 24-in. x 6-in. (61.0 - cm x 61.0 -cm x 15.2 -cm) concrete slabs prepared and dried to constant weight. These slabs were impregnated by bolting on the pressure impregnation unit on top and pressurizing with the monomer at various pressures. Figure B-2 shows the results of these tests as compared with those from laboratory experience. It can be seen that the results from concrete cylinders and slabs are consistent, i. e., all results follow the predictions of the Rideal-Washburn equation with respect to time, though not with respect to pressure. (See Appendix D.)

Impregnation of Concrete Cylinders from Top Surface

A series of cylinders were made with PennDOT AA concrete and after 28 days of moist curing the lateral sides were coated with epoxy. These cylinders were then impregnated from the top surface with MMA-TMPTMA-AZO (100:10:0.5 by weight) at various over-pressures in an impregnation chamber described by Weyers (4).

These cylinders were impregnated at 0, 25, 50, and 75 psig (0, 170, 340, and 520 kPa). Table B-2 gives some of the data concerning these impregnations. The cylinders were not impregnated to achieve full penetration except in the case of 0 psig. Figure B-3 represents photographs of the cross section cut from

the four cylinders impregnated from the top surface only. The dark areas indicate the presence of polymer and one can observe from the tone of the dark areas that loading was nonuniform, with the highest loadings occurring at the top. The presence of the light lines in the middle and bottom sections of the cylinders are cracks that are not filled completely with PMMA. Figure B-3 also shows decreasing penetration with increasing pressure for approximately the same weight gain of monomer. Hence it appears that for a given increase in pressure and same amount of monomer, the percent void volume filled with monomer will increase and the depth of penetration will decrease.

Figure B-4 presents the weight of monomer gained as a function of the square root of time for pressures of 0, 25, 50, and 75 psig (0, 170, 340, and 520 kPa). Linear regression analysis, slope intercept, and error of regression data are given in Table B-2. The data indicate a linear relationship between the monomer weight gain and the square root of time.

Figure B-5 presents a plot of this data between the rate of impregnation and the pressure. This curve appears to be a linear relationship in agreement with data discussed above (5). The values for the slope, intercept, and error of regression data are given in Table B-2.

Effect of Contaminants on Penetration Rate

The effects of contaminants on impregnation of concrete bridge deck cores and cast cylinders are discussed in detail in Appendix F. These cylinders were oven-dried and impregnated from the top surface only. In general, the effects of deicer salts appear to decrease the rate of impregnation at atmospheric pressure, but this effect appeared to be

Table B-2. Pressure Impregnation of Concrete Cylinders

from Top Side Only

Pressure (psig)	Slope[1] $(g/hr^{1/2})$	Total Monomer Gained (g)	Error of Regression	Intercept
0	9.5	95.1	0.998	-4.84
25	27.7	92.2	0.997	4.68
50	32.7	91.3	0.999	10.99
75	49.6	92.3	0.999	-9.08
Rate vs. Pressure	0.50	---	0.980	11.0

Unit Conversion: 1 psig = 6.89 kPa.

1. Slope corresponds to data plotted in Figures B-4 and B-5.

overcome by the application of over-pressure (75 psig [520 kPa] was

the only over-pressure tested on salt-contaminated specimens). The

quantity of MMA uptake by the cylinders did not appear to be influenced

by the deicer salts at 0 and 75 psig (520 kPa).

Penetration Rate as Affected by Degree of Drying

A group of 30 cylinders were cast (4 in. [10.2 cm] in diameter by

8 in. [20.3 cm] long) using PennDOT AA concrete (6). The purpose of

this series of tests was to determine the moisture contents in the

cylinders when dried with an infrared joint heater applied to the top

surface of the cylinders, the rate and maximum monomer uptake when monomer

is ponded on the top surface of the cylinder after drying, and to observe

if different ambient temperatures affect the impregnation.

These cylinders were divided into five groups of six cylinders each.

Three cylinders from each group after drying were used for ponding

impregnation at an ambient temperature of 68°F (20°C) and the other three

cylinders were used for ponding at 40°F (4.4 °C). All cylinders prior to

drying were cured in a fog room for 28 days at 100 percent relative

humidity at 68°F (20°C). After the hydration period was complete,

six cylinders (Group I) were placed in a forced air oven at 302°F (150°C)

for drying to constant weight. The weight total of moisture removed from

each of these cylinders dried at 302°F (150°C) was obtained and expressed

as a percentage of its saturated weight. The average value for this

ratio was calculated and used to estimate the amount of water in each of

the 24 remaining cylinders (Groups II to V) by multiplying this ratio

by the saturated weight of each cylinder.

The perimeters of all cylinders were coated with epoxy resin in order to prevent water or monomer from egressing through the sides. The coating was done when the oven-dried specimen (Group I) was cooled to room temperature after drying and before the saturated cylinders of Groups II to V were subjected to infrared drying technique.

For infrared drying, the top surfaces of Groups II to V cylinders were placed about 11 in. (27.9 cm) below a 120,000 BTU (130 MJ) infrared heater. The cylinders were supported by a steel grid (5 in. [12.7 cm] above the ground) which allowed the moisture to move out freely from the bottom of the laterally coated cylinders. Aluminum foil was placed around and flush with the top surface of the cylinders. Using this method, the radiant infrared heat was only absorbed by the specimens from their top surfaces and the moisture could only be removed from the specimens from their bottom surfaces, which approximates drying of a concrete slab or bridge deck from one surface only. Certain cylinders during casting had copper-constantan thermocouples embedded at 4 in. (10.2 cm) from the surface so that the temperature could be correlated with the measured temperature from large-scale slab and bridge deck trials, reported in Appendices G and H.

Table B-3 gives the drying data, estimated moisture content, and temperature at the centers of the cylinders for the series of tests (6).

After the cylinders were dried, they received an extra epoxy resin coating on the lateral surfaces prior to impregnation. In order to contain the monomer on the top surfaces of the cylinders, a section of tin can was placed around the cylinder top. Silastic rubber was applied to seal the gap between the top of the cylinder and the can. When the

Table B-3. Drying Data on 4-in. Diameter by 8-in. Concrete Cylinders

Specimen[1]	Drying Method	Estimated Average[2] Moisture Content in Top 4 in. of Cylinder	Estimated Average[3] Moisture Content in 8-in. Cylinder	Final Temp. Center of Cylinder (°F)
Group I - A & B	Oven	0	0	302
Group II - A & B	Infrared	53	77	195
Group III - A & B	Infrared	44	72	220
Group IV - A & B	Infrared	30	65	245
Group V - A & B	Infrared	19	60	250

Unit Conversions: 1 in. = 2.54 cm

$$°F = (\frac{9}{5}) \ °C + 32.$$

1. Each group has 6 cylinders, 3 to be impregnated at ambient temperature of 68°F (A) and 3 to be impregnated at ambient temperature of 40°F (B).

2. Based on the assumption that all the water removed during infrared drying from the top surface of the cylinder was from the upper 1/2 of the cylinder. Its mathematical form is:

   Average M.C. (upper 1/2) = $100 - \frac{\text{cylinder weight loss}}{0.5 \text{ ave TW}}$ X 100

   where average T.W. is the average total water removed from 6 cylinders in Group I during oven drying.

3. Same mathematical equation as average MC (upper 1/2) except the 0.5 factor is removed.

silastic rubber was cured, MMA-TMPTMA-AZO system (100:10:0.5 by weight) was ponded on the surface and pools were covered with aluminum foil to reduce evaporation. Weight gain of the specimens was recorded at the 3rd, 12th, and 24th hr after ponding and every 24 hr thereafter until the monomer uptake was less than .035 oz (1 g) per day. As previously mentioned, three cylinders from each group of specimens were impregnated at an ambient temperature of 68°F (20°C) and three at 40°F (4.4 °C). Polymerization was achieved after the specimens had achieved an equilibrium state of impregnation by placing the cylinders in a hot water bath for 24 hr which was maintained at 167°F (75°C).

Table B-4 lists the monomer loading and depths of penetration for the oven-dried specimens. One result of this data shows that it may be possible to impregnate completely through 8 in. (20.3 cm) of concrete if the specimen or deck is dry enough but the length of time may be prohibitive. Another result indicates that ambient temperature may affect the depth of penetration achieved (6.5 in. [16.5 cm] for 40°F [4.4 °C] versus 8 in. [20.3 cm] for 68°F [20°C]), but the percent of total monomer uptake versus time is nearly the same for the different ambient temperatures.

Table B-5 gives the data for monomer loading and estimated depth of penetration for the infrared-dried specimens. Thermal expansion cracks appeared in the top surfaces of all infrared-dried cylinder specimens. These cracks were uniformly and radially distributed on the top surfaces. They were shallow and not serious enough to cause any concrete separation. However, as evident from the data in Table B-5, these cracks appeared to influence the rate of monomer impregnation as compared to the oven-dried

specimens. In 24 hr after impregnation began, all infrared-dried

specimens had taken up about 87 percent of the total monomer uptake as

compared to about 37 percent for the oven-dried specimens, and in 48

hr all the infrared-dried specimens had taken up about 95 percent ·

as compared to about 47 percent for the oven-dried specimens. Although

the final depth of penetration is different, this percentage of the total

monomer uptake for the infrared-dried specimens is about the same regardless

of the final temperature at 4 in. (10.2 cm) below the surface. It

must be pointed out that it took about 4 days to achieve this maximum

monomer loading in the infrared-dried specimens. This is one of the reasons

why 4 days was chosen for the ponding time in the large slab and bridge

deck trial experiments discussed in Appendix G. This study also shows

that even though an estimated 20 percent of the total moisture may remain

in the top 4 in. (10 cm) of concrete after drying to $250^{\circ}F$ ($121^{\circ}C$) at 4 in.

(10.2 cm) with an infrared heater, heavy penetrations of monomer to a

depth of about 3.5 in. (8.9 cm) can be achieved.

WETTING PROPERTIES OF MMA ON CONCRETE

Surface Energy Measurement

For a given solid surface, the surface energy of the liquid is useful

in predicting the wettability of the liquid which is an important

parameter in capillary flow of the liquid. If the surface energy of the

liquid is low, one would expect it to spread easily on the solid, particularly

if the solid has a high surface energy. The surface energy of MMA was

obtained on a Fisher Scientific Co. Model 21 Surface Tensiomat (Du Nuoy

ring method). A series of measurements were taken with the tensiomat on

Table B-4. Monomer Loading and Depth of Penetration for Oven-Dried Specimens

(4 in. Diameter x 8 in.)

Specimen[1]	Final temp. at center °F	Impregnation[2] temp. °F	Percent Total Monomer[3] Uptake and Est. Depth of Penetration[4] at Various Impregnation Times					
			3 hr/depth(in.)		12 hr/depth(in.)		24 hr/depth(in.)	
Group I-A	302	68	12.5	0.99	25.5	2.04	34.7	2.78
Group I-B	302	40	12.3	0.80	28.5	1.85	38.4	2.49

	Percent Total Monomer Uptake and Est. Depth of Penetration at Various Impregnation Times								
Specimen	2 days/depth(in.)		4 days/depth(in.)		6 days/depth(in.)		8 days/depth(in.)	10 days/depth(in.)	
Group I-A	45.2	3.62	72.0	5.76	82.6	6.61	88.1	7.05	93.6	7.49
Group I-B	47.9	3.11	67.2	4.37	77.7	5.05	84.3	5.48	90.8	5.90

	Percent Total Monomer Uptake and Est. Depth of Penetration at Various Impregnation Times						
Specimen	12 days/depth(in.)		14 days/depth(in.)		15 days/depth(in.)[5]		Total Wt(g) of Monomer Gained
Group I-A	97.5	7.80	100.0	8.0	100.0	8.0	170.1
Group I-B	96.2	6.25	99.4	6.46	100.0	6.5	152.0

Table B-4. Monomer Loading and Depth of Penetration for Oven-Dried Specimens

(4 in. Diameter x 8 in.) (Continued)

Unit Conversions: 1 in. = 2.54 cm

$$°F = (\frac{9}{5}) \ °C + 32$$

1 oz = 28.35 g.

1. Groups I-A and I-B were comprised of 3 cylinders each. Data are averages of 3 cylinders.

2. The lateral sides of the cylinders were coated with epoxy and monomer was ponded on the top
    surface only.

3. Monomer system was MMA-TMPTMA-AZO (100:10:0.5 by weight).

4. The estimated depth of penetration is the percent of total monomer uptake at various times
    multiplied by the total depth of penetration (heaviest loading--visible to the eye).

5. The cylinder that was cut to measure the final depth of penetration (heaviest loading--
    visible to the eye) had a total monomer uptake that was about the mean of the 3 cylinders
    in its group.

Table B-5. Monomer Loading and Depth of Penetration for Infrared-Dried Specimens

Specimen[1]	Final temp. at center °F	Est. M.C. top 4 in.	Impregnation[2] temp. °F	Percent Total Monomer Uptake[3] and Est. Depth of Penetration[4] at Various Impregnation Times					
				3 hr	/depth(in.)	12 hr	/depth(in.)	24 hr	/depth(in.)
Group II - A	195	53.0	68	41.2	0.72	71.2	1.25	90.5	1.58
Group II - B	195	53.0	40	39.9	0.80	66.7	1.33	85.6	1.71
Group III - A	220	44.0	68	44.8	1.01	74.0	1.67	90.5	2.04
Group III - B	220	44.0	40	37.8	0.94	63.1	1.58	86.5	2.16
Group IV - A	245	30.0	68	38.3	1.15	67.5	2.03	85.4	2.56
Group IV - B	245	30.0	40	37.6	1.22	66.2	2.15	83.5	2.71
Group V - A	250	19.0	68	37.0	1.29	72.8	2.55	88.4	3.09
Group V - B	250	19.0	40	40.5	1.42	69.2	2.42	87.2	3.05

Table B-5. Monomer Loading and Depth of Penetration for Infrared-Dried Specimens (Continued)

Percent Total Monomer Uptake[3] and Est. Depth of Penetration[4]

at Various Impregnation Times

Specimen[1]	48 hr/depth(in.)		72 hr/depth(in.)		96 hr/depth(in.)		120 hr/depth(in.)[5]		Total Wt (g) Monomer Gained
Group II - A	95.3	1.67	98.8	1.73	100	1.75			58.1
Group II - B	96.7	1.93	99.4	1.99	100	2.0			58.5
Group III - A	96.1	2.16	98.8	2.22	100	2.25			61.3
Group III - B	96.5	2.41	99.3	2.48	100.	2.50			64.1
Group IV - A	93.2	2.80	96.7	2.90	99.7	2.99	100	3.0	83.2
Group IV - B	95.8	3.11	97.3	3.16	99.5	3.23	100	3.25	79.8
Group V - A	95.0	3.32	99.2	3.47	99.5	3.48	100	3.5	88.7
Group V - B	94.0	3.29	97.3	3.41	99.9	3.49	100.	3.5	93.5

Table B-5. Monomer Loading and Depth of Penetration for Infrared-Dried Specimens (Continued)

Unit Conversions: 1 in. = 2.54 cm

$$°F = (\frac{9}{5}) \ °C + 32$$

1 oz + 28.35 g.

1. Each group (Group II-A, etc.) was comprised of 3 cylinders. Data are average of 3 cylinders.

2. The lateral sides of the cylinders were coated with epoxy and monomer was ponded on the top surface only.

3. Monomer system was MMA-TMPTMA-AZO (100:10:0.5 by weight).

4. The estimated depth of penetration is the percentage of total monomer uptake at various times multiplied by the total depth of penetration (heaviest loading--visible to the eye).

5. The cylinder that was cut to measure the final depth of penetration (heaviest loading--visible to the eye) had a total monomer uptake that was about the mean of the 3 cylinders in its group.

MMA monomer at 73°F (22.8°C). Five readings were taken and the average

value of these readings is 0.16 lb/in. (28   mN/m). The MMA value is about

1/2 the value of water (0.39 lb/in. [69 mN/m]), and since water readily wets

concrete one would expect that the MMA would also wet the concrete surface.

More detailed information concerning these measurements is given by Pu (6).

Contact Angle Measurement

The solid liquid contact angle is another important measurement in

establishing the wetting properties of a monomer. If all other conditions

are held constant, the maximum monomer penetration according to capillary

flow theory would be when the monomer concrete contact angle is zero

degrees. A contact angle of zero degrees implies spontaneous spreading of

a liquid on a solid surface.

The contact angle measurements were obtained on a goniometer which has,

on an optical track, two rotatable cross hairs, a specimen stage with a tilt

device, and an illuminator. The contact angle is measured directly

from the monomer sessile drop formed on the prepared concrete surfaces.

Concrete specimens for this experiment were made of Class AA cement

concrete according to Pennsylvania Department of Transportation specifica-

tions except that no air-entraining agent was used in order to obtain a

less porous specimen. All test surfaces were ground to obtain a smooth

surface.

The polished specimens were placed in the goniometer and a drop of

MMA was placed on the surface. Readings were obtained quickly because

of the volatility of MMA. The MMA monomer quickly wetted the concrete

surface and no readable contact angle could be obtained. The MMA drops

were placed on other spots on the specimen for consideration of the

heterogeneity of the concrete. No readable contact angle could be obtained. The same results were obtained when crosslinking agent (TMPTMA) and catalyst (AZO) were added to the monomer.

This spontaneous wetting of the clean polished concrete surface by MMA or the MMA monomer system could possibly be caused by the high porosity of the concrete system. To investigate this area, highly compressed cement paste specimens containing less than 1 percent porosity were substituted for the concrete. The instantaneous spreading behavior was again observed and no readable contact angle could be obtained.

Another series of tests were conducted in which the concrete surface was slightly wetted with a clean wet facial tissue. The thin water film on the concrete did not change the spreading characteristics of the MMA monomer system.

The effects on the contact angle of the contaminated concrete and MMA monomer system were also investigated. The polished concrete specimens were contaminated with salt, linseed oil, motor oil, and grease. The contact angle on the contaminated concrete was too small to be measured. It must be pointed out that linseed oil, motor oil, and grease readily dissolve in the MMA monomer solution and probably would be carried into the concrete during an impregnation. Another series of tests were conducted on contaminated concrete with t-butyl styrene and epoxy. Measurable contact angles were obtained with the epoxy; details concerning this work are given by Weyers (4).

Detailed descriptions of all contact angle tests are given by Pu (6) and Weyers (4). Based on the MMA contact angle tests, one would expect to obtain deep penetration of the concrete with MMA monomer system.

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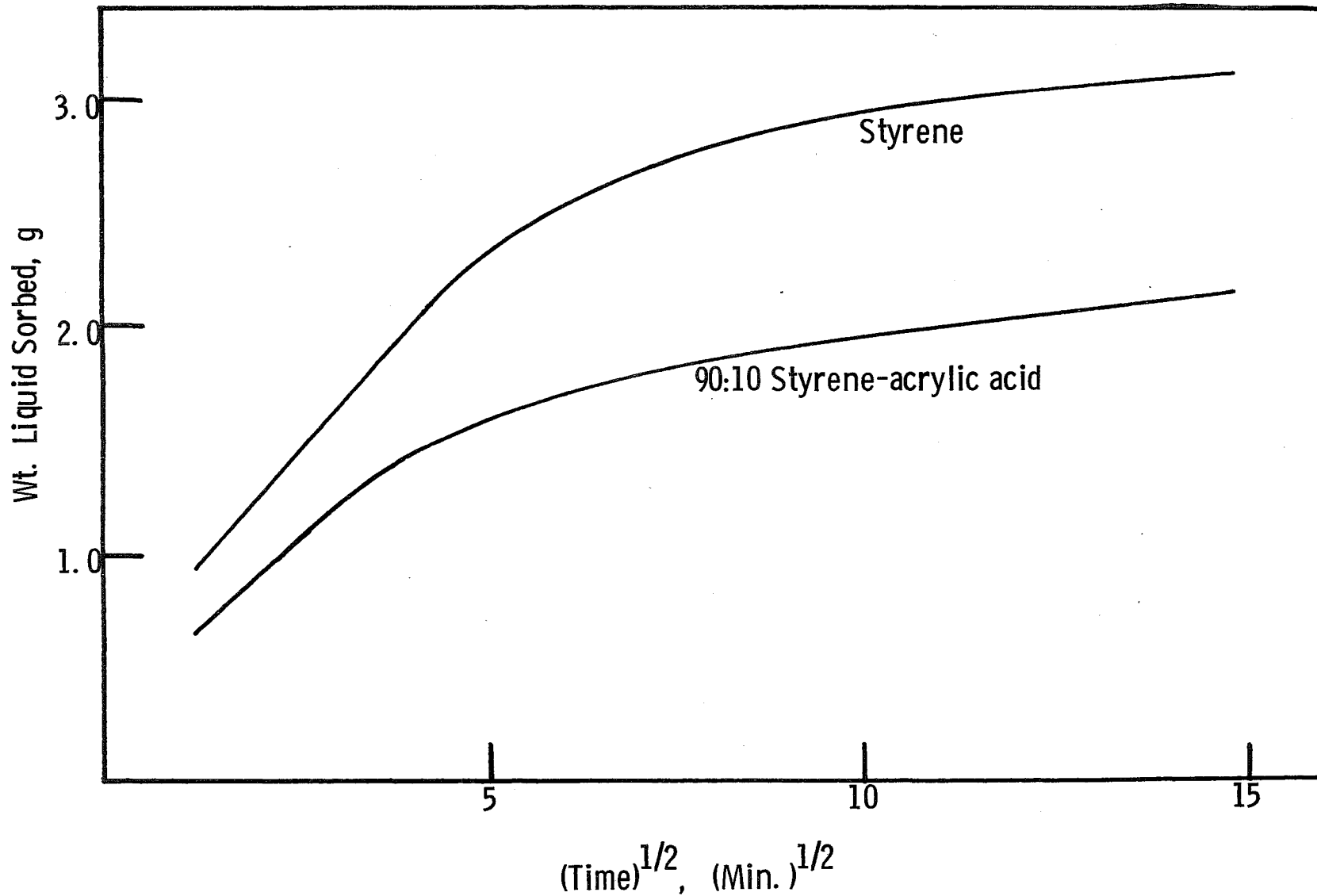
Fig. B-1 Variation of Sorption of Monomer into Mortar with Square Root of Time: 0 Styrene; 0 90:10 Styrene-Acrylic Acid
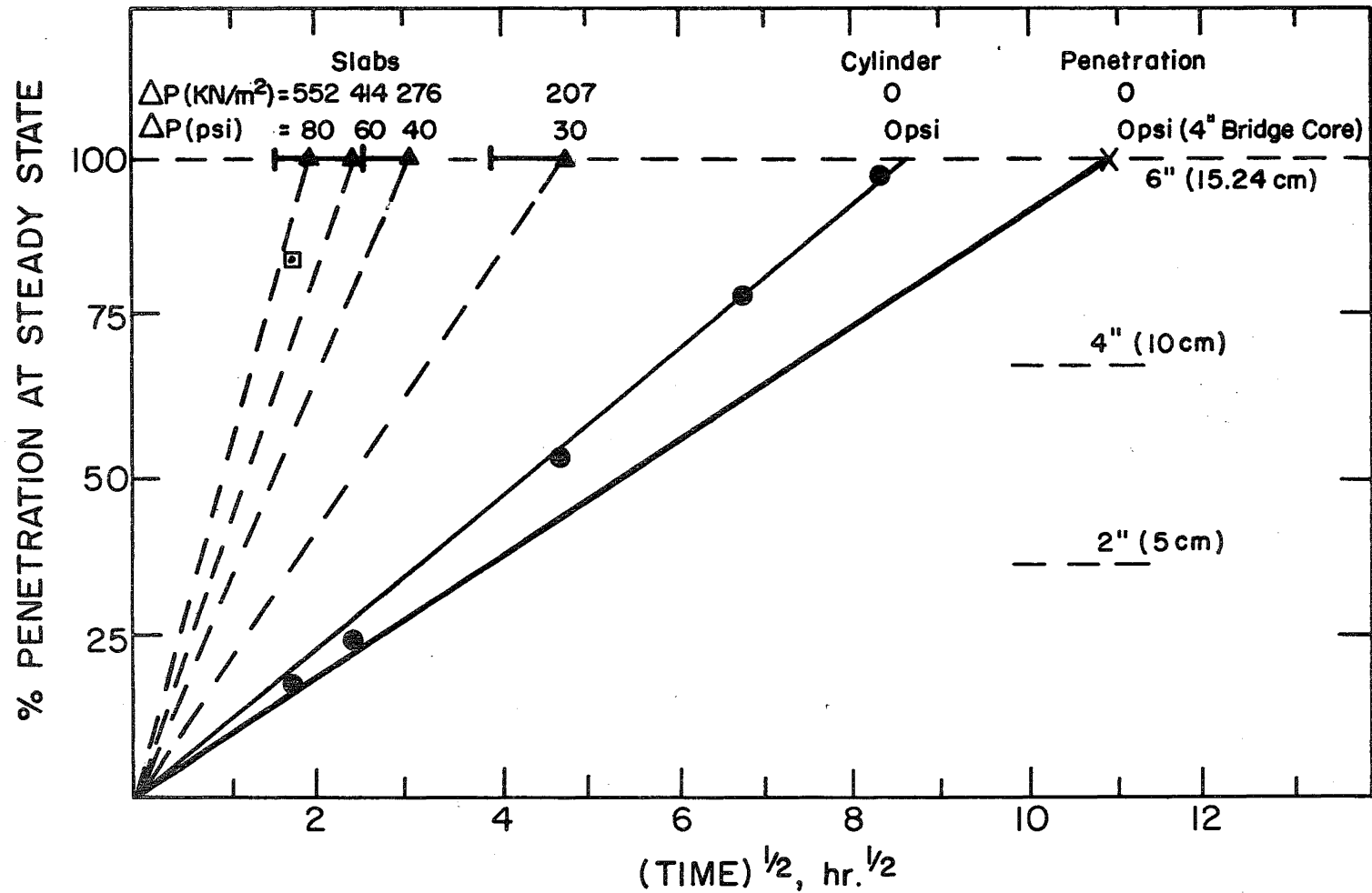
Fig. B-2 Variation of Monomer Penetration into 6-in. (150-mm) Concrete Slab with Time as Function of Applied Pressure; 0 = Cylinder; Δ = Slab (Note for Comparison, Bridge Deck Core Impregnated in Laboratory (14) at = 75 psi; X = 0 psi)

0 psig

25 psig

50 psig

75 psig

Fig. B-3 Cross-Section of Cylinders Impregnated at Four Different
Pressures

FIGURE B-4 WEIGHT GAINED AS A FUNCTION OF SQUARE ROOT OF TIME.
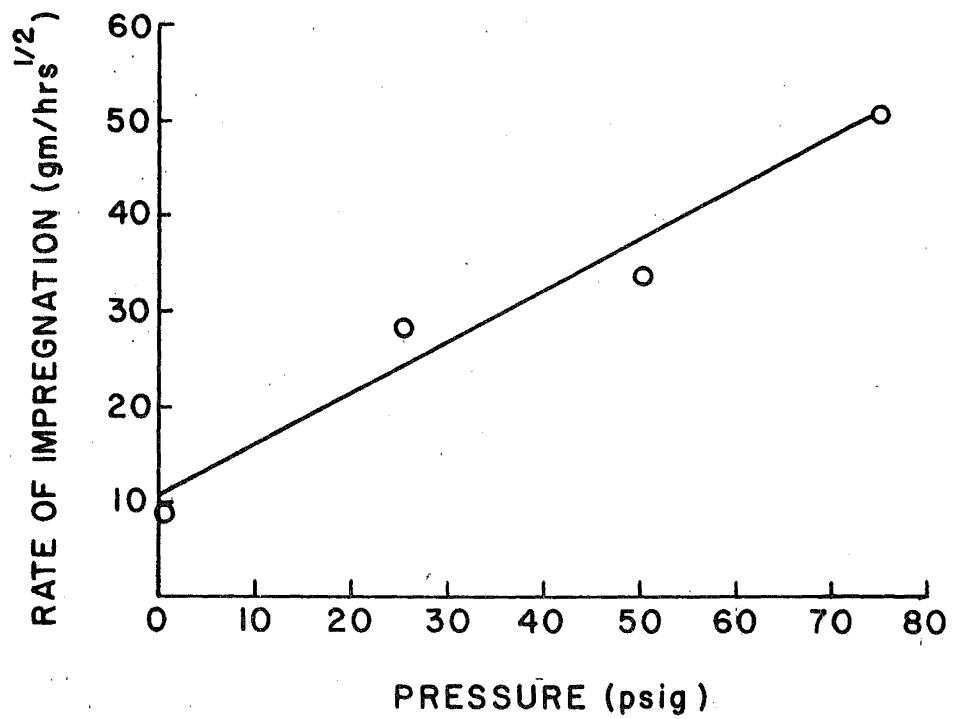
FIGURE B-5 RATE OF IMPREGNATION AS A FUNCTION OF PRESSURE.
(1 psi = 6.89 kPa)

APPENDIX C

DRYING STUDIES

BACKGROUND

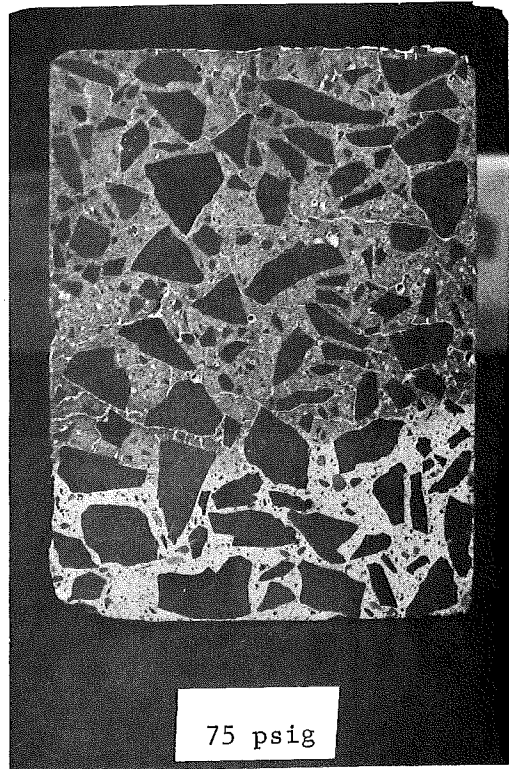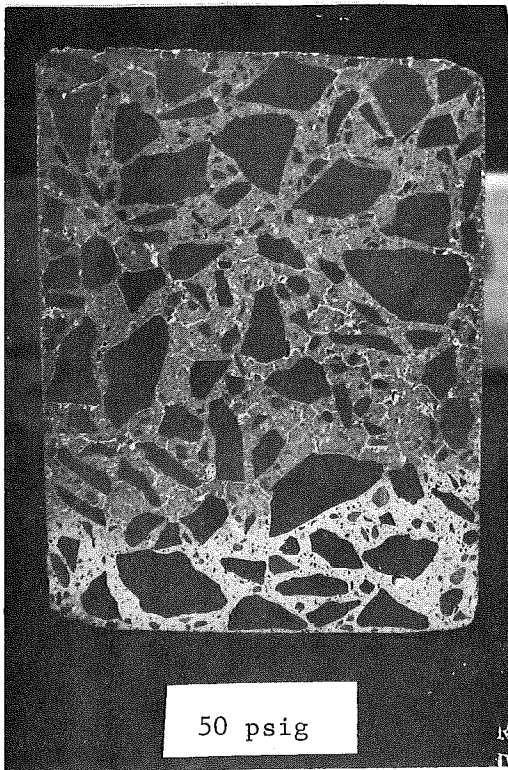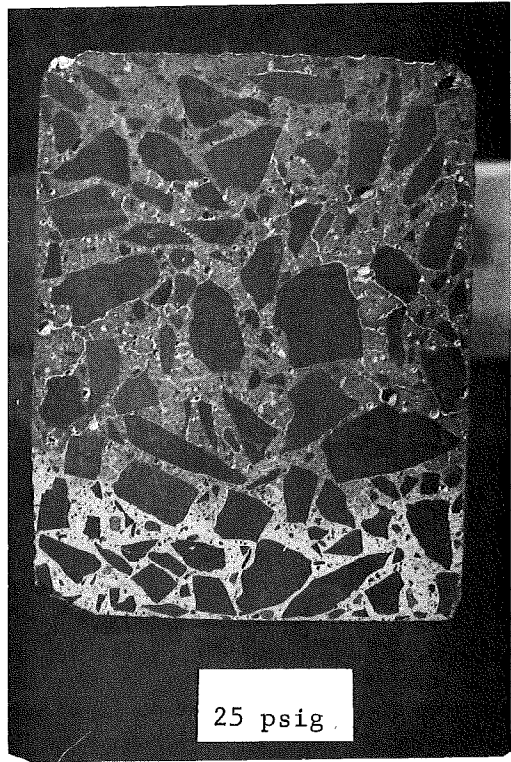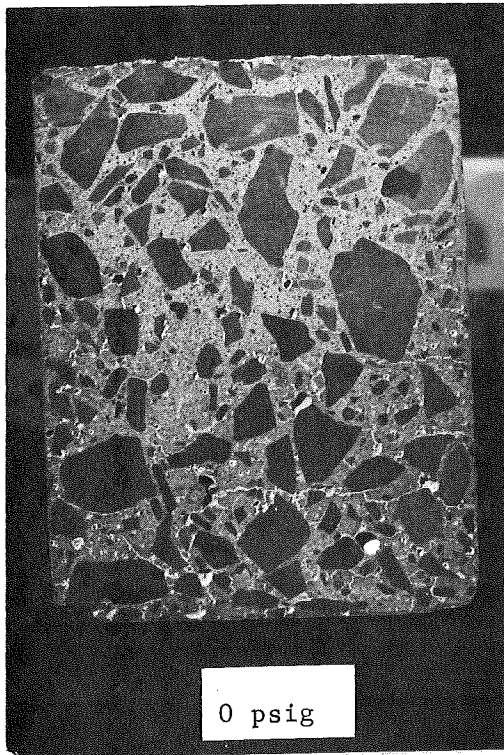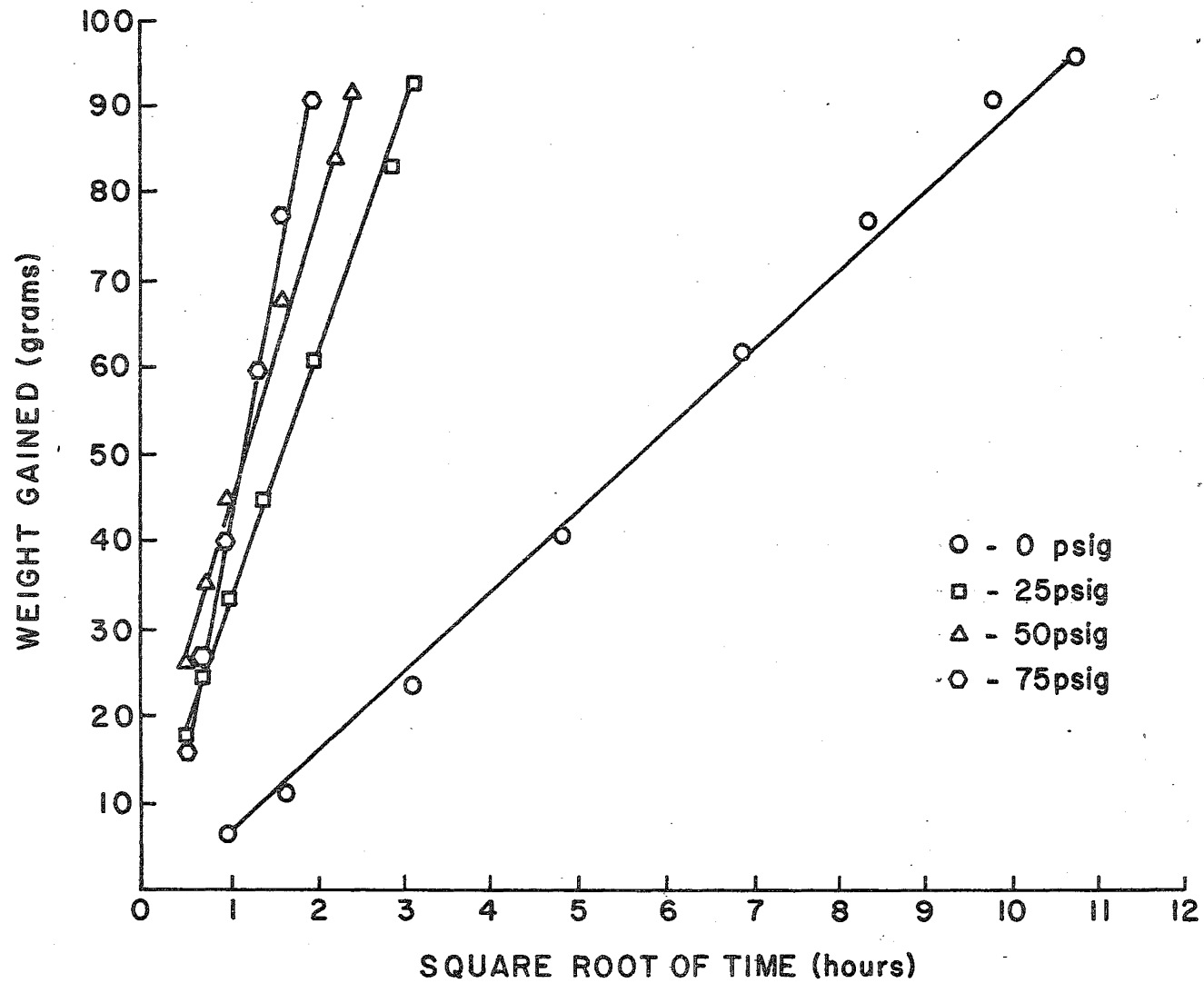It was realized early in the research effort that adequate drying of the concrete would be a major concern in preparing the material for polymer impregnation. Various methods of drying had been reported by others such as BNL (1), BuRec (1), University of Texas (2), and the Kansas Highway Commission (3), e.g., methods based on gas-fired infrared heating, microwave heating, hot-air heating, flame heating, and electro-osmosis devices (3). Since the goal of this project, however, generally posed different drying requirements; namely, deep drying from one side using available techniques capable of easy scale-up, extensive drying tests were carried out to determine the best method. Tests were conducted both in the laboratory and in the field; some were begun prior to this study and funded by other sources.

Studies were conducted to determine which techniques might be best utilized, and some were conducted to establish a practical criterion for drying in the field. Experiments were made with mortar cubes, concrete cylinders, and slabs at the bridge deck of the Pennsylvania Transportation Research Facility.

GENERAL REQUIREMENTS

For preliminary studies, standard portland cement mortar cubes (ASTM C 109-70T) and slabs were prepared and cured. These were then dried under different schedules by a variety of methods such as ambient air, hot air, infrared, radio frequency, and oven drying. A smooth inverse relationship was generally found to exist between surface temperature reached

(regardless of the heat source) and the amount of moisture remaining.

INVESTIGATIONS OF VARIOUS METHODS

Hot Air (Kerosene-Fired Blower and Electrically Heated Blower)

In typical experiments using high-velocity hot air (heated electrically or by a kerosene burner) concrete pieces up to 24 in. x 24 in. x 6 in. (61.0 cm x 61.0 cm x 15.2 cm) were subjected to rapid moving air above 200° F (93°C). Although considerable drying occurred in the concrete, drying the slab at up to 240° F (116°C) for a total of 4 days yielded a net moisture loss of only 76 percent. Since slowness in drying and low degrees of moisture removal were shown to be detrimental to the deep impregnation of concrete, these methods were not favored.

Infrared (IR) Heating

Following earlier work by others, additional studies were made using small cubes and 8-in. x 8-in. x 4 1/2-in. (20.3-cm x 20.3-cm x 11.4-cm) concrete blocks. Large-scale use of IR drying on slabs and on bridge decks themselves was also demonstrated (reported later in this appendix).

In investigations of drying methods, two points regarding IR methods are of special importance:

1. The drying of concrete by such equipment as electrically powered IR heaters requires amounts of power that may be very difficult to obtain in the field because concrete typically has a high total heat capacity per unit area. Relatively high concrete surface temperatures are also required (somewhat > 200°F [93°C]) for sufficient drying for deep impregnations. Thus, electrical power requirements are large.

2. In spite of these power requirements, IR heating tends to be
    relatively efficient compared to other methods such as hot-air
    drying. Depending on the exact conditions, propane-fired IR
    drying may be three times as efficient (relative to propane required)
    as propane-fired hot air, for instance. Shielding from wind in the
    field is conveniently accomplished, so that the high surface temp-
    eratures required may be easily reached.

Microwave or Radio Frequency (RF)

Microwave or radio frequency heating of concrete can result in
rather rapid drying. Since the RF energy is coupled directly with the
water, the time required to heat the system depends only on the materials
present and the power density available. In fact, the rate of RF drying
probably can be as high or higher as with any method thus far reported.
Tests on mortar cubes gave complete drying within minutes.

Several points were considered. First was the cost of RF power. The
generation of electric power utilizes only about one-third of the heat of
combustion in a power plant; the generation of RF power from 60 Hz power
requires another significant loss. It is only once the RF power is at-
tained that the efficiency of transforming RF to heat in the concrete is
high.

Second, radiation hazards and electrical interference must be reck-
oned with in using RF power to dry concrete on a large scale. Portable
RF drying units are under development elsewhere for patch repair of
roads and structures; care is being taken to minimize such problems.

Third, a too rapid release of energy in wet concrete can cause in-
ternal damage due to the sudden vaporization of the water. Thus, an

upper limit may be set on the drying rate by this factor rather than by the deliverable power per se.

In any case, at least during the period of this contract, the use of RF did not appear to be feasible for large-scale use in drying bridge decks for subsequent impregnation.

Oven Drying

Oven drying is often advantageous for laboratory studies. In tests on concrete slabs 24 in. x 24 in. x 6 in. (61.0 cm x 61.0 cm x 15.2 cm), it was also shown to be an effective way to carry out evaluation of parameters such as the change in moisture content with time. Thus, drying 45 hr at 250° F (121 ° C) resulted in complete drying; the rate depended on the square root of time (4), as expected for a diffusional process.

In larger-scale tests, it is possible in principle to field-dry concrete by building ovens to encompass some or all of a structure or slab. Fuel efficiency may be expected to be high, but construction may be expected to be complex and expensive, especially if deep drying is required, as is the case here.

Electro Osmosis

The motion of liquid through membrane-like media under the influence of an electric field (electro osmosis) has been previously investigated for possible use in drying concrete (3). Some preliminary tests were made.

Although success has been reported informally by others, at this time the feasibility of using the method does not appear to be sufficiently established for use in this work. Preliminary experiments in

these laboratories did not yield the relative dryness that is required for rapid penetration of monomers. However, further basic studies in the future would be important in establishing the degree of usefulness for concrete structures. In the case of some potentially useful monomer systems, the applicability of electro osmosis definitely would need to be reevaluated.

Propane-Fired Torch

Application of the technique using a propane-fired torch to dry concrete in the current research was developed and reported (4). The method is quite capable of producing relatively high surface temperatures leading to rapid, deep drying. Typically, the torch is programmed to travel a given route repetitively. The use of a sand covering to protect the surface from flame-induced degradation was found to be desirable.

In comparison with IR drying, the torch method requires more propane per unit dried, and is probably more readily susceptible to decreases in efficiency due to wind, etc. However, the use of propane to obtain heat may be efficient compared to using electricity generated from oil or other fuel. Only small amounts of electricity are required to move and control the torch. In addition, this method has several other practical advantages: low cost, simplicity, and ease of scale-up.

Electric Resistance Heating

For laboratory work on small scale, such as for controlled drying studies, electric resistance heating can be advantageous. This is either through the concrete system or by utilizing the reinforcing steel. However, while it is possible that resistance drying will be developed for large-scale field applications at some later date, for the purposes of

the current contract, it was decided that other methods are more applicable, at least at present.

Several disadvantages hinder such large-scale use. The heat capacity of wet concrete is such that very large electrical power requirements result. Very large electrical generators would be required to dry large slabs of concrete in the field. Further, it is difficult to even approximately match impedances between the electrical source and the concrete load in order to obtain efficient power transfer. In general, the impedance and heat capacity can be expected to change with time as drying progresses.

LABORATORY DRYING TESTS ON LARGE SLABS

Using funding from the Pennsylvania Science and Engineering Foundation and The Pennsylvania State University, laboratory experiments were designed to obtain research data for use in field applications, with emphasis on drying rates as a function of parameters such as surface temperature, moisture content, and size. The basic research was also directed toward seeking relationships between specimen temperature, temperature distribution rate of temperature change, and moisture content.

After consideration of the results of investigations of various drying methods, as reported in the previous section, it was decided that IR drying and propane torch drying were the most feasible for studies which would be useful within the period of this contract and provide relatively efficient use of fuel, time, and cost.

A 6-ft x 6-ft x 6-in. (18.29-m x 18.29-m x 0.15 m) slab was constructed on a raised steel framework with one layer of typical bridge deck reinforcing steel. Thermocouples were placed at depths of 1/2 in.

(1. 3 cm), 1 in. (2.5 cm), 2-1/2 in. (6.4 cm), and 4 in. (10.2 cm) from
the top for five different locations in the slab. The reinforcing used was
composed of No. 4 bars placed on 6-in. (15.2 -cm) centers in one direc-
tion and No. 5 bars placed on 8-in. (20.3-cm) centers in the other
direction. A second slab 6 ft x 6 ft x 8 in. (18.29 m x 18.29 m x
0.20 m) was cast with two layers of reinforcing steel, similar to con-
struction of bridge decks in Pennsylvania. Thermocouples, in this case,
were placed at depths of 2-1/2 in. (6.4 cm) and 4 in. (10.2 cm) from
the top surface for monitoring temperature as drying progressed. Design
details for these slabs and the concrete mixtures used for them are given
in Appendix G.

The two methods--gas-fired infrared (IR) and propane torch--were
used in various experiments to determine suitable drying criteria. Using
moisture gages placed in concrete specimens, the moisture content associ-
ated with different drying methods and temperatures was established. In some
cases, moisture gages were placed in slab positions. Gas-fired IR heaters have
a high relative efficiency compared to some other methods, resulting in a
propane consumption of about 2.9 lb/hr (1.3 kg/hr) for 60,000 BTU/hr
(63 MJ/hr) output. This heater (size 2 ft x 1 ft [6.10 m x 3.05 m])
could dry about 2 ft^2 (0.2 m^2). It was secured from Pavement Reclaiming
Corp., Buffalo, New York (Model TPRC JH2 - Joint Heater).

Curves in Figures C-1 and C-2 present the temperature profile data
of the 6-ft x 6-ft x 6-in. (18.29-m x 18.29-m x 0.15 m) slab and the
6-ft x 6-ft x 8-in. (18.29-m x 18.29-m x 0.20 m) slab, respectively,
during drying tests using the gas-fired infrared heater. Many

drying tests were ∧conducted using different sources and the temperature profiles presented are considered to be typical (5). Some of the slab drying tests produced severe cracking (however, on drying a bridge deck, severe cracking was not observed).

For drying of concrete using gas-fired heaters, one can either maintain a constant surface temperature (as in oven drying) or maintain the heater at a constant distance above the concrete. To maintain a constant surface temperature, the surface temperature must be observed and the heater distance above the concrete controlled, as is evident in Figures C-1 and C-2. To avoid the constant monitoring required to maintain a constant surface temperature, one can also choose to maintain a constant difference between the heater and the slab. This was done in this case.

There are two distinct drying periods evident in the curves. In the first period, average moisture content decreases fairly fast and the temperature rises, after which it remains about constant. This is sometimes called the constant rate period and capillary flow is believed to be (6) the principal mechanism of moisture migration. This period terminates when the slab temperature begins to increase. A second period is called the falling rate period. Here moisture movement is believed to be mainly by an evaporation and condensation mechanism. In this period, the rate of temperature rise throughout the concrete steadily decreases until equilibrium with the surroundings is reached.

Establishing Criteria for Drying

To predict if the concrete is dry to a prescribed level at 4 in. (10 cm), using IR, a thermocouple can be placed at a depth of 4 in.

(10 cm) or one can use the surface temperature as an indication of the
temperature at 4 in. (10 cm). The best indication using surface temp-
erature seems to be to observe the rate of surface temperature change
once per hour, and when the rate of increase per hour is 10° F (5.5° C)
or less, the temperature at 4 in. (10 cm) approaches equilibrium.
This rate occurred about 2 hr after the temperature at 4 in. (10.2 cm)
reached about 212° F (100° C). Table C-1 presents the rate of surface
temperature change along with the temperature at 4-in. (10-cm) depth.
In summary, there appear to be two ways of expressing the criteria.
First, when the rate of temperature change at the surface is 10° F/hr
(5.5° C/hr) or less, drying equilibrium in the concrete is nearly
attained at 4 in. (10 cm). Alternately, when the temperature at 4 in.
(10 cm) is above 230°F (110°C), drying equilibrium is practically at-
tained. The temperature at 4 in. (10 cm) during the test appeared to
level out at about 260° F (127°C) when the ambient temperature was
70° F (21°C).

Effect of Drying on Monomer Loading and Moisture Absorption

In order to establish a criterion for drying in terms of impregnation
characteristics, a typical MMA monomer system was employed in evaluating
monomer penetration: 100:10:0.5 mixtures of MMA, trimethylolpropane
trimethacrylate (TMPTMA) and azobisisobutyronitrile (AZO). This system
has been very useful in laboratory experiments with bridge deck cores,
cast cylinders, and slab and field work.

Drying to 230° F (110° C) or higher at a depth of 4 in. (10 cm)
results in ease of penetration under pressure above atmospheric values.
It has also been shown by Weyers (7) that the MMA system will soak

through 5 in. (12.7 cm) of bridge deck cores in 4 to 11 days if these are

properly dried (specimens were oven-dried and then vacuum oven-dried).

In the Weyers' experiments, soaking occurred from the top only and sides

were sealed. Additional data are given in Appendices B, D, and F.

Effects of Heating Rate

After the drying criterion (230°F at 4 in. [110°C at 10 cm]) was

adopted, preliminary experiments were also made with 24-in. x 24-in. x

6-in. (61.0 -cm x 61.0 -cm x 15.2 -cm) slabs to correlate moisture loss

directly with temperature and rate of drying. For this study, 24-in. x

24-in. x 6-in. (61-cm x 61-cm x 15-cm) concrete slab specimens were

prepared from a conventional non-air-entrained 1.00:1.92:6.10:6.75 water-

portland cement (type 1)--coarse sand-limestone aggregate (1 in. [2.5 cm]

maximum) mix with a cement factor of 485 lb/cu yd (287 kg/m^3) and a

28-day average compressive strength of 4,750 psi (32,800 kN/m^2). The

measured air content was 3 percent with a slump of 2.5-3.0 in. (6.4-7.6 cm).

The slabs were given a normal trowel finish and were cured in the fog room

(90-100 percent RH) for at least 28 days before the drying and impregnation

tests. All slabs contained a nominal steel reinforcement at a 4-in.

(10-cm) depth to simulate the structure of the bridge deck. The slabs

were tested between 9 to 12 months after casting and were stored in

a moist room at 90-100 percent RH prior to testing. Six thermocouples

were embedded in each of slabs 1, 2, and 3 at various depths and posi-

tions. The gas propane torch was used for drying, and the slabs weighed

to monitor moisture content.

Results showed that, as expected, the higher the heating rate, the

shorter the time required to reach 230° F (110°C) at any depth (Figure

Table C-1. Surface Temperature Rate Compared To Temperature at 4 in.[1]

Test	Surface ΔT (°F)[2] for each hr after 212°F is reached at 4 in.		Temperature (°F) at 4 in. at end of each hr
6' x 6' x 8"		36	212
	1 hr	18	243
	2 hr	5.4	264
6' x 6' x 6"		27	212
Position 1	1 hr	18	236
	2 hr	5.6	254
6' x 6' x 6"		27.6	218
Position 3	1 hr	7.2	238
	2 hr	0	251
6' x 6' x 6"		25.2	213
Position 4	1 hr	16.2	235
(crack)	2 hr	12.6	254

Unit Conversions: $°F = \frac{9}{5} °C + 32$

1 in. = 2.54 cm

1 ft = 0.305 m.

1. Ambient temperature was about 70°F.

2. ΔT = temperature at end of hour − temperature at beginning of hour.

C-3). However, the shorter the time, the lower the amount of water lost. Although those results cannot be correlated directly with the IR experiments (large slabs or bridge decks), the results might suggest that more work is needed in terms of moisture loss/monomer pickup for a greater variety of concretes and conditions.

It was also found in preliminary experiments that alternate drying could be more efficient than continuous drying (Figure C-4). During cooling, water continues to evaporate as long as a positive thermal gradient exists with respect to the surroundings. It may be possible, therefore, to reduce the costs of drying by making use of this effect.

FIELD DRYING TESTS

Infrared Dryer

A slab portion of the deck of the Pennsylvania Transportation Research Facility was first used for field drying studies (termed Field #1). This was followed by a second field test on a larger section of the facility using IR drying only (termed Field #2). Subsequently, a portion of a bridge deck in Bethlehem, Pa., was also IR dried (termed Field #3), adding more experience to drying in the field. In all cases, the dried sections were impregnated with MMA, followed by polymerization to ascertain the drying procedure.

In the first case, drying was accomplished by both propane torch and flame infrared, followed by both "ponding" and by pressure types of impregnation. Polymerization was accomplished by both hot water and steam. This illustrates the various combinations that can be used in the field to get more than 4-in. (10-cm) penetration of polymer.

In field test #1, thermocouples were placed in the bridge deck by

drilling holes in the concrete. As noted in Figure C-5, the form of the temperature profile with time is similar to that noted in Figures C-1 and C-2 for research slabs. Time to reach a given temperature seems to be longer, compared to the slab tests, because of the low ambient temperature and cooling effect of winds. The equipment failure occurred when the heater was extinguished by high winds. This problem was solved by using a shield around the IR heater. The areas dried were relatively small (3.75 ft^2 [0.35 m^2]), but impregnation to 4 in. (10 cm) with subsequent polymerization was obtained, indicating adequate drying. Table C-2 presents a summary of temperature rate data.

Field test #1 for drying indicates that both IR and propane torch drying could achieve adequate results in the field. The IR system--as mentioned earlier--tends to use less propane and may be less affected by wind. Propane torch systems could conceivably be cheaper to construct, however.

Field tests 2 and 3 were limited to gas-fired IR drying using a 4-ft x 5-ft (1.22-m x 1.52-m) IR system of 180,000 BTU/hr (130 MJ/hr) capacity. Table C-3 summarizes the findings.

Flame Dryer

As described in Appendix H, the torch unit was used successfully to dry several sections of the Pennsylvania Transportation Research Facility bridge deck. The subsequent impregnation was successful to 4-in. (10-cm) depths.

Drying Criterion

Since the laboratory tests showed that a temperature of 230° F

Table C-2. Surface Temperature Rate Compared
to Temperature at 4 in.[1]

Test	Surface ΔT (°F)[2] for each hr after 212°F is reached at 4 in.	Temperature (°F) at 4 in. at end of each hr
Bridge Deck	22	212
(Field Test #1)	1 hr 36	223
PSU Test Track	2 hr 9	231

Unit Conversions: 1 in. = 2.54 cm

$$°F = \left(\frac{9}{5}\right) °C + 32.$$

1. Ambient temperature was about 31°F (-0.56°C).

2. ΔT = temperature at end of hour minus temperature at beginning of hour.

Test[1]	Drying Times	Max. Surface Temp. °F
Field Test 2, PSU Test Track	4 hr	630
Field Test 3, Bethlehem, Pa.	7 hr	680

Table C-3. Summary of Drying Times

Unit Conversion: °F = $\frac{9}{5}$ °C + 32.

1. Ambient temperatures were about 77°F and 50°F, respectively. Drying time is time to reach 230°F at 4 in.

(110° C) resulted in drying to 80 percent or more of oven dry weight,
this criterion was tested in the first small-scale field trials (see
Appendix G). Since the trials were successful, the criterion was
adopted. Additional trials may be necessary if the mix design is changed
or a high absorption type aggregate is used. Slight alterations of the
drying criteria may be necessary to accommodate these variables.

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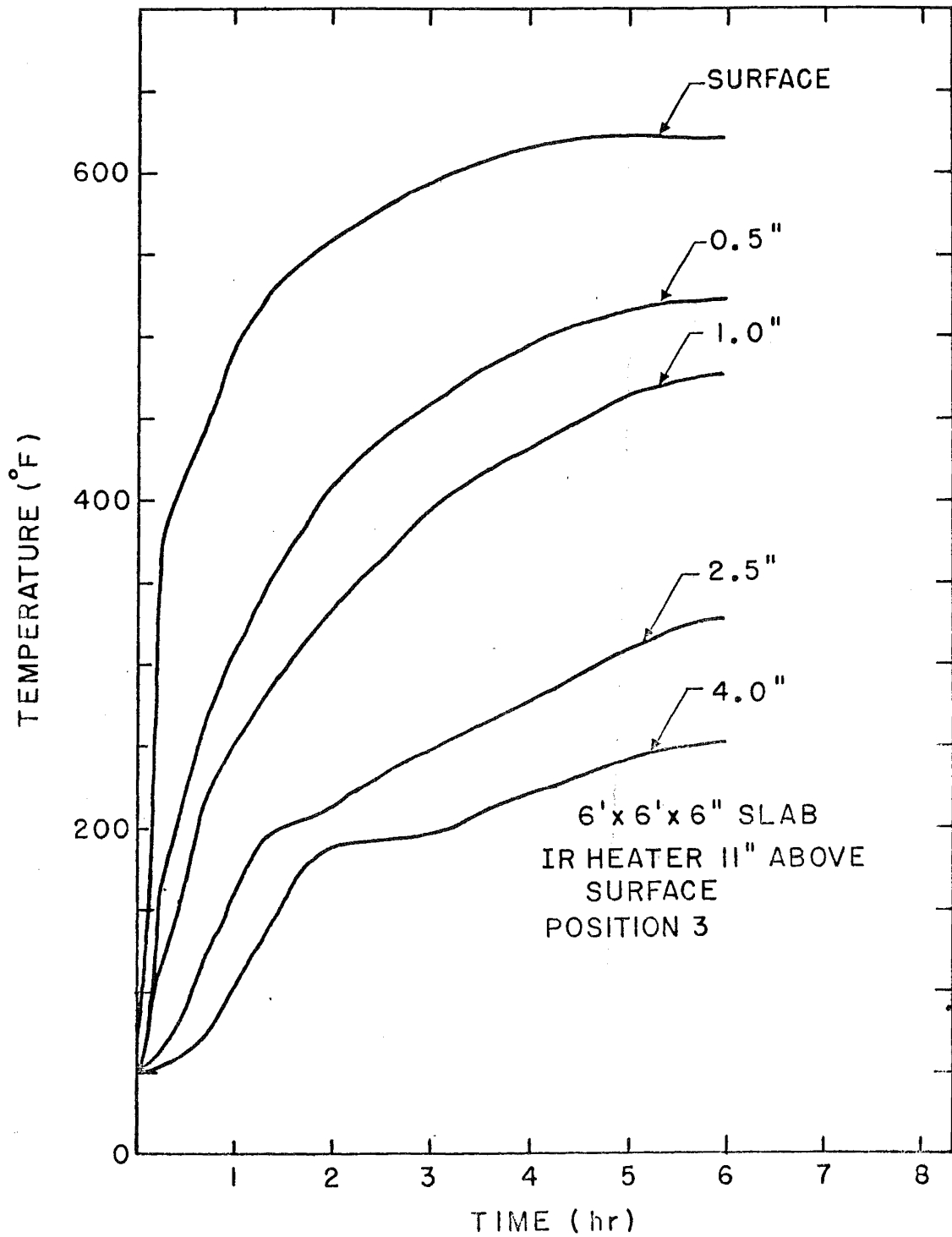
Fig. C-1 TEMPERATURE PROFILE vs TIME FOR 6' x 6' x 6"
SLAB TRIAL. Ambient Temperature 70°F (One Inch
$= 2.54$ cm; $^\circ$F $= \frac{9}{5}^\circ$C $+32$)
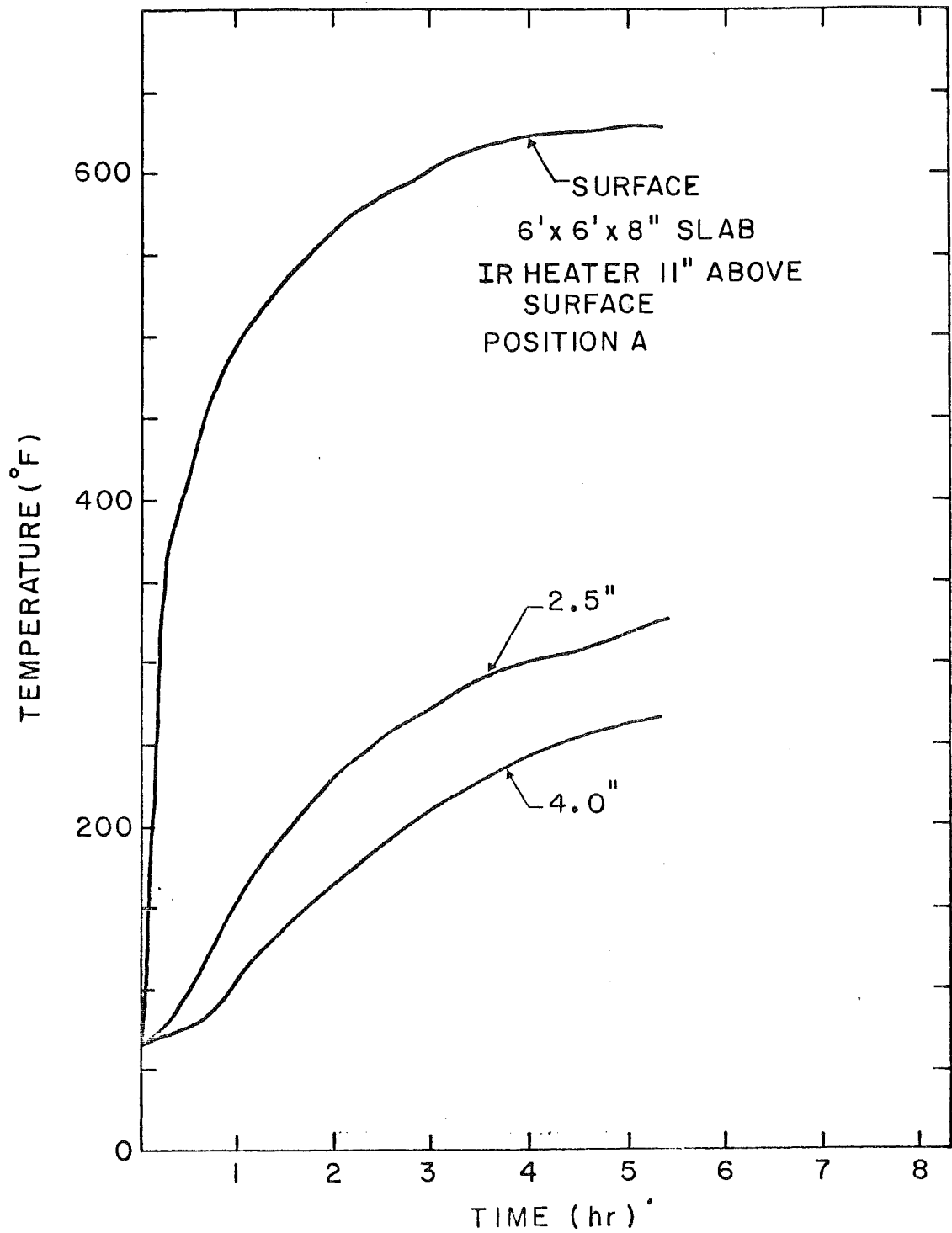
Fig. C-2 TEMPERATURE PROFILE vs TIME FOR 6' x 6' x 8"
SLAB TRIAL. Ambient Temperature $70^{\circ}F$ (One Inch =
2.54 cm, $^{\circ}F = \frac{9}{5}^{\circ}C + 32$)
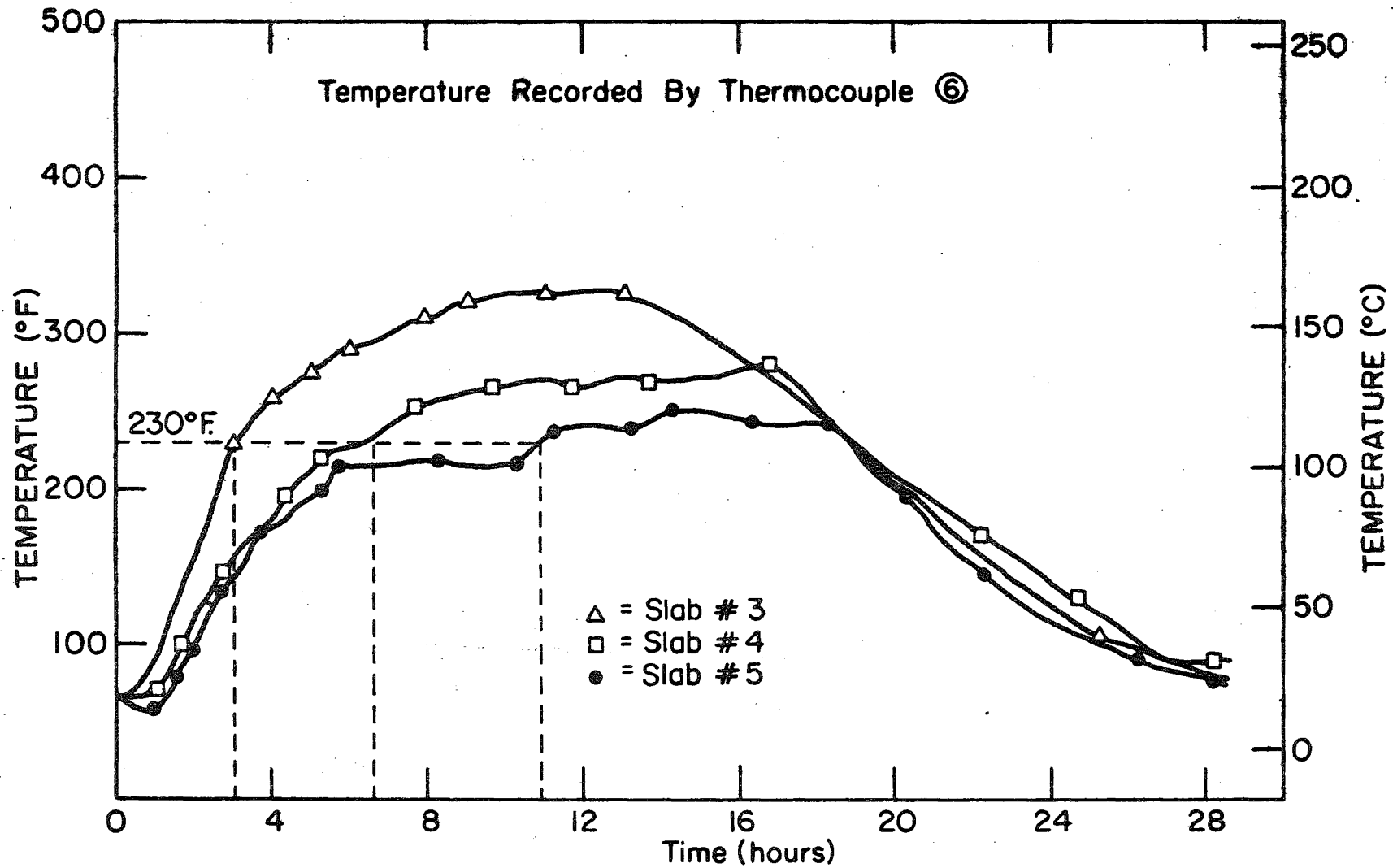
Fig. C-3 Temperature Vs. Time for Underside of 24"x24"x6" Slabs (One Inch = 2.54 cm, $^\circ F = \frac{9}{5} {}^\circ C + 32$)
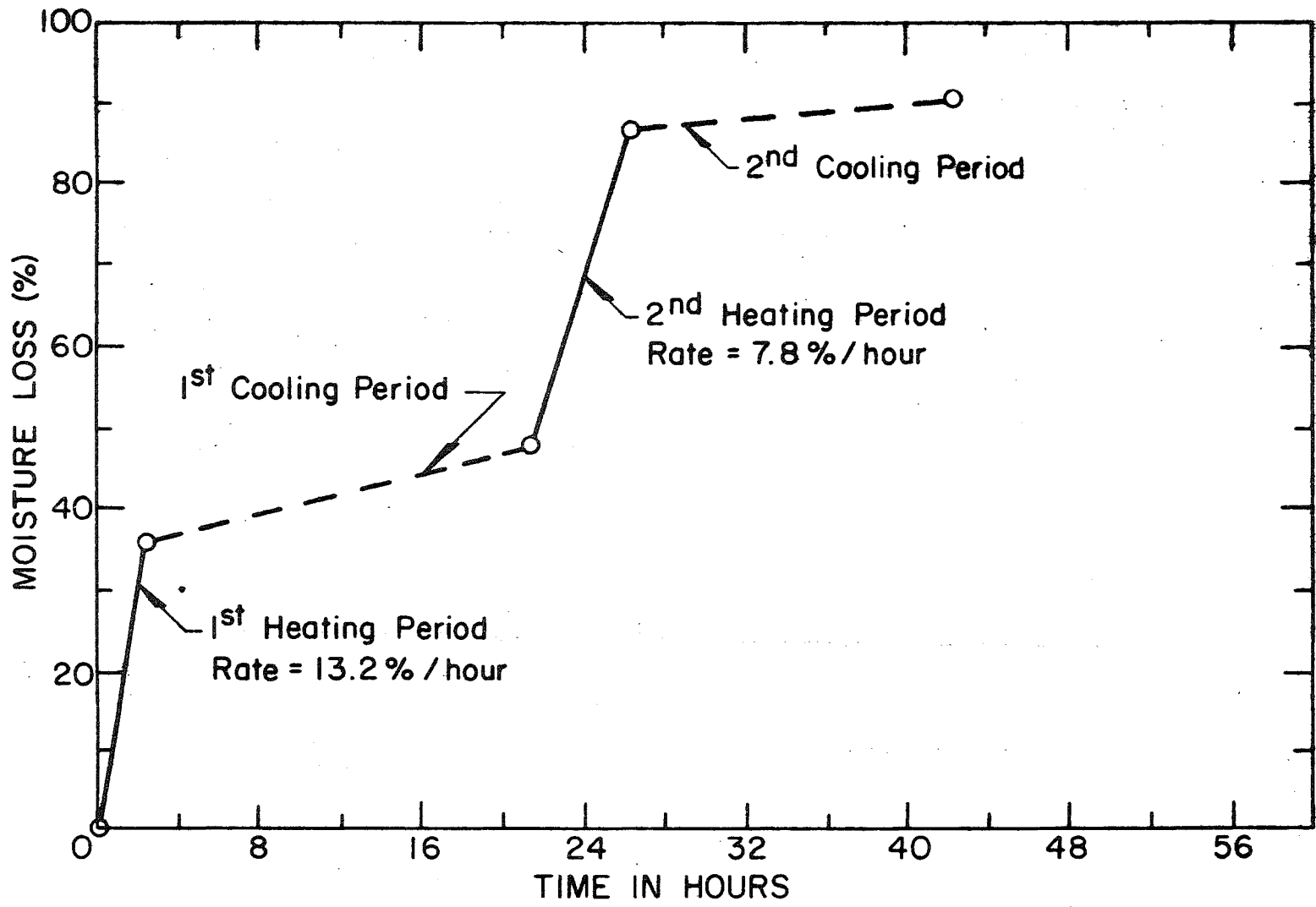
Fig. C-4 Moisture Loss Curve for 24"x24"x6" Slab Dried by Alternate Heating and Cooling (One Inch = 2.54 cm)

Fig. C-5 TEMPERATURE PROFILE vs TIME FOR BRIDGE DECK DRYING TRIAL.

APPENDIX D

IMPREGNATION STUDIES

THEORETICAL ASPECTS

Although the morphology of concretes and mortars is complex, the solid phase may be considered to be a single-component, rigid, isotropic material containing a network of interconnected pores (1). Since these pores have a broad distribution of sizes and contain both air and water, the rate of penetration and equilibrium sorption of a given fluid depend on the thermal-curing 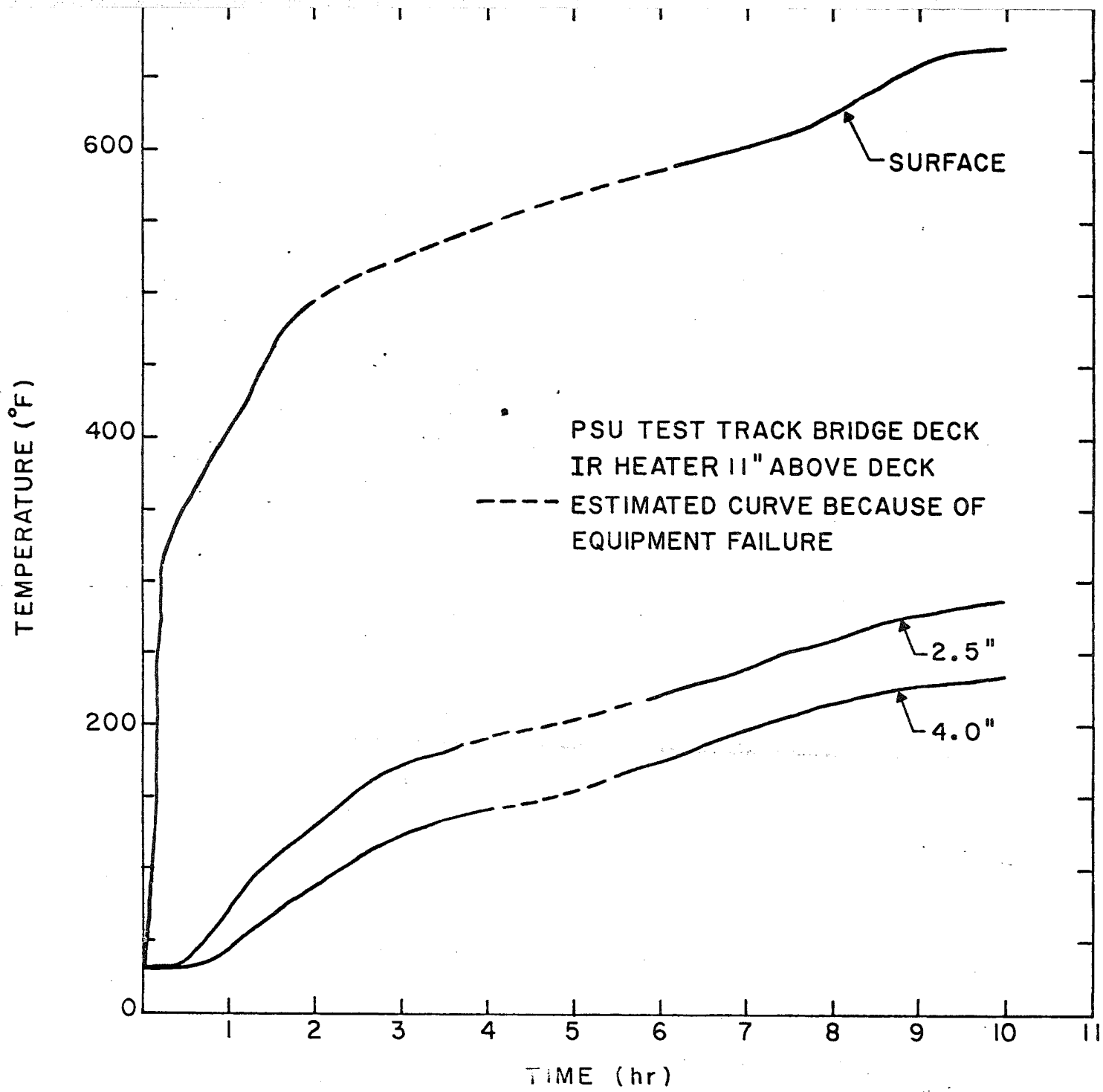and atmospheric history of the substrate. As will be shown below, however, a mortar specimen with a given porosity and history can give reproducible rates of penetration with a given monomer, so that the different rates observed with various monomers reflect real differences attributable to such properties as interfacial energy and viscosity.

Several approaches have been taken to characterize fluid flow through porous media. Assuming a constant porosity and pressure gradient in the x direction, the application of Darcy's law (2) leads to the following expression for the permeability constant P (the volume of fluid of unit viscosity passing through a unit cross-sectional area in unit time):

$$P = \eta q \ L/A\Delta P \tag{D-1}$$

where η is the viscosity, q the rate of flow through area A (dependent on the porosity), and ΔP the pressure drop through the medium of thickness L. Poiseuille's equation has also been modified by several investigators to give equations which involve such

measurable parameters of the substrates as the surface area per unit volume S_w:

$$q = \left[kA\, \upsilon_w^3 / \eta S_w^2 \right] (\Delta P/L) \tag{D-2}$$

where S_w is the specific surface area of the substrate with υ voids per unit length, and k is a constant.

Equations D-1 and D-2 account for the viscosity of the fluid and the porosity of the substrate; however, they do not account for the capillary-rise phenomenon. The height of rise h of a fluid ascending a capillary pore of radius r is given by the Rideal-Washburn equation (3):

$$r \cos \theta = 2\eta h^2 / \gamma t \tag{D-3}$$

where θ is the contact angle, γ the surface tension of the fluid, and t the time. Thus for a given contact angle and pore size, the value of h should vary directly with the product $(\gamma t/\eta)^{1/2}$.

The penetration of a fluid into a porous substrate should proceed according to Equations D-1 to D-3 (until it is counterbalanced by evaporation from the surface or stopped by entrapped air or water vapor); however, at the time this work was begun these equations had not yet been tested with conctete substrates nor was the moisture known. Studies of penetration rate per se are discussed in Appendix B; the studies discussed here were concerned primarily with effects of moisture content and techniques.

CONCRETE AND MORTAR LAB SPECIMENS

Effects of Moisture Content on Monomer Loading

Mortar cubes 2 in. x 2 in. x 2 in. (5.1 cm x 5.1 cm x 5.1 cm) were molded and dried for different periods of time in an oven (221°F [105°C]. When 30, 40, 50, 60, 80, and 100 percent of the water that could be

removed from the mortar cubes under the drying conditions stated had

been removed, two cubes for each condition were taken from the oven.

These cubes were allowed to cool and then were soaked in the MMA-TMPTMA-AZO

system for 3 days. The cubes were then polymerized by a thermo-catalytic

procedure. The important result of this test was that if 20 percent

of the water that could be removed from the mortar under the drying

condition stated remained, impregnations of approximately 90 percent

of the monomer that could be impregnated at zero percent moisture

content could be achieved. This implies that good monomer loadings

could be achieved at 20 percent or less moisture contents. Detailed

discussion and results of this test are given by Pu (4).

PRESSURE METHOD

Slabs

Concrete slab specimens, 24 in. x 24 in. x 6 in. (61 cm x 61 cm x

15 cm), were prepared from a conventional non-air-entrained 1.00:1.92:

6.10:6.75 water-portland cement (type 1)-coarse sand-limestone aggregate

(1 in. [2.5 cm] maximum) mix with a cement factor of 485 lb/cu yd (287

kg/m^3) and a 28-day average compressive strength of 4,750 psi (32,800

kPa). The measured air content was 3 percent with a slump of 2.5 in.

to 3.0 in. (6.4 cm to 7.6 cm). The slabs were given a normal trowel

finish and were cured in the fog room (90 - 100 percent relative

humidity) for at least 28 days before use in drying and impregnation

tests. All slabs contained a nominal steel reinforcement at a 4-in.

(10-cm) depth to simulate the structure of the bridge deck, and

one 72-in. x 72-in. x 8-in. (180-cm x 180-cm x 20-cm) slab was prepared to the PennDOT AA specification.

In these tests, the 24-in. x 24-in. x 6-in. (61-cm x 61-cm x 15-cm) slabs were oven-dried at 257°F (125°C) while the 72-in. x 72-in. x 5-in. (183-cm x 183-cm x 20.32-cm) slabs were dried using the propane-torch assembly (Appendix C).

Impregnation and Polymerization

The completely dried 24-in. x 24-in. x 6-in. (61-cm x 61-cm x 15-cm) concrete slabs were positioned on supports with their lower surfaces exposed and subjected to impregnation from their upper surfaces. Details of the equipment used are presented in Appendix G.

The first slab was dried and impregnated at a pressure of 30 psi (210 kPa). After 17 hr, a dark spreading patch of monomer appeared on the underside of the slab; by 24 hr this patch had grown to a diameter of 18 in. (46 cm), larger than the diameter of the area impregnated from the upper surface. At this point, the impregnation device was removed and a 0.5-in. (1.3 cm) layer of sand was spread over the area enclosed by the gasket and wetted with additional monomer, to minimize evaporative losses during polymerization (5, 6). The slab was then wrapped in polyethylene film and live steam was played on its surface for 5 hr to polymerize the monomer mixture. After polymerization, the polymer loading of this slab was determined to be approximately 5.5 percent.

When the slab was broken, only a slight odor of monomer was detected, indicating that the polymerization had proceeded to high conversion. Moreover, the appearance of the fracture cross section was

and 0.750 percent by weight of mortar for 1.0, 2.5, 4.0, and 6.0 percent

salt solutions, respectively.

After the specimens were salt contaminated, they were again

dried in a forced air oven to constant weight. The lateral sides

were coated with epoxy, and the cylinders were then impregnated from

the top surface with MMA-TMPTMA-AZO (100:10:05 by weight) at 75 psig

(517.1 kPa) over-pressure in an impregnation chamber described by

Weyers (8).

The impregnation data for the salt-contaminated cylinders are

presented in Table D-1. The error of regression showed that the

impregnation level tends toward a linear function of the monomer

weight gain in grams as a function of the square root of time. However, the

slope of the curve (rate of impregnation) varied by about 25 percent among

the cylinders prepared from a single batch mix.

In order to analyze the variability in the impregnation rates for the

cylinders, the percent MMA gained at 2 hr and the total percent volume

filled with MMA was compared with the percent salt used. The

correlation coefficients were compared for significance at the 95 percent

confidence level. Since correlation was not established for the

percent salt solutions and the total percent volume filled with MMA

or the percent MMA gained in 2 hr, the presence of 0.750 percent chloride

appeared to have no effect on penetration.

Additional impregnation studies for salt-contaminated are discussed

below and in Appendix F.

PONDING METHOD

Cores

The impregnation of cast cylinders by ponding MMA-TMPTMA-AZO

Table D-1. Laboratory Cylinders Impregnation Data

(Impregnated at 75 psig)

Cylinder Number	Slope $(g/hr^{1/2})$	Error 6f Regression	Monomer Gained in 2 hr (g)	Total Monomer Gained (g)	Percent at 2 hr	Percent Volume Filled	Percent Salt Solution	Total Pressure Time (hr)
PS 1-1	61.5	0.998	78.7	108.0	78.7	11.2	1.0	3.5
PS 1-2	68.1	1.000	80.8	114.0	80.8	11.8	1.0	3.0
PS 1-3	55.3	0.998	78.7	102.2	78.7	10.6	1.0	3.5
PS 2-1	64.7	1.000	76.0	113.4	76.0	11.7	2.5	3.5
PS 2-2	63.2	0.997	85.3	109.0	85.3	11.3	2.5	3.0
PS 2-3	64.0	0.999	73.1	115.0	73.1	11.9	2.5	3.5
PS 3-1	55.2	0.996	75.8	108.9	75.8	11.3	4.0	4.0
PS 3-2	56.1	0.993	83.9	106.0	83.9	11.0	4.0	3.5
PS 3-3	66.0	0.978	93.9	111.5	93.9	11.5	4.0	3.0

similar to that of other polymer-impregnated specimens. The dark polymer-impregnated region can be distinguished readily from the light unimpregnated region. The diameter of the impregnated region was 21 in. (53 cm) on the upper surface and 18 in. (46 cm) on the lower surface of the slab, indicating that the impregnating monomer had spread laterally beyond the 16-in. (41-cm) diameter enclosed by the gasket. Also, the lighter 0.25-in. (0.6-cm) surface layer on the bottom indicated that some monomer was lost from the lower surface by evaporation. Examination of the fracture cross section with a magnifying glass showed that, in the polymer-impregnated region, fracture usually occurred through the aggregate particles, but in the unimpregnated region, it typically occurred around the particles.

This first slab impregnation was successful in that it achieved the deepest impregnation in sound concrete reported to date. To confirm and extend this result, other slabs were dried and impregnated. The parameters investigated included the pressure applied during impregnation, the substitution of isobutyl methacrylate for methyl methacrylate in the monomer mixture, the use of hot-water ponding instead of steam to polymerize the monomer, and the presence of salt as a contaminant in the concrete substrate (see Appendix F).

In these experiments, the pressure was varied from 30 psi to 80 psi (210 kPa to 550 kPa). The impregnation proceeded smoothly in all cases, but there was some leakage of monomer around the gasket at pressures greater than 60 psi (410 kPa). An increase in the pressure decreased the time required for penetration to the full 6-in. (15-cm) depth, e.g., from 17 - 24 hr for 30 psi (210 kPa) to 2.0 - 3.5

hr for 80 psi (550 kPa). These times are expressed as ranges; the first value denotes the first appearance of monomer on the underside of the slab, and the second value the time required for complete impregnation. Apparently, the monomer mixture penetrates first through the channels and microcracks from which the water has been removed and only later fills the micropores and large voids as it spreads both downward and laterally through the slab.

Isobutyl methacrylate was substituted for methyl methacrylate in two slabs in this study because it is less volatile and therefore less subject to loss by evaporation. Moreover, polyisobutyl methacrylate is more flexible and less brittle than polymethyl methacrylate and thus may be better able to withstand repetitive freezing-and-thawing cycles.

All of the slabs were polymerized by heating for 5-8 hr using steam except for one slab which was polymerized overnight using hot-water ponding on its surface. During the course of the polymerization, the temperature of the water decreased from 140°F (60°C) to 100°F (43°C) and some monomer was lost by evaporation from the underside of the slab.

Cylinders

A series of concrete cylinders were cast with a concrete mixture used by the Pennsylvania Department of Transportation. After 28 days of moist curing (100 percent relative humidity at 68°F [20°C]) these cylinders were dried to constant weight and impregnated with salt solutions. A mixture of one part $CaCl_2$ to three parts NaCl was used in preparing the salt solutions. The cylinders were impregnated with a 1.0, 2.5, 4.0, and 6.0 percent salt solution (by weight). The acquired salt contents were analyzed by a titration procedure developed by Berman (7). The concrete speciments acquired chloride levels of 0.125, 0.318, 0.500,

and 0.750 percent by weight of mortar for 1.0, 2.5, 4.0, and 6.0 percent

salt solutions, respectively.

After the specimens were salt contaminated, they were again

dried in a forced air oven to constant weight. The lateral sides

were coated with epoxy, and the cylinders were then impregnated from

the top surface with MMA-TMPTMA-AZO (100:10:05 by weight) at 75 psig

(517.1 kPa) over-pressure in an impregnation chamber described by

Weyers (8).

The impregnation data for the salt-contaminated cylinders are

presented in Table D-1. The error of regression showed that the

impregnation level tends toward a linear function of the monomer

weight gain in grams as a function of the square root of time. However, the

slope of the curve (rate of impregnation) varied by about 25 percent among

the cylinders prepared from a single batch mix.

In order to analyze the variability in the impregnation rates for the

cylinders, the percent MMA gained at 2 hr and the total percent volume

filled with MMA was compared with the percent salt used. The

correlation coefficients were compared for significance at the 95 percent

confidence level. Since correlation was not established for the

percent salt solutions and the total percent volume filled with MMA

or the percent MMA gained in 2 hr, the presence of 0.750 percent chloride

appeared to have no effect on penetration.

Additional impregnation studies for salt-contaminated are discussed

below and in Appendix F.

PONDING METHOD

Cores

The impregnation of cast cylinders by ponding MMA-TMPTMA-AZO

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PS 1-3	55.3	0.998	78.7	102.2	78.7	10.6	1.0	3.5
PS 2-1	64.7	1.000	76.0	113.4	76.0	11.7	2.5	3.5
PS 2-2	63.2	0.997	85.3	109.0	85.3	11.3	2.5	3.0
PS 2-3	64.0	0.999	73.1	115.0	73.1	11.9	2.5	3.5
PS 3-1	55.2	0.996	75.8	108.9	75.8	11.3	4.0	4.0
PS 3-2	56.1	0.993	83.9	106.0	83.9	11.0	4.0	3.5
PS 3-3	66.0	0.978	93.9	111.5	93.9	11.5	4.0	3.0

Table D-1. Laboratory Cylinders Impregnation Data

(Impregnated at 75 psig) (Continued)

Cylinder Number	Slope $(g/hr^{1/2})$	Error of Regression	Monomer Gained in 2 hr (g)	Total Monomer Gained (g)	Percent at 2 hr	Percent Volume Filled	Percent Salt Solution	Total Pressure Time (hr)
PS 4-1	60.5	0.990	85.7	112.8	85.7	11.7	6.0	3.5
PS 4-2	43.2	0.987	81.3	107.2	81.3	11.1	6.0	4.0
PS 4-3	67.6	0.999	91.7	108.0	91.7	11.2	6.0	3.0
PS 5-1	54.8	0.994	84.2	102.0	82.5	10.5	0.0	3.5
PS 5-2	64.6	0.993	94.3	101.6	92.8	10.5	0.0	2.5
PS 5-3	70.0	0.997	100.0	100.0	100.0	10.3	0.0	2.0

Unit Conversions: 1 psi = 6.9   -kPa

1 oz = 28.4 g.

(100:10:0.5) is discussed in detail in Appendix B. It appears from these data that,if the cylinder is sufficiently dry, deep impregnations (up to 8 in. [20.3 cm]) can be achieved. Also, when the cylinders are dried from the top surface using infrared heat, heavy impregnations of up to 3.5 in. (8.9 cm) from the surface can easily be achieved.

Cores obtained from three salt-contaminated bridge decks were impregnated with MMA-TMPTMA-AZO (100:10:0.5)by weight) by ponding on the top surface only. Prior to impregnation, the lateral sides of these cores were coated with epoxy, and these cylinders were dried in a forced air oven (240°F [116°C]) for 3 days after which they were placed under vacuum in an oven at 250°F (121.1°C) for 24 hr. The MMA system was ponded on the top surface and the impregnation was continued until the monomer system soaked through about 5 in. (13 cm) of the core. The deicer salts appeared to decrease the rate of impregnation (8). The study is discussed in detail in Appendix F.

Slabs

Large-scale slab studies (6 ft x 6 ft x 6 in. [18.29 m x 18.29 m x 15.2 cm]and 6 ft x 6 ft x 8 in.[18.29 m x 18.29 m x 20.3 cm]) showed that after drying with infrared heat to a prescribed drying schedule, ponding over the dried area with a MMA-TMPTMA-AZO (100:10:0.5 by weight) system produced impregnation to about 4-in. (10-cm) depth in 4 days. These results are discussed in more detail in Appendix G.

PRESSURE MAT

The foregoing results show that the bolt-down impregnation unit was suitable for carrying out impregnation at greater-than-atmospheric pressure. However, this type of apparatus is limited in terms of weight and mobility. A better method of pressure impregnation was sought: a pressure

mat impregnation unit.

The first pressure mat experiment used a molded rubber door mat comprised of diamond shape cells about 0.5 in. (1.3 cm) deep except for an elliptical area in the center, which was marked "Welcome." This mat was inverted with the cell-side down on a dried 24-in. x 24-in. x 6-in. (60.96-cm x 60.96-cm x 15.24-cm) concrete slab and held in place by a bolted-down metal sealing strip around the edge of the slab and the mat. Monomer was introduced into the cells of the mat through the same pressurizing apparatus used before, but this time arranged so that the monomer was injected into the cells between the back of the mat and the concrete substrate. This whole assembly was mounted in a hydraulic press which was subjected to an unloading and loading cycle to simulate the effect of a roller going over and over such a pressure mat in actual practice (Figure D-1).

It was found after 5 hr of impregnation that the monomer struck through the bottom of the slab and, about the same time, the center of the mat around the "Welcome" sign deteriorated so that it disintegrated. The monomer infused into the slab was polymerized in the conventional way, and the slab was broken to determine the depth of penetration. It was found that monomer had penetrated to a depth of at least 5 in. (12.7 cm) throughout the slab under the area covered by the mat and a black layer of dissolved rubber showed the forefront of the monomer impregnation. These results showed that the pressure mat technique is feasible.

Therefore, a mat was designed and prepared from Neoprene rubber specially for this purpose. This rubber mat was clamped into position

in the same manner and subjected to the loading and unloading cycle as before. Again, the impregnation was virtually complete.

These experiments demonstrate that the pressure mat technique, although not yet developed to commercial scale, has considerable promise and should be developed further (9).

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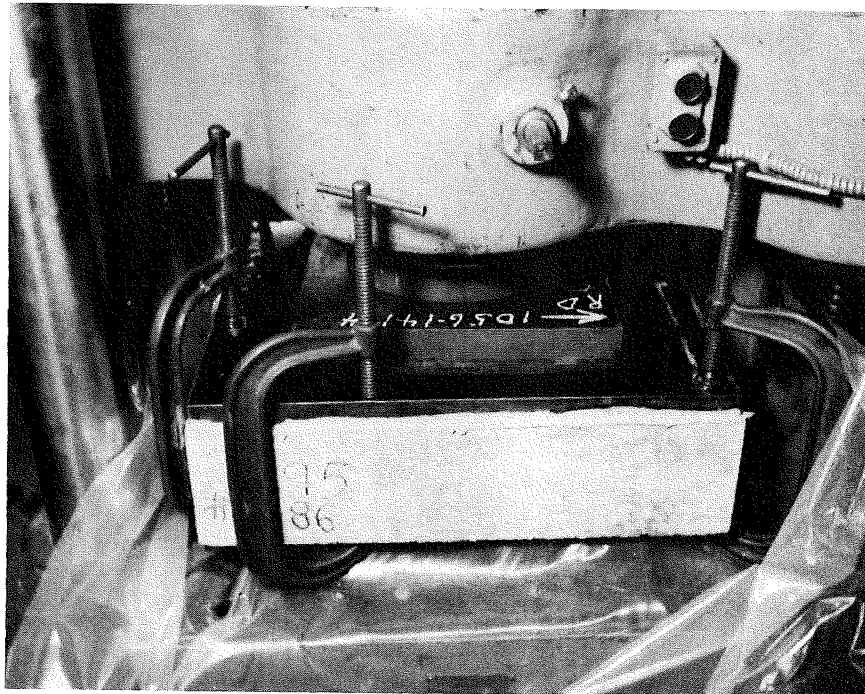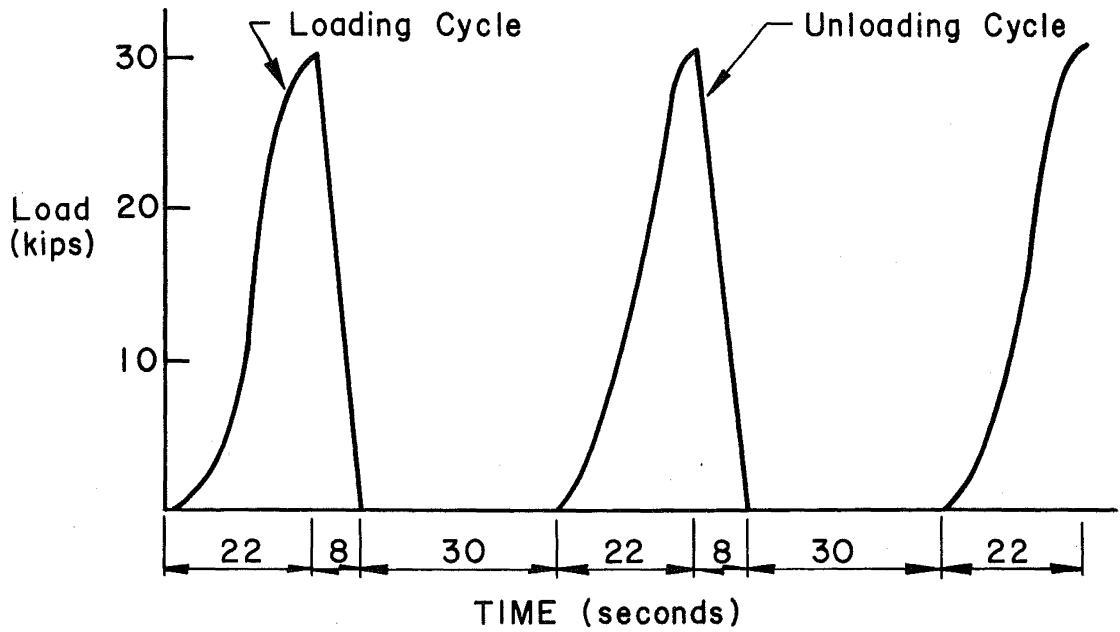
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Loading   Area = 240 sq. inches

Fig. D-1   Pressure Mat Impregnation Method
(a) Typical Load Cycle
(b) Apparatus

APPENDIX E

PROPERTIES OF POLYMER-IMPREGNATED CONCRETE

GENERAL

Several monomers are of potential interest in bridge deck impregna-
tion, for example, MMA and BA; from a longer-range point of view, other

impregnants are also worth consideration. Since properties such as

strength and durability presumably depend on the nature of the impregnant,

several studies of these and related properties were made using cement

mortars and concrete cylinders, slabs, and cores (1-5). The effects of

salt on mechanical properties are discussed in Appendix F.

MECHANICAL PROPERTIES

Stress-Strain Behavior: Concrete and Mortar Cylinder Specimens--

Monomer Systems

Experimental Details (1, 2). Portland cement mortar cylinders (1 in.

[2.5 cm] diameter; 2 in. [5.1 cm] height) were prepared using a 12:24:64

water-type II portland cement-Ottawa silica sand (ASTM C-109) mix and

cured under water for 28 days at room temperature. The cylinders were

dried in an air oven for 3 hr at 302°F (150°C), placed in a vacuum cham-

ber, and subjected to vacuum for 15 min, then immersed in monomer (various

mixtures of MMA and BA) containing 0.5 percent azobisisobutyronitrile for

up to 3 hr at atmospheric pressure. Unless specified otherwise, these

monomer-impregnated cylinders were immersed in a 158° F (70° C) water

bath for 4 hr to polymerize the monomer. The polymer loadings were 5-7

percent based on dried weight for 3-hr impregnations, and less for short-

er times.

Compression tests were run on these polymer-impregnated mortar cylinders using an Instron tester operated at a constant strain of 0.01 in. (0.025 cm)/min. To ensure reproducible results, the circular ends of the cylinders were ground flat before testing. It was also necessary to preload the specimens to 1000 lbf- 2000 lbf(4.5 kN - 8.9 kN) and unload, before loading to failure. Each series of tests used four to six specimens.

Concrete cylinders (3 in.[7.6. cm] diameter; 6 in. [15.2 cm] height) were prepared using water, type 1 portland cement, sand, and gravel (3/8 in.[1.0 cm]) according to ASTM C33-67. After one day at room conditions, the cylinders were cured for 28 days in a moist room (90-100 percent RH), then stored for 14 days at room conditions. They were then dried, impregnated with monomer (MMA, BA, MMA/BA mixtures, and MMA/BA/TMPTMA mixtures), and polymerized in a manner similar to that of the smaller mortar cylinders. The polymer loadings were between 4 and 6 percent, based on dried weight. Typical compositions and loadings are given in Table E-1.

Compression (ASTM C39-66) and split tensile (ASTM C496-66) tests were run on these polymer-impregnated concrete cylinders using a Baldwin hydraulic tester (300,000 lbf[1.33 MN] capacity). The tester was operated at constant hydraulic flow rate, and hence, at an approximately constant load rate (40-50 lbf[180 - 220 N]/sec.), during the loading phase. Thus, the crosshead speed was not constant throughout the test, but increased after rupture of the specimen began. The strain was plotted as a function of stress, using the output from strain gages attached to various parts of the specimen.

Effect of Monomer Loading. As shown in other studies (6-9), the compressive strength of polymer-impregnated mortar or concrete is a direct

Table E-1. Typical Polymer Loadings in 3-in. x 6-in. Concrete Cylinders

Specimens (1)	Number of Specimens (2)	Polymer, as a Percentage (3)	Average Polymer Loading, as a Percentage by Weight (4)
AI	4	100 MMA	4.8
AII	8	60 MMA + 40 BA	4.3
BI	4	90 MMA + 10 TMPTMA	5.2
BII	8	70 MMA + 20 BA + 10 TMPTMA	4.6
BIII	8	60 MMA + 30 BA + 10 TMPTMA	4.9
BIV	8	50 MMA + 40 BA + 10 TMPTMA	5.1

Unit Conversion: 1 in. = 2.54 cm.

function of the polymer loading. Typical results are shown for a 90:10 MMA:BA mixture (Figure E-1). It may also be seen that polymerization by intermittent heating to 140° F (60° C) rather than at a steady 158° F (70°C) yields higher strengths at a given loading, perhaps due to the formation of a higher molecular weight polymer.

Effect of Polymer Composition. Figures E-2 through E-10 and Table E-2 show typical results of the stress-strain measurements. It is obvious that the modulus, strength, ultimate strain, and energy-to-break of the portland cement mortar are increased dramatically by impregnation with polymethyl methacrylate (PMMA). This is in agreement with data reported by others (6, 7, 10, 11). Although the absolute values and relative improvement of these properties are smaller than those reported by Auskern and Horn (12, 13), the polymer loading is also proportionately lower. Also, as reported earlier (12), the stress-strain curves show a high degree of linearity, with only a slight tendency to yield at very high strains. Thus, the impregnation of portland cement mortar with PMMA gives a dramatic increase in strength, stiffness, and overall toughness, accompanied by a corresponding decrease in ductility due to progressive yielding (this ductility is not obvious in the control specimen of Figure E-2, probably because of the small specimen size). It is interesting to note that a high level of elastic and brittle behavior is achieved by impregnation of the mortar with PMMA, which by itself is normally ductile in compression.

However, as the proportion of BA in the monomer impregnation mixture is increased past 25 percent, the tensile and compressive

Table E-2. Typical Mechanical Properties of Polymer-Impregnated[a]

3-in. x 6-in. Concrete Cylinders

Specimen (1)	Tensile Strength, in kips Per square inch (2)	Compressive Strength, in kips per square inch (3)	Young's Modulus[b], in kips per square inch x 10^3 (4)
AI	1.38	18.6	7.5
AII	1.13	14.4	4.0[a]
A Control	0.50	5.5	3.4[a]
BI	1.10	16.1	7.8
BII	0.94	16.4	7.1
BIII	1.01	18.4	7.1
BIV	1.18	17.8	7.1
B Control	0.44	5.4	4.1[a]

Unit Conversions: 1 psi = 6.89 kN/m² = 6.89 kPa.

1 in. = 2.54 cm.

a. For compositions, see Table E-1.

b. Young's modulus for AII and all controls is the "secant modulus" measured

at a stress one half the ultimate value. The "tangent modulus" is given

for the other specimens. Values based on compressive tests.

strengths* show a corresponding decrease, confirming results of a

separate study (14). By controlling the percent BA in the mixture, a

wide range of stress-strain behavior from brittle to ductile may be

obtained.

Effects of adding the crosslinking agent, TMPTMA, are shown in Table

E-2 and Figures E-9 and E-10, for specimens BI to BIV, inclusive; compo-

sitions are given in Table E-1. It is seen that the addition of 10 percent

TMPTMA as crosslinking agent of various combinations of MMA and BA increases

the Young's modulus of PIC, but has a complex effect on strength. While

10 percent TMPTMA causes a decrease in both tensile and compressive

strengths for the case of 100 percent MMA, the compressive strengths for

---

*Because of the small specimen size, which results in catastrophic

failure once cracking begins, caution must be exercised in interpreting

the variation of stress as a function of strain. Thus, the decrease in

ultimate strain at high proportions of BA may reflect the test method as

much as the properties of the specimen, at least at the strain rate used.

The stress concentration in the cementitious matrix will be higher, the

lower the modulus of the polymer, so that failure will occur first in the

BA-rich samples as long as the specimen must follow the crosshead motion

without relaxation. Even so, the incorporation of BA in the monomer mix-

ture confers a significant degree of yielding prior to failure, and a peak

stress is observed for compositions containing 50 percent or more BA.

Thus, ductility is conferred by the BA, although under these testing con-

ditions, it is not reflected in the breaking strain. This is consistent

with the observation that not only those specimens containing 75 percent

or more MMA broke with sharp audible cracks.

the MMA-BA combinations with TMPTMA pass through a maximum for a 60:30:10 mixture, the maximum value being similar to the value for 100 percent MMA. However, in all cases the use of TMPTMA tends to reduce ultimate strain and ductility (in the sense of yielding).

In summary, the brittle behavior of PIC impregnated with MMA can be modified by incorporating a monomer, BA, which confers a degree of rubberiness to the resultant copolymer. For example, a 60/40 MMA/BA combination shows a pronounced increase in ductility, or the ability to yield and deform at stresses close to the maximum observed before failure, compared to a 100 percent MMA-impregnated specimen, at the expense of only a 20 percent reduction in the ultimate strength and some 20 percent reduction in Young's modulus. Incorporation of a crosslinking agent, TMPTMA, in the monomer mixture has several effects: (1) A slight decrease in tensile and compressive strengths in the case of MMA alone; (2) a slight decrease in tensile strength for all MMA/BA compositions studied (up to 40 percent BA); (3) a slight decrease to a negligible change in compressive strength, depending on the concentration of BA; and (4) a general reduction in ultimate strain and ductility, along with an increase Young's modulus. Thus, a wide variety of stress-strain and ductility characteristics can be obtained by suitable variation in monomer composition. In any event, in contrast to the predictions of a simple pore-filling model (12), the modulus (and probably other properties) of the polymer must play a significant role in whatever relationship is used to predict behavior of the polymer-impregnated composite. This observation is consistent with the findings of Gebauer et al. (15), namely, that the strength of polymer-impregnated ceramic depends on whether the measurements are made at a temperature

above or below the second-order transition temperature of the polymer.

The fact that significant reinforcement requires a polymer to be in the glassy and not the rubbery state is further supported by tests with mortar specimens containing mixtures of BA and MMA polymers. As shown in Figure E-11, about the same degree of reinforcement (in terms of compressive strength) is obtained with any compositions as long as it is at a temperature below its glass temperature, T_g. As temperature is raised above T_g, the degree of reinforcement is reduced, eventually becoming negligible. Interestingly, it may be noted that the inflection point of the transition for the MMA systems (this point usually corresponding closely to the T_g) is higher than for the homopolymer ($T_g \cong 302°$ F [150° C]). In contrast, the BA systems display the inflection point close to that reported for the homopolymer ($T_g \cong 126$ °F [52° C]). It thus seems likely that the rigid polymer within the pores is in a highly strained configuration.

The Role of the Polymer

The foregoing results show that the polymer in PIC plays an active role in the reinforcement of the cementitious matrix and not merely a passive pore-filling role. Unfortunately, several expressions proposed for the quantitative prediction of composite properties in terms of constituent properties do not work well with PIC. Although the present study has not progressed far enough to permit rigorous evaluation of these expressions, the preliminary results indicate that neither the porosity model of Auskern and Horn (12) nor the model of Hobbs (16) can account for the observed effect of polymer modulus. The variations in PIC modulus as a function of polymer modulus predicted by these models are less than 10

percent, compared with the observed variation of 36 percent. The flat-shaped pore model proposed by Hasselman et al. (17) does predict a more significant variation (about 27 percent) for a probably-not-unrealistic length-to-width ratio of 5.

Nevertheless, it is interesting to consider the effects of polymer modulus on stress concentrations both in the cementitious matrix and in the polymer phase (18). For inclusions of PMMA, the stress concentration in the matrix is reduced almost three-fold for a flat-shaped pore with a length to width ratio of 5; on the other hand, the stress concentration in the polymer is increased significantly. These effects are almost (but not quite) negligible for inclusions of the lower-modulus PBA. Thus, even if the modulus of PIC cannot yet be predicted accurately, and the fact that the polymer does not fill the pores completely, the higher-modulus polymer must not only reduce the stress concentration in the matrix, but also aid in the stress transfer to the polymer-filled pore. This conclusion complements the findings of Isenburg and Vanderhoff (19), i.e., that a latex polymer incorporated in the mix plays an active role in minimizing stresses when microcracks form during curing, and the conclusion of Tazawa and Kobayashi (20), and Auskern and Horn (21), i.e., the inclusion of polymer in PIC increases the fracture energy significantly.

Stress-Strain Behavior: Slabs and Cores--Monomer Systems

In order to characterize the effectiveness of impregnation in slabs used to model bridge deck concrete, stress-strain behavior, which is close-ly related to the percent loading with polymer, was determined for several kinds of specimens: slabs and cores impregnated with different monomer systems, both before and after freeze-thaw testing. The effects of salt

contamination are discussed in Appendix F.

Experimental Details. The concrete slab specimens (24 in. x 24 in. x 6 in. [61.0 cm x 61.0 cm x 15.2 cm], were prepared from a conventional non-air-entrained 1.00:1.92:6.10:6.75 water-portland cement (type 1)-coarse sand-limestone aggregate (1 in. [2.5 cm] maximum) mix with a cement factor of 485 lb/yd^3 (287 kg/m^3) and 28-days-average compressive strength of 4750 psi (32800 $_{Pa}$). The measured air content was 3 percent with slump of 2.5-3.0 in. (6.4 -7.6 cm). The slabs were given a normal trowel finish and were cured in the fog room (90-100 percent relative humidity) for at least 28 days before use in drying and impregnation tests. All slabs contained a nominal steel reinforcement at a 4-in. (10 -cm) depth to simulate the structure of the bridge deck. All slabs were dried for 45 hr in an oven at 257° F (125° C). Impregnation of the slabs and cores taken from them was effected as described in Appendix D--in the case of slabs impregnated from one side, and in the case of cores, by vacuum-pressure impregnation in a closed chamber. With the exception of two slabs which were impregnated with isobutyl methacrylate (IBMA) the monomer system used was 90:10 MMA:TMPTMA, with 0.5 percent AZO. One of the slabs impregnated with IBMA was impregnated only partially.

Results and Discussions. Table E-3 compares strength measurements made both in direct compression and split tension of cores subjected to freeze-thaw testing (see also Appendix H) and control cores not subjected to this test. The core identification is the same as that used in Table E-2. The variations include cores from both unimpregnated and polymer-impregnated slabs, cores from unimpregnated control slabs that were impregnated and polymerized in the laboratory, and the

Table E-3. Compressive and Tensile Strengths of Polymer-Impregnated

Concrete before and after Freeze-Thaw Testing (ASTM C671)

| | | Before Freeze-Thaw Testing | | | | | |
| | Salt | Compressive Strength | | | Tensile Strength | | |
Impregnation[1]	Content	Core	in psi	(kN/m^2)	Core	in psi	(kN/m^2)
Surface Impregnation of Slab[2]	None	$1\text{-}6^3$	8850	(61000)	$1\text{-}1^3$	910	(6280)
Surface Impregnation of Slab[4]	$0.3\%^5$	2-3	10260	(70800)	2-5	850	(5870)
None (Unimpregnated Control Slab)	None	4-6	3790	(26100)	4-8	530	(3620)
None (Unimpregnated Control Slab)	$0.3\%^5$	5-6	3540	(24400)	5-6	420	(2860)
Surface Impregnation of Slab[6]	None	$6\text{-}6^3$	8850	(61000)	$6\text{-}4^3$	830	(5710)

Table E-3. Compressive and Tensile Strengths of Polymer-Impregnated
Concrete before and after Freeze-Thaw Testing (ASTM C671) (Continued)

| | | Before Freeze-Thaw-Testing | | | | | |
| Impregnation[1] | Salt Content | Compressive Strength | | | Tensile Strength | | |
		Core	in psi	(kN/m^2)	Core	in psi	(kN/m^2)
Lab Impregnation of Core from Unimpregnated Slab[7]	None	----	-----	-------	----	---	-------
Lab Impregnation of Core from Unimprenated Slab[7]	0.3%[5]	----	-----	-------	----	---	-------

Table E-3. Compressive and Tensile Strengths of Polymer-Impregnated

Concrete before and after Freeze-Thaw Testing (ASTM C671) (Continued)

| | | After Freeze-Thaw Testing | | | | | |
| | Salt | Compressive Strength | | | Tensile Strength | | |
Impregnation[1]	Content	Core	in psi	(kN/m^2)	Core	in psi	(kN/m^2)
Surface Impregnation of Slab[2]	None	1-3[3]	8520	(58800)	1-5[3]	900	(6240)
Surface Impregnation of Slab[4]	0.3%[5]	2-2	12030	(83000)	2-1	1050	(7240)
None (Unimpregnated Control Slab)	None	4-3	4080	(28100)	4-2	560	(3850)
None (Unimpregnated Control Slab)	0.3%[5]	5-1	2970	(20500)	5-2	310	(2160)
Surface Impregnation of Slab[6]	None	----	----	-------	---	---	------

Table E-3. Compressive and Tensile Strengths of Polymer-Impregnated

Concrete before and after Freeze-Thaw Testing (ASTM C671) (Continued)

		After Freeze-Thaw Testing					
	Salt	Compressive Strength			Tensile Strength		
Impregnation[1]	Concrete	Core	in psi	(kPa)	Core	in psi	(kPa)
Lab Impregnation of Core from Unimpregnated Slab[7]	None	4-5 I	11610	(80080)	4-4 I	1020	(7010)
Lab Impregnation of Core from Unimpregnated Slab[7]	0.3%[5]	5-9 I	11130	(76760)	5-5 I	980	(6750)

Table E-3.   Compressive and Tensile Strengths of Polymer-Impregnated Concrete

before and after Freeze-Thaw Testing (ASTM C671) (Continued)

1. 90:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture containing 0.5% azobisisobuty-

ronitrile initiator.

2. 2.0 hr vacuum (25 in. or 63.5 cm Hg); 40 psi (280   kPa) pressurization.

3. Partially impregnated.

4. 1.5 hr vacuum (28 in. or 71 cm Hg); 60 psi (410   kPa) pressurization.

5. 0.3% salt = 12 lb/yd^3 or 7.1 kg/m^3.

6. 1.5 hr vacuum (28 in. or 71 cm Hg); 60 psi (410   kPa) pressurization; isobutyl methacrylate sub-

stituted for methyl methacrylate.

7. Laboratory vacuum (1.5 hr)-pressure (60 psi [410   kPa]) chamber.

substitution of isobutyl methacrylate for methy methacrylate in the mono-mer mixture. In general, the strengths of these cores were not as great as those of 3-x 6-in. (7.5-x15.0cm) cylindrical specimens cast in the lab-oratory, presumably because of possible distortion and cracking during the core-drilling operation and incomplete impregnation (for the polymer-impregnated cores).

Although the number of specimens tested is ~~necessarily~~ small and the results show the usual experimental scatter, some generalizations can be made. Before freeze-thaw testing, the strengths of the polymer-impregnated cores were 2.5-3.0 times greater than those of the unimpregnated cores. After freeze-thaw testing, the strengths of the polymer-impregnated cores were the same or even slightly greater because of the annealing during heating for 60 hr at 212°F (100°C) (after freeze-thaw testing, the cores were subjected to the water absorption test, redried, and then used in the strength tests). The strengths of the unimpregnated cores from salt-contaminated slabs decreased after freeze-thaw testing because the cores were dried at high temperatures (>>212°F [100°C]) before they were con-taminated with salt and redried for the water absorption test (this is observed even for specimens not subjected to freeze-thaw testing, e.g., compare the strengths of cores 4-6 and 5-6 in compression and cores 4-8 and 5-6 in tension). The strengths of the uncontaminated, unimpregnated cores were slightly greater after freeze-thaw testing, however, because the control cores not subjected to freeze-thaw testing were not dried before the strength test, while the corresponding cores subjected to freeze-thaw testing were dried only once at low temperatures (220°F [104°C]), for the water absorption test. The polymer impregnation seems

to heal the microcracks formed during high-temperature drying as no such strength reduction was observed for salt-contaminated cores after impregnation from this work and other tests on laboratory specimens. The presence or absence of salt contamination, or the substitution of isobutyl methacrylate for methyl methacrylate in the monomer mixture, had little or no effect on the strengths of the polymer-impregnated cores before or after freeze-thaw testing.

Several slabs were broken open to observe fracture patterns. Typically, the appearance of the fracture cross section (Figures E-12 through E-14) was similar to that of other polymer-impregnated specimens. The dark polymer-impregnated region can readily be distinguished from the light unimpregnated regions. The lighter 0.25-in. (0.6'-cm) surface layer on the bottom indicated that some monomer was lost from the lower surface by evaporation. Examination of the fracture cross section with a magnifying glass showed that, in the polymer-impregnated region, fracture occurred <u>through</u> the aggregate particles, but in the unimpregnated region, it occurred <u>around</u> the particles.

No evidence was found for a plane of weakness at the interface between the monomer front and the unimpregnated portion of a partially impregnated specimen (Figures E-13, E-14). As expected, however, strengths are somewhat lower than for fully impregnated specimens (Table E-3).

It may be concluded that the benefits noted for the impregnation of cylinders are maintained in slabs, and, at least with cores, are maintained after rigorous freezing and thawing.

<u>Stress-Strain Behavior: Cylinders--Other Impregnants</u>

From a long-range point of view, the use of impregnants that are cheaper than typical vinyl monomers would be desirable. Although such

impregnants will tend to be more viscous than vinyl monomers, the combination of deep drying and pressurization may offer considerable potential for process development. For this reason, exploratory studies (3) were conducted using sulfur, whose use as a concrete impregnant had been described previously (22, 23), a low-viscosity tar, tar -sulfur mixtures, and barium hydroxide (24). Impregnation details are given in Ref. 24.

Experimental. Experiments with sulfur impregnation were conducted using 3-in. x 6-in. (8-cm x 15-cm) cylindrical specimens prepared from a conventional non-air-entrained 1:2.0:3.42:4.16 water-portland cement (type I) coarse sand-limestone aggregate (1 in. [3 cm] maximum) mix with a 28-day average compressive strength of 4000 psi (28 MPa). The measured air content was 3 percent with a slump of 4.5 in. (11 cm). All cylinders were cured in a fog room (90-100 percent relative humidity).

For experiments with the other systems, mortar specimens (1.0 in. x 2.0 in. [2.5 cm x 5.0 cm]) were prepared using a water-portland cement (type I)--Ottawa sand mix in the proportions 0.5:1.0:2.7, and cured for 28 days.

Results_ and Discussion. Typical results for the other systems are shown in Table E-4 and Figure E-15. It may be seen that sulfur impregnation yields a two-fold improvement in compressive strength and Young's modulus; a similar improvement (not shown) is observed for the split-tensile strength. The sulfur-tar mixture gives a lesser improvement in compressive strength, while tar alone has no significant effect. These results are quite consistent with the discussion above concerning the need

Table E-4. Strength of Impregnated Mortar Specimens

Impregnant	Specimen	% Loading	Compressive Strength (psi x 10^3)
Sulfur[1]	29	10.2	1.50
	30	10.1	1.48
	31	11.5	1.53
Sulfur-Tar (80-20)	39	11.6	1.14
	40	11.9	1.05
	41	10.7	1.18
Tar	43	7.3	0.64
	44	6.7	0.64
	45	6.9	0.64
Control Specimens	48	--	0.65
	49	--	0.77
	50	--	0.70

Unit Conversion: 1 psi = 6.9 kN/m^2 = 6.9 kPa.

1. Impregnation time, 60 hr; not predried.

for high modulus in a reinforcing impregnant. No results could be obtained with the barium hydroxide, which appeared to attack the specimens.

CHLORIDE PENETRATION IN PIC

In view of the generally improved resistance of PIC to corrosion, e.g., by acids and sulfates, it may be expected that penetration by chloride ion may also be reduced, in comparison with the unimpregnated matrix. Indeed such an effect has been noted already (24). However, several questions do arise: (1) in practice, polymer impregnation does not fill all the available capillary pores; (2) the matrix-polymer bond may conceivably undergo degradation during service, especially under freeze-thaw cycling; and (3) in principle, both the inherent permeability to salts and the stability of the matrix-polymer bond depend on the state of polymer (i.e., whether it is glassy and brittle, or rubbery and tough).

To determine the relative effectiveness of various polymers in PIC on reducing chloride penetration, static tests using standard portland cement mortar specimens were conducted for a period of 12 months. Two monomers were used: MMA, which yields a glassy, brittle polymer at room temperature, and BA, which yields a rubbery, tough polymer. For the chloride determination, a new technique was developed using electron microprobe analysis to follow salt migration into the concrete.

Experiments

Standard portland cement mortar cylinders, 1 in. x 2 in. (2.5 cm x 5.0 cm),were used for the salt penetration experiments; MMA and BA monomer systems were used to represent a glassy and rubbery polymer, respectively. The cylinders were prepared using a 12:24:64 water-type II portland cement-

Ottawa silica sand (ASTM C-109) mix and cured under water for 28 days at room temperature. After drying in an air oven for 3 hr at 302° F (150° C), specimens were placed in the vacuum for 15 min, then immersed in monomer (MMA or BA) for 3 hr at atmospheric pressure. The monomer-impregnated cylinders were then immersed in a 158° F (70° C) water bath for 4 hr, to polymerize the monomer. These conditions of drying, impregnating, and polymerization were sufficient to ensure reasonably complete filling of the specimen void space; the polymer loadings were based on dried weight. Since BA is 20 percent less dense than MMA, the volumetric loadings were close in each case.

After impregnation by the procedures described above, the mortar cylinders were exposed to 8 percent aqueous $CaCl_2 \cdot 2H_2O$ solutions. Following the convenient procedure of Ost and Montfore (25), solutions were contained in covered polyethylene sheaths tightly fitted on the cylinders and adjusted to extend above the top surface for about 1 in. (2.5 cm). The curved surfaces of the cylinders were closely wrapped with waterproof tape to insure the axial flow; a screen support was used to provide free circulation of air underneath. After different exposure periods, cylinders were broken and the chloride concentration in the past phase determined at different depths by electron microprobe analysis (26). At a given depth, small specimens were removed, coated with a thin carbon layer, three areas in the cement phase--3.1 to 3.9 x 10^{-3} in. (8 to 10 μm)--scanned, and 10-sec counts (for chloride ion) taken in duplicate.

Although the absolute numerical values include all chloride content, and thus exceed those corresponding to "free" chloride determinations by

other techniques, the values provide a sensitive measure of total chloride penetrated and also a relative measure of chloride ions available for corrosive reactions. Thus, comparison with results obtained by the potentiometric analysis of cores (Appendix F) reveals that the microprobe technique "sees" chloride concentrations which are about 3 x those measured for the "available" chloride.

Results. After only one month of exposure, the plain mortar showed a significant amount of chloride([1.6 percent Cl or 6 percent $CaCl_2 \cdot 2H_2O$] at a depth of 0.25 in [0.6 cm]) at different depths in the mortar (Figure E-16). However, for both BA- and MMA-impregnated mortars, only traces of chloride (< 0.1 percent Cl [= 0.4 percent $CaCl_2 \cdot 2H_2O$] by weight of cement paste) were found at a depth of 0.25 in. (0.6 cm). At lower depths, the chloride values from electron microprobe fall into the range of background scatter, so that detection of deeper penetration in the impregnated mortars will require much larger exposure times. At least for a one month exposure, both BA- and MMA-impregnated mortars gave similar results. As time progressed, chloride continued to penetrate; after one year, the concentration reached 5.5 percent at a 0.25-in. (0.6 cm) and 0.6 percent at a 1.5-in. (3.81 cm) depth (Figure E-17). In contrast, the concentration in the BA-impregnated specimens was much less--0.4 percent at a 0.25-in. (0.6 cm) depth and ∿ 0.1 percent (background of detection) at a 0.5-in. (1. 3 cm) depth. However, the BA specimens were not as effective after one year; chloride concentrations reached 2 percent at a 0.25-in. (0.6-cm) depth and 0.6 percent at a 0.5-in. (1.3 cm) depth.

Conclusions. Impregnation of portland cement mortar with polymers of

MMA or BA(glassy and rubbery, respectively) reduces calcium chloride penetration, after one month's exposure to an 8 percent solution, by an order of magnitude, regardless of the state (rubbery or glassy) of the polymer used. Preliminary tests show, however, that BA is not as effective after a 12-month exposure. Freeze-thaw cycling tests will, of course, be necessary to complete the picture of the role of the polymer.

CORROSION TESTS

Some slabs (Table E-3) were cored in such a way that a section of the steel reinforcing rods placed at the 4-in. (10-cm) depth was removed as an integral part of the core. This was done deliberately to determine whether the monomer had permeated the porous concrete matrix around the rods and whether the filling of the pores in this matrix by polymer would inhibit corrosion of the rods. If the channels left around the rods by evaporation of water were not filled with polymer, water could permeate these channels during the freeze-thaw tests and corrode the rods, causing severe dilation and eventual failure of the concrete.

The reinforcing rods in cores from uncontaminated slabs, both polymer-impregnated (slab 1) and unimpregnated (slab 4), showed no sign of corrosion after freeze-thaw testing (see Appendix F), indicating that the presence of salt is necessary for corrosion. However, the reinforcing rods in cores from the unimpregnated salt-contaminated slab 5 showed considerable corrosion after freeze-thaw testing, while those in cores from the polymer-impregnated, salt-contaminated slab 2 showed no visible signs of corrosion. Figure E-18 shows scanning electron ~~photo~~micrographs of the near-end sections of the reinforcing rods, depicting corrosion in core 5-3 and none in

core 2-1. Thus, although no quantitative measurements have been made, the impregnation of porous concrete with monomer and its subsequent polymerization prevents corrosion of the reinforcing rods, perhaps by immobilizing the contaminating salt by eliminating the water flux that carries it through the concrete to the rods. Evidently a loading of 5 wt percent of polymer is sufficient. Further tests will be needed to determine the limiting loading possible.

ACID ETCHING

One core from each concrete slab (Table E-3) was sawed lengthwise; one half was etched by soaking in 18.5 percent aqueous hydrochloric acid for 2 hours, and the other was polished to show the morphology and coloration. Figure E-19 compares the appearance of the acid-etched half with that of the polished half after freeze-thaw testing (control cores 2-7 and 4-1 were not subjected to freeze thaw). Acid etching caused disintegration of the unimpregnated cores; the cementitious matrix was broken down and the aggregate particles were attacked and dissolved. The polymer-impregnated cores showed remarkable resistance to the acid-etching; the cementitious matrix was unaffected by the acid while the aggregate particles were eaten away. The polished sections show clearly the uniform coloration of the polymer-impregnated cores.

Figure E-20 shows cores from the highway bridge deck treated in the same manner. These polymer-impregnated cores show the same remarkable resistance to acid etching as did the polymer-impregnated cores from the slabs; the cementitious matrix was unaffected by the acid etching while the aggregate particles were eaten away. This resistance to acid etching

was uniform over the whole 5-in. (12.7-cm) depth of the core, indicating

that the impregnation and polymerization were complete to that depth.

This is supported by the uniform coloration of the polished sections. The

polymerized monomer-sand-topping was also unaffected by the acid etching.

Sulfur impregnation was also shown to inhibit etching (3).

FREEZE-THAW TEST

Laboratory Specimens

Freeze-thaw tests, in accordance with ASTM Designation C671, were

carried out on non-salt-contaminated and salt-contaminated specimens of

polymer-impregnated concrete. Control specimens of nonimpregnated con-

cretes of each type were also tested for purposes of comparison. The

specimens consisted of 3-in. (7.6 -cm) diameter cores drilled from 6-in.

(15.2 -cm) thick test slabs. Two types of impregnation were employed,

surface impregnation of the slabs and impregnation of cores in a vacuum-

pressure chamber. The monomer system used throughout was MMA + 10 percent

TMPTMA. Three specimens were tested for each treatment level. The freeze-

thaw tests were carried out until specimen failure occurred, as defined in

ASTM C671, or until 10 cycles had been run.

The results of the freeze-thaw tests are shown on Table E-5. It

should be mentioned that while ASTM C671 defines the end of the period of

frost immunity as the point at which the dilation is more than twice the

dilation of the previous cycle, the concrete may also be considered as

having failed when the dilation exceeds approximately 400 to 500 micro in.

(1.0 to 1. $\times 10^{-3}$ cm). This is the elastic limit for a 6-in. (15.2 -cm)

specimen (approximately 70 to 80 microstrain).

Table E-5. Freeze-Thaw Resistance (ASTM C671)

Specimen Number	Impregnation Procedure	Type of Concrete	Dilation, micro in. (cycle)									
			(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
4-2	None (Control)	No salt contam-	60	30	660	930	1000	1560	1250	1500	1480	1460
4-3		ination	70	180	1130	1230	1520	1900	1830	+	+	+
4-4			70	30	1100	1220	1700	2080	+	+	+	+
5-1	None (Control)	Salt-contaminated	+	+	----	----	----	----	----	----	----	----
5-2		slab (salt con-	+	+	----	----	----	----	----	----	----	----
5-3		tent 0.3 wt %)	+	+	----	----	----	----	----	----	----	----
5-5	1-1/2 hr vac &	Salt-contaminated	30	20	20	20	20	30	20	30	30	30
5-8	60 psi pres-	slab	30	30	20	20	30	30	0	40	30	30
5-9	sure vac.-press.		20	20	0	30	40	30	0	50	40	30
	chamber.											

Table E-5. Freeze-Thaw Resistance (ASTM C671) (Continued)

Specimen Number	Impregnation Procedure	Type of Concrete	Dilation, micro in. (Cycle)									
			(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
4-4	1-1/2 hr vac &	Non-salt-con-	100	30	40	40	20	50	30	20	20	10
4-5	60 psi pres-	taminated	60	30	30	30	20	40	20	20	10	30
4-9	sure vac.-press.	slab	50	30	30	20	20	20	30	20	20	30
	chamber.											
2-1	1-1/2 hr vac &	Salt-contamin-	40	10	10	30	20	30	30	*	30	40
2-2	60 psi pres-	ated slab	30	20	10	20	20	20	20	*	40	30
2-6	sure - slab		840	1690	2500	----	----	----	----	----	----	----
	surface impreg.											
1-2	2 hr vac & 40	Non-salt-	40	20	0	30	0	30	0	30	20	*
1-3	psi pressure -	contaminated	20	20	10	20	10	20	0	20	20	20
1-5	slab surface	slab	40	40	20	20	20	20	0	20	10	30
	impreg.											

Table E-5. Freeze-Thaw Resistance (ASTM C671) (Continued)

\+   - Off scale

\----   - No test run

*   - Equipment malfunction

NOTE:

(1) Monomer used: MMA + 10% TMPTMA

(2) After 3rd cycle, specimen 2-6 was cycled an additional 25 times. Bottom portion of specimen

(apparently not impregnated) visibly deteriorated.

Unit Conversions: 1 micro in. = 2.54 x 10^{-6} cm

1 psi = 6.89. kPa.

As shown in Table E-5, the nonimpregnated specimens all failed early--
the salt-contaminated ones in the first cycle and the non-salt-contaminated
ones in the third cycle. It should be noted that in order to sensitize
the test, none of the concretes in this study were air entrained; the poor
frost resistance of the control specimens is thus to be expected. Also, it
is interesting to observe that the salt-contaminated control specimens
failed sooner than non-salt-contaminated ones, in agreement with field ob-
servations. With one exception, all of the polymer-impregnated specimens
displayed exceptional resistance to freezing and thawing. Moreover, no
evidence for corrosion of the rebar was noted even in the presence of salt.
The single anomalous result (Specimen 2-6) was subjected to an additional
25 freeze-thaw cycles (noninstrumented) in order to visually expose the
susceptible portion of the specimen. Confirming suspicions, the lower por-
tion of the specimen deteriorated badly, indicating incomplete impregnation.
The exceptional performance of PIC in the presence of salt loadings as high
as 12 lb/cu yd (7.1 kg/m^3) confirms related observations by different
tests (27), and shows the potential of polymer-impregnated concrete as a
means to alleviate deterioration of highways and bridge decks.

Specimens from Field Impregnation Study

One core specimen from each of the 3-ft x 12-ft (0.91-m x 3.66-m)
areas impregnated on the research facility bridge (see Appendix H) were
subjected to 11 freeze-thaw cycles in accordance with ASTM C671. Control
specimens from nonimpregnated concrete adjacent to each of the impregnated
areas were tested also. In all cases (impregnated and control) the dila-
tions(expansions during freezing) were very small (averaging about 10 per-
cent of the elastic limit of the concrete), transitory, and failed to show

any tendencies to increase with time. The high quality, air-entrained concrete in this deck is obviously very frost resistant. Therefore, while polymer impregnation will most certainly improve its frost resistance, it would take either a much larger number of freeze-thaw cycles or a more severe freeze-thaw test to demonstrate the improvements.

ABRASION TESTS

To determine whether polymer impregnation can improve surface wearability, an accelerated test method was sought that would be representative of the field conditions of rolling and sliding friction accompanied by high impact. Of the many test methods proposed, no one method can predict the actual abrasion resistance of concrete in service because of the sensitivity of abrasion resistance of concrete to the details of testing, proportioning, placing, finishing, curing, and protection.

Test Apparatus

For this work, the ball bearing abrasion test method was selected in preference to sand blasting, grinding wheels, and other abrasive devices because it comes the closest to the actual abrasive action in the field. This method depends on the abrasive action of rapidly rotating steel balls under load on a wet concrete surface. Water is used to flush loose particles from the test path, bringing the ball into contact with sand and stone particles still bonded to the concrete surface, thus providing impact as well as sliding friction.

Figure E-21 shows that the apparatus consists of a motor-driven hollow vertical shaft resting on and turning ball bearings which rest on the concrete surface. As the ball bearings cut into the concrete surface, depth-

of-wear readings can be taken continuously as a function of time without stopping the test. The abrasion tool is comprised of eight 23/32 or 0.71875-in. (1.83-cm) diameter steel balls equally spaced in a retaining ring, to form a ball circle of 2.50 (3.65-cm) diameter. The wear tool is given a breaking-in period of 300 sec, during which the balls become slightly textured and distorted so that their apparent diameter is slightly larger. During the remainder of the tests, the balls were reduced in diameter to a value slightly less than the original diameter due to the sliding friction. The wear tool was discarded when the diameter of the steel balls was reduced to 0.7175 in. (1.82 cm).

The hollow vertical drive shaft is provided with a flanged bearing plate at its lower end grooved to match the ball circle of the abrasion tool and a centered 1/8-in. (0.32-cm) diameter orifice to permit a constant flow of water. The drive shaft is provided with an adjustment of plumbness to the test surface. The total load on the ball bearing is 27 lb (12.3 kg) including the weight of the drive motor, hollow drive shaft, and contained water. The motor is capable of turning the drive shaft at 1000 rpm under load. The dial indicator has a 0.5-in. (1.28-cm) travel and reads to the nearest 0.0001 in. (.00025 cm).

A 1-gal (3.8 x 10^{-3} m^3) plastic tank mounted on the motor base supplies water, which flows by gravity through the hollow drive shaft and orifice in the flange plate onto the concrete surface. The machine base is provided with a vacuum hold-down device with three support points.

Test Specimens. Eight 24-in. x 24-in. x 6-in. (61-cm x 61-cm x 15-cm) slabs were prepared and impregnated with various monomer mixtures (Table

E-6). The slabs were aged for 30 days, dried thoroughly, impregnated with

monomer, and polymerized. Slab 13 was impregnated with partially polymer-

ized styrene; after two hours, this viscous solution had penetrated less

than 0.033 in. (0.8 cm) into the substrate so the impregnation was discon-

tinued. The excess monomer solution was removed from the surface and mixed

with dry sand in 1:1 ratio. This mixture was spread over the surface of

the slab, the slab was wrapped with polyethylene film, and steam-polymerized.

Slab 14 was prepared similarly by mixing dry sand with the excess 90:10

methyl methacrylate-trimethylolpropane trimethacrylate mixture on the sur-

face and polymerizing.

For the abrasion test, the slabs were clamped securely on rigid stands

and leveled, to approximate the rigidity of a slab in place. This proced-

ure was considered satisfactory, even though the rate of wear measured by

this method is affected by sample sizes smaller than a slab in place, be-

cause the purpose of this work was to compare the abrasion resistance of

polymer-impregnated concrete with that of unimpregnated concrete rather than

to determine the abrasion resistance of a polymer-impregnated concrete slab

in place per se.

Abrasion Test Results. Three or more tests were made on representative

surfaces of each slab and averaged to give the depth of wear-time curves

shown in Figures E-22 and E-23 and the values for average depth of wear

given in Table E-6. The average depth of wear of the polymer-impregnated

slabs was significantly smaller than that of the unimpregnated control

slabs. For example, the improvement in abrasion resistance measured at

1200 sec was 80-90 percent for the methyl methacrylate monomer mix-

ture, 50-60 percent for the isobutyl methacrylate monomer mixture, and

Table E-6. Abrasion Resistance of Polymer-Impregnated Concrete

Slab	Figure	Curve	Monomer[1]	Impregnation[2]	Average depth of wear at 1200 seconds in inches (cm)	Percent improvement in abrasion resistance
9	11	2	90:10 MMA-TMPTMA	Partially Impregnated	0.06725 (0.1708)	80
10	11	3	90:10 MMA-TMPTMA	Partially Impregnated		
11	11	4	90:10 IBMA-TMPTMA	Partially Impregnated	0.0778 (0.1976)	55
12	11	5	90:10 IBMA-TMPTMA	Partially Impregnated		
13	12	8	Partially Poly-merized Styrene	0.25-in. Styrene-sand Topping	0.0170 (0.0432)	608
19	12	9	90:10 MMA-TMPTMA	0.25-in. 90:10 MMA-TMPTMA-sand Topping	0.0640 (0.1626)	88

Table E-6. Abrasion Resistance of Polymer-Impregnated Concrete (Continued)

Slab	Figure	Curve	Monomer[1]	Impregnation[2]	Average depth of wear at 1200 seconds in inches (cm)	Percent improvement in abrasion resistance
15	11	1	None (Unimpregnated Control Slab)			
16	12	6	None (Unimpregnated Control Slab)		0.1205 (0.3061)	---

1. MMA = methyl methacrylate; IMBA = isobutyl methacrylate; TMPTMA = trimethylolpropane trimethacrylate; monomer mixture contained 0.5% azobisisobutyronitrile initiator.

2. 1.5 hr vacuum (28 in. or 71 cm Hg); 60 psi (410 kPa) pressurization.

600-700 percent for the styrene-sand topping.

The polymer-impregnated slabs also showed more uniform abrasion re-sistance than the unimpregnated control slabs; those curves of Figures E-22 and E-23 for the polymer-impregnated slabs resemble more a half-parabola inclined toward the time axis than the unimpregnated control slabs, which show more abrasion on the surface than at greater depth.

The styrene-sand topping on slab 13 proved remarkably resistant to abrasion (curve 8, Figure E-23); the abrasion test gave only a slight pol-ishing action to the surface. When the styrene-sand topping was removed before testing, the initial rate of wear was much greater, about 50 per-cent of that for the unimpregnated control slab; as the surface was worn away, the rate of wear decreased but eventually exceeded that of the con-trol slab, indicating that the viscous, partially polymerized styrene used for the impregnation had penetrated only slightly below the surface.

The rate of wear for the methyl methacrylate-sand topping (slab 14, curve 9, Figure E-23) was considerably greater than for the styrene-sand topping of slab 13, perhaps because polystyrene is harder and more brit-tle than polymethyl methacrylate. However, the rate of wear for the methyl methacrylate-sand topping of slab 14 was the same as that for the slabs impregnated with the methyl methacrylate monomer mixture, perhaps because in this case the impregnation proceeded to some distance below the surface. The rate of wear for the slab impregnated with the isobutyl methacrylate monomer mixture was slightly greater than that for the slab impregnated with the methyl methacrylate monomer mixture.

It is interesting that the steel balls used for abrasion testing of

the polymer-impregnated slabs were worn away very little or not at all during the test compared with the substantial reduction in diameter of the steel balls used for the unimpregnated control slabs.

WATER ABSORPTION

Experimental

In the case of water absorption tests (2) run on various freeze-thaw-tested cores and control cores, the cores were saturated by soaking in water for 24 hr at room temperature and then weighed to the nearest gram (1 oz = 28.4 g). The water-saturated cores were heated in an oven for 60 hr at 220° F (104° C) to drive off the evaporable water and were then reweighed; the difference between the two weights was taken as the total water absorption of the core.

Results and Discussion

Results for the various polymer-impregnated cores (core identifications the same as in Tables E-3 and E-5) are summarized in Table E-7.

Several generalizations can be made from these results. First, the water absorption of the polymer-impregnated cores was less than 0.5 - 1.5 percent of the total weight of the core and was only 10 - 20 percent of that of the unimpregnated cores, in good agreement with the 83 - 95 percent reduction in water absorption reported for polymer-impregnated cylindrical specimens cast and impregnated in the laboratory under controlled conditions (28). Also, there was no significant difference in water absorption between freeze-thaw-tested polymer-impregnated cores and polymer-impregnated cores not subjected to

Table E-7. Water Absorption of Polymer-Impregnated Concrete before and after Freeze-Thaw Testing

Impregnation[a] (1)	Salt Content, as a Percentage (2)	Core (3)	Water Absorption, in grams (4)	Water Absorption as a Percentage, Based on Concrete (5)	Reduction in Water Absorption, as a Percentage Compared to Controls Subjected to Freeze-Thaw (6)	Compared to Controls Not Subjected to Freeze-Thaw (7)
Surface Impregnation of Slab[b]	None	1-2[c]	27	1.6	78	76
		1-3[c]	24	1.4		
		1-5[c]	22	1.3		
Surface Impregnation of Slab[d]	0.3[e]	2-1	12	0.67	87	87
		2-2	13	0.74		
		2-6[f]	14	0.88		

Table E-7. Water Absorption of Polymer-Impregnated Concrete before and after Freeze-Thaw Testing (Continued)

Impregnation[a] (1)	Salt Content, as a Percentage (2)	Core (3)	Water Absorption, in grams (4)	Water Absorption as a Percentage, Based on Concrete (5)	Reduction in Water Absorption, as a Percentage	
					Compared to Controls Subjected to Freeze-Thaw (6)	Compared to Controls Not Subected to Freeze-Thaw (7)
Lab Impregnation of Core from Unimpregnated Slab[g]	None	4-41	18	1.1	83	82
		4-51	19	1.1		
		4-91	17	1.0		
Lab Impregnation of Core from Unimpregnated Slab[g]	0.3[e]	5-51	21	1.2	81	80
		5-91	19	1.1		
		5-81	20	1.2		

Table E-7. Water Absorption of Polymer-Impregnated Concrete before and after Freeze-Thaw Testing (Continued)

Impregnation[a] (1)	Salt Content, as a Percentage (2)	Core (3)	Water Absorption, in grams (4)	Water Absorption as a Percentage, Based on Concrete (5)	Reduction in Water Absorption, as a Percentage	
					Compared to Controls Subjected to Freeze-Thaw (6)	Compared to Controls Not Subjected to Freeze-Thaw (7)
Impregnated Bridge Deck Core	----	----	12	0.54	92	89
None (Unimpregnated Control Slab)	None	4-2	104	6.07	--	--
		4-3	113	6.55		
		4-7	110	6.36		

Table E-7. Water Absorption of Polymer-Impregnated Concrete before and after Freeze-Thaw Testing (Continued)

Impregnation[a] (1)	Salt Content, as a Percentage (2)	Core (3)	Water Absorption, in grams (4)	Water Absorption as a Percentage, Based on Concrete (5)	Reduction in Water Absorption, as a Percentage Compared to Controls Subjected to Freeze-Thaw (6)	Compared to Controls Not Subjected to Freeze-Thaw (7)
None (Unimpreg-nated Control Slab)	0.3[e]	5-1	105	5.82	--	--
		5-2	107	5.96		
		5-3	107	5.94		
Surface Impregnation of Slab[d,h,i]	None	6-6	10	0.59	91	91
		6-4	9	0.5		
Surface Impregnation of Slab[d,i]	0.3[e]	2-7	9	0.5	91	91

Impregnation[a] (1)	Salt Content, as a Percentage (2)	Core (3)	Water Absorption in grams (4)	Water Absorption as a Percentage, Based on Concrete (5)	Reduction in Water Absorption, as a Percentage Compared to Controls Subjected to Freeze-Thaw (6)	Compared to Controls Not Subjected to Freeze-Thaw (7)
None (Unimpregnated Control Slab)[i]	None	4-1	108	6.17	--	--
None (Unimpregnated Control Slab)[i]	0.3[e]	5-4	102	5.9	--	--

Table E-7. Water Absorption of Polymer-Impregnated Concrete before and after Freeze-Thaw Testing (Continued)

Unit Conversion: 1 oz = 28.35 g.

a. 90:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture containing 0.5%

azobisisobutyronitrile initiator.

b. 2.0 hr vacuum (25 in. [640 mm] Hg); 40 psi (280-kPa) pressurization.

c. Partially impregnated.

d. 1.5 hr vacuum (28 in. [710 mm] Hg); 60 psi (410-kPa) pressurization.

e. 0.3% salt = 12 lb/cu yd (7.1 kg/m^3).

f. Unimpregnated region of core failed in freeze-thaw test.

g. Laboratory vacuum (1.5 hr)-pressure (60 psi [410 kPa]) chamber.

h. Isobutyl methacrylate substituted for methyl methacrylate.

i. Cores not subjected to freeze-thaw test.

this test, demonstrating again that polymer-impregnated concrete is remarkably resistant to freezing and thawing. Second, the water absorption was greater for cores taken from control slabs and impregnated in the laboratory vacuum-pressure chamber than for cores taken from polymer-impregnated slabs (e.g., compare the average of 19.3 percent for cores 5-51, 5-81, and 5-91 with 12.9 percent for cores 2-1, 2-2, and 2-6), even though the polymer loading was greater for the former. (Perhaps the polymer fills the pores of the latter type in a different manner.)

Finally, a single polymer-impregnated core taken from a bridge deck impregnated in the field (See Appendix H) showed lower water absorption than cores taken from polymer-impregnated slabs, indicating that equally good or better results may be expected from the field trials than from the laboratory impregnations.

Additional results on bridge deck cores (29) confirm the efficacy of impregnation in reducing water absorption.

Results for the other impregnants are given in Table E-8. Again, significant reductions up to 99 percent were noted for the sulfur, tar, and sulfur-tar combinations.

SKID RESISTANCE

Extensive studies by Fowler et. al. (27) showed that the impreg-
nation of highway-type concrete with PMMA resulted in a significant
improvement in the skid resistance (as measured by the British portable
skid tester) of dry unworn specimens and in a slight (5-10%) improvement
(wet) relative to unimpregnated controls after wear and polishing had
occurred. Researchers at BNL also reported only small effects in the case
of impregnation with a polyester-styrene mixture (30): a slight decrease
in the direction of the broom grain, and essentially no change in the
transverse direction.

In view of these results, measurements were confined in this
study to the area of the large-scale field trial (Appendix H) on the PSU
test track deck and were made only after 13 months of service. Tests were
run in triplicate using a newly calibrated British portable skid tester
following the general test procedure outlined in ASTM E303 , with the
help of Mr. B. Bright of the Transportation Research Institute. Air and
water temperatures were $62^{o}F$ ($17^{o}C$) and $60^{o}F$ ($16^{o}C$) respectively.

Two areas were selected within the impregnated area, and one
control area outside; each area was scrubbed, washed, and conditioned by
preliminary tests. The following scale readings were obtained: control,
84 ($\pm$ 0); area 1, 84 ($\pm$ 1); and area 2 (a slightly rougher area), 88 ($\pm$ 3).
Clearly, these results support the observation by others (see above) that
impregnation with PMMA does not induce a degradation of skid resistance in
concrete. (Tests on the Rte. 378 deck will probably be made by PennDOT
after at least one year has elapsed since impregnation.)

Table E-8. Water Absorption of Impregnated Mortar Specimens

Impregnant	Specimen No.	Average[1] Percent Loading	Average Water Absorption (g)	Average[2] Percent Reduction in Water Absorption
B_a (OH)$_2$ Solution[3]	1- 7	2.3	2.02	47
Molten Sulfur[4]	8-14	12.5	0.03	99
	29-33	10.5	0.06	98
Tar[5]	15-21	6.8	0.10	97
Sulfur-Tar (80-20)	22-28	11.2	0.05	99
Water (Control)	34-38	7.8	3.84	--

Unit Conversion: 1 oz = 28.35 g.

1. Percent Loading = $[\frac{\text{impregnated weight-dry weight}}{\text{dry weight}} \times 100]$; immersion time =24 hr.

2. Percent reduction in water absorption = $[\frac{\text{water required for saturation-water absorbed}}{\text{water required for saturation}} \times 100]$.

3. Ba(OH)$_2$ dissolved in its own water of crystallization; surface of concrete specimens severely attacked by the solution.

Table E-8. Water Absorption of Impregnated Mortar Specimens (Continued)

4. Specimens 8-21 and 34-38 immersed in water for 24 hr; the remaining specimens immersed in water

for 72 hr.

5. Tar used was AASHO Specification M-214-65; specific gravity, 1.08.

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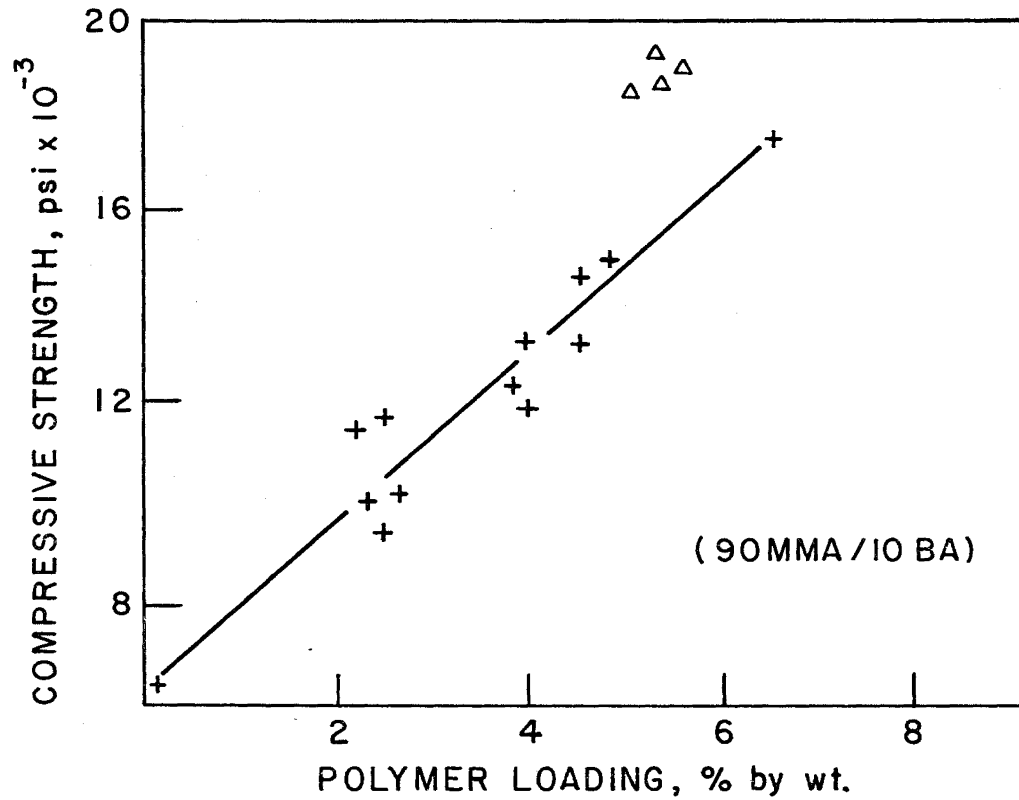
Fig. E-1 Effect of Polymer Loading on Compressive Strength (by Instron Tester: Crosshead Speed, 0.01 in/min) for Mortar Specimens (1"x2") Impregnated with MMA/BA Copolymers (90/10) Polymerization: Continuous at 70°C, + ; Intermittent at 60°C, Δ, 1 in. = 2.54 cm, $°F = \frac{9}{5}°C$ +32, 1 psi = 6.89 kN/m^2
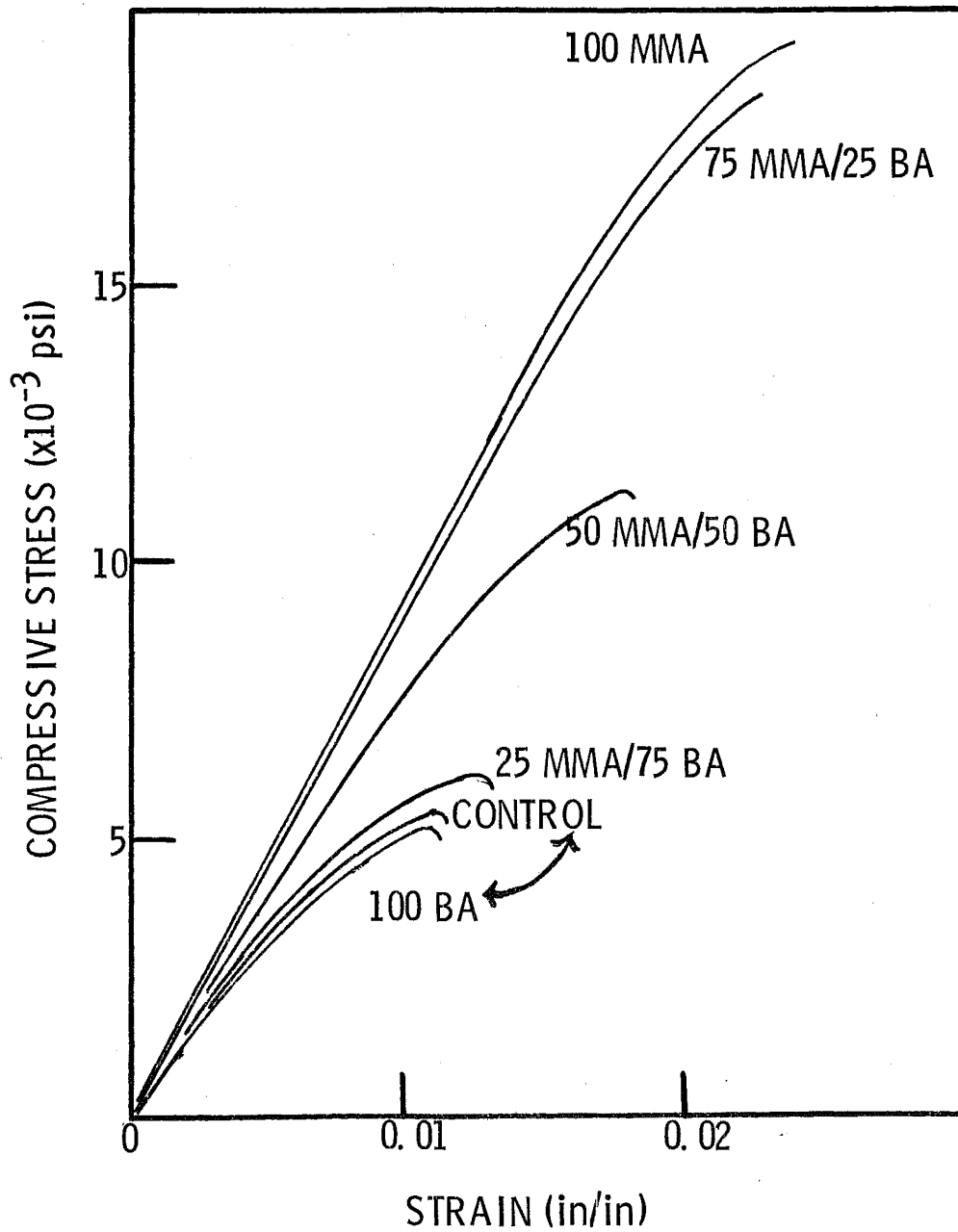
Fig. E-2   Polymer-Impregnated Mortar: Typical Compressive
Stress-Strain Curves

MMA = Methyl Methacrylate
BA = Butyl Acrylate

COMPRESSIVE STRESS-STRAIN CURVES
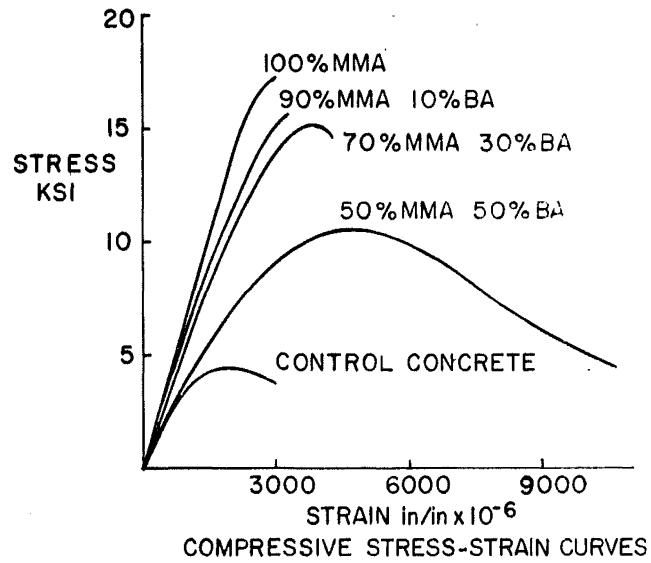
Fig. E-3 Polymer-Impregnated Concrete: Compressive
          Stress-Strain Curves as a Function of
          Polymer Composition

Tensile Load-Strain Curves
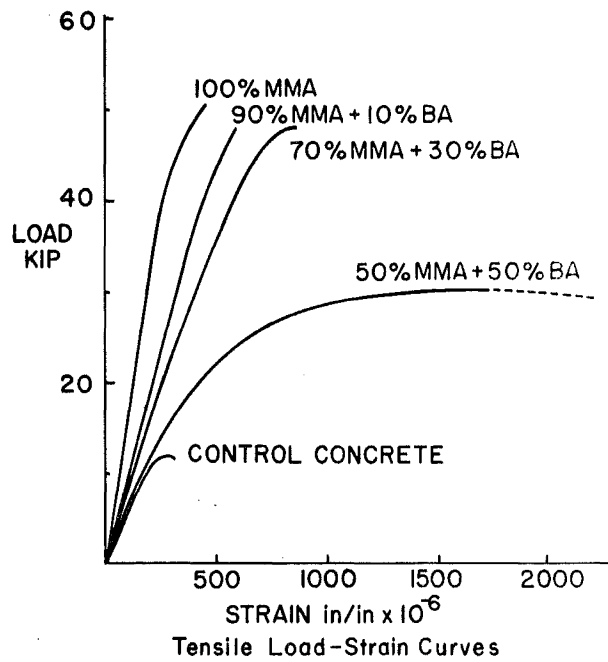
Fig. E-4 Polymer-Impregnated Concrete: Tensile Load-
          Strain Curves as a Function of Polymer
          Composition
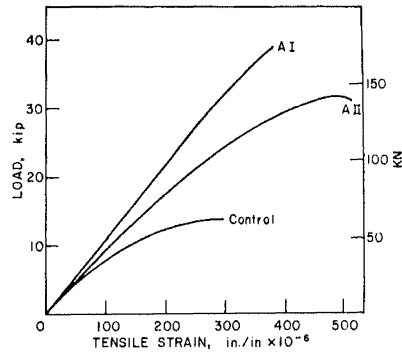
Fig. E-5 Tensile Load-Strain Curves (Hydraulic
          Tester) for 3-in. x 6-in. Concrete Cylinders
          Impregnated with MMA/BA 60/40 Mixture
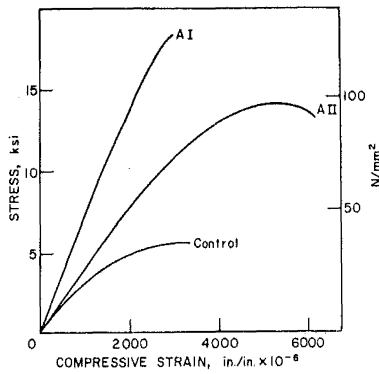
.Fig. E-6 Compressive Stress-Strain Curves (Hydraulic
           Tester) for 3-in. x 6-in. Concrete Cylinders
           Impregnated with MMA/BA 60/40 Mixture
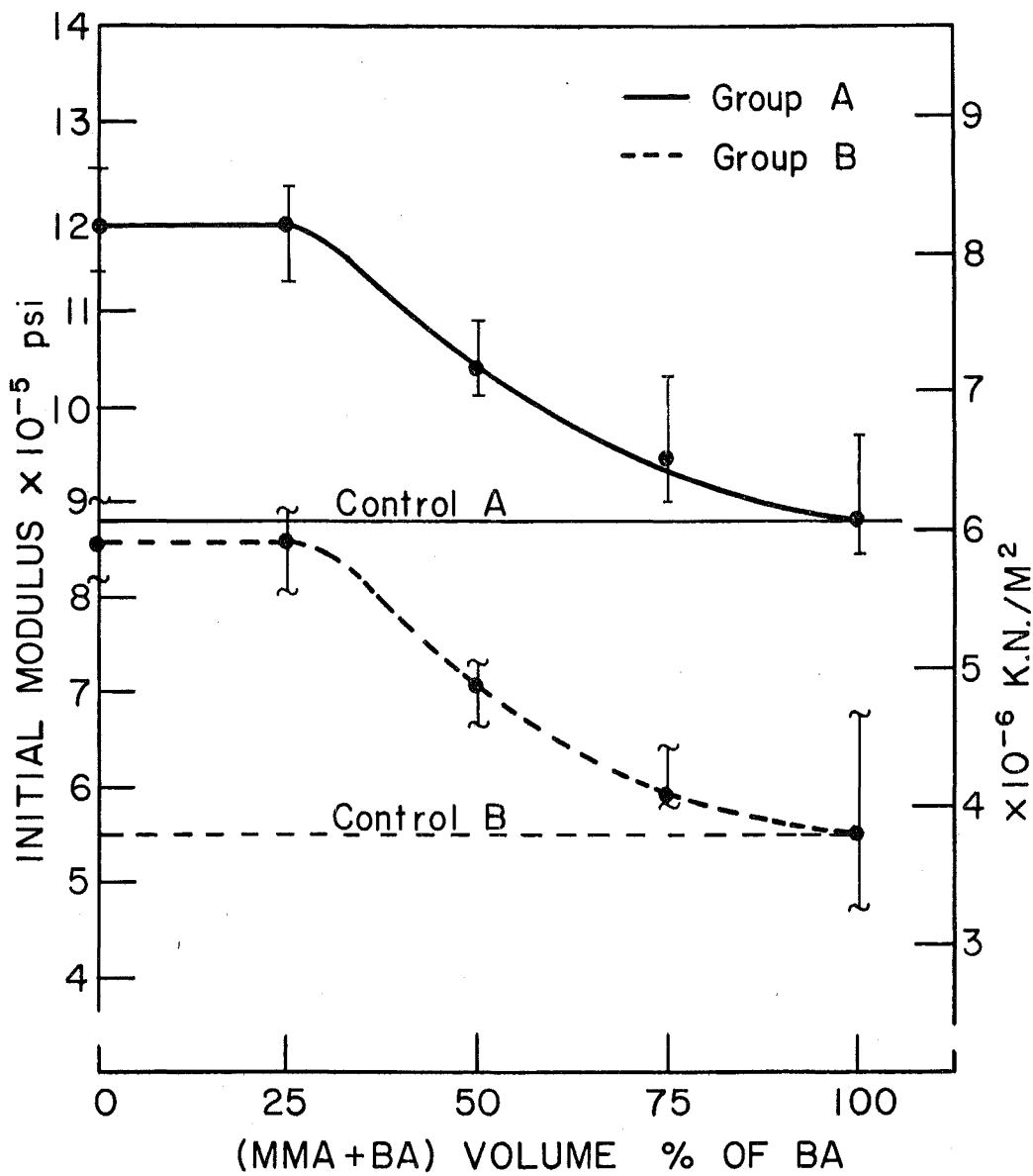
Fig. E-7 Polymer-Impregnated Mortar: Variation of Compressive Modulus with Strain Rate as a Function of Polymer Composition (Instron)
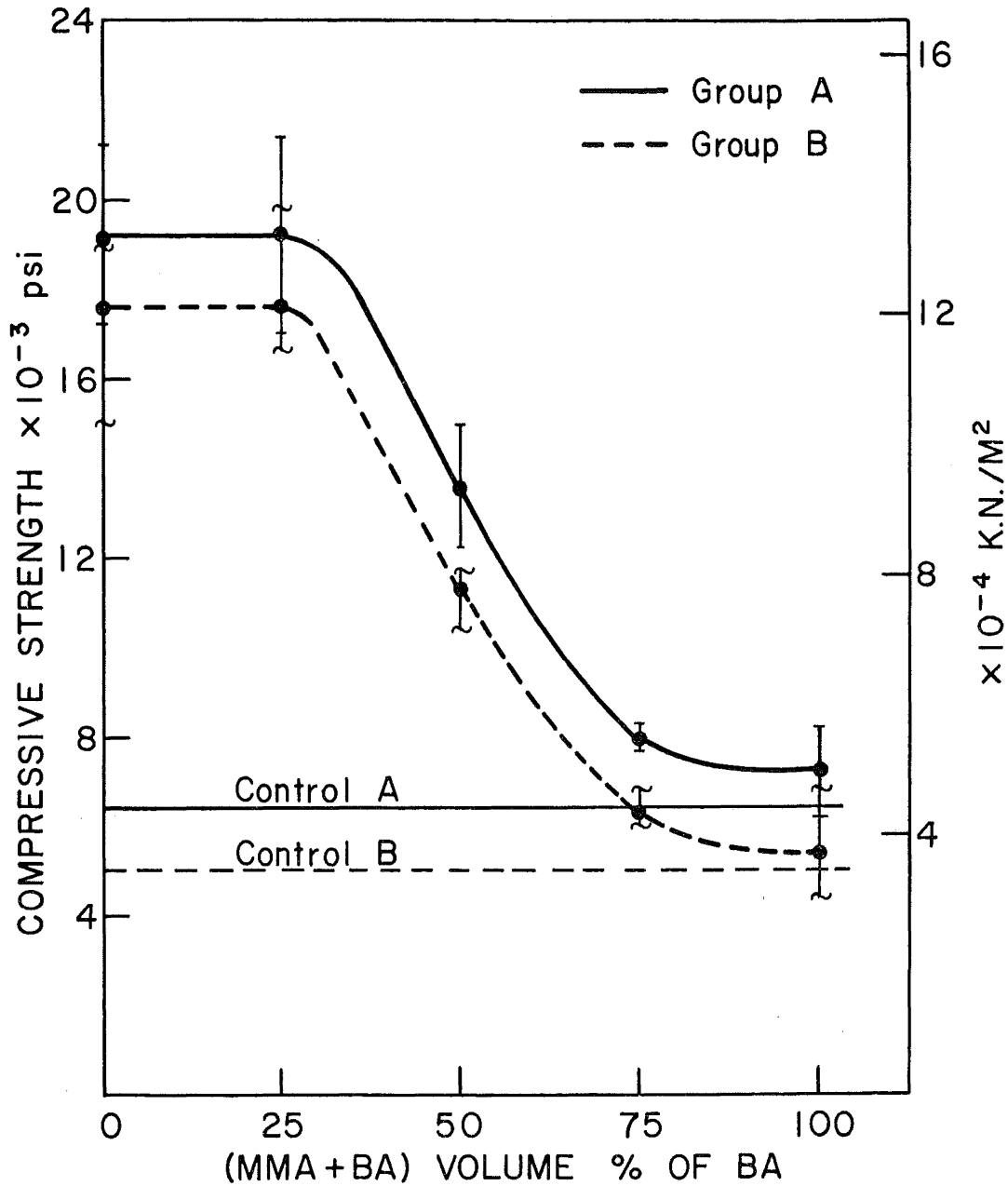
Fig. E-8 Polymer-Impregnated Mortar: Variation of Compressive Strength
with Strain Rate as a Function of Polymer Composition (Instron)
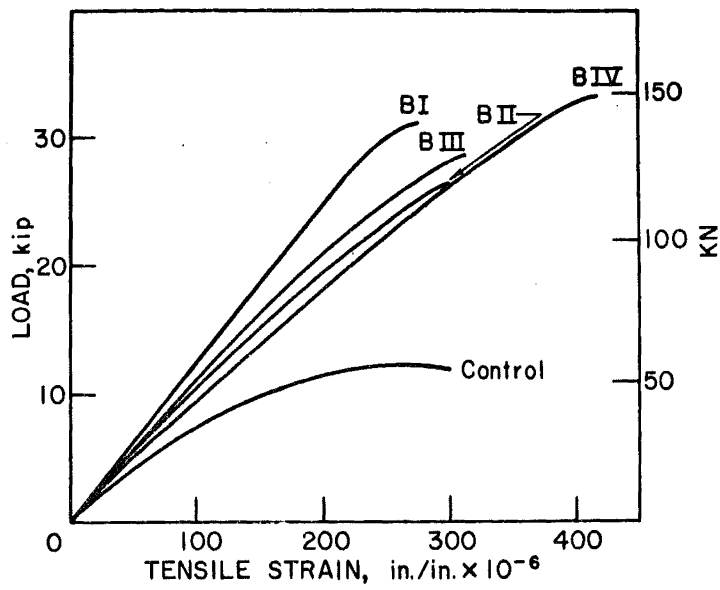
Fig. E-9   Tensile Load-Strain (Hydraulic Tester) for
            3-in. x 6-in. Concrete Cylinders Impregnated
            with Various MMA/BA/TMPTMA Mixtures
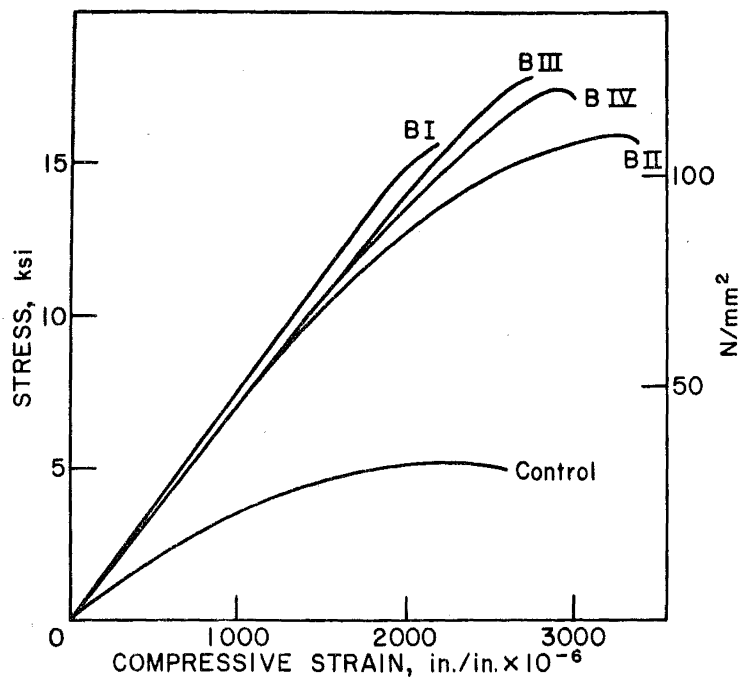
Fig. E-10   Compressive Stress-Strain Curves for Concrete
            Impregnated with Various Composition of MMA,
            BA, and TMPTMA

E-56
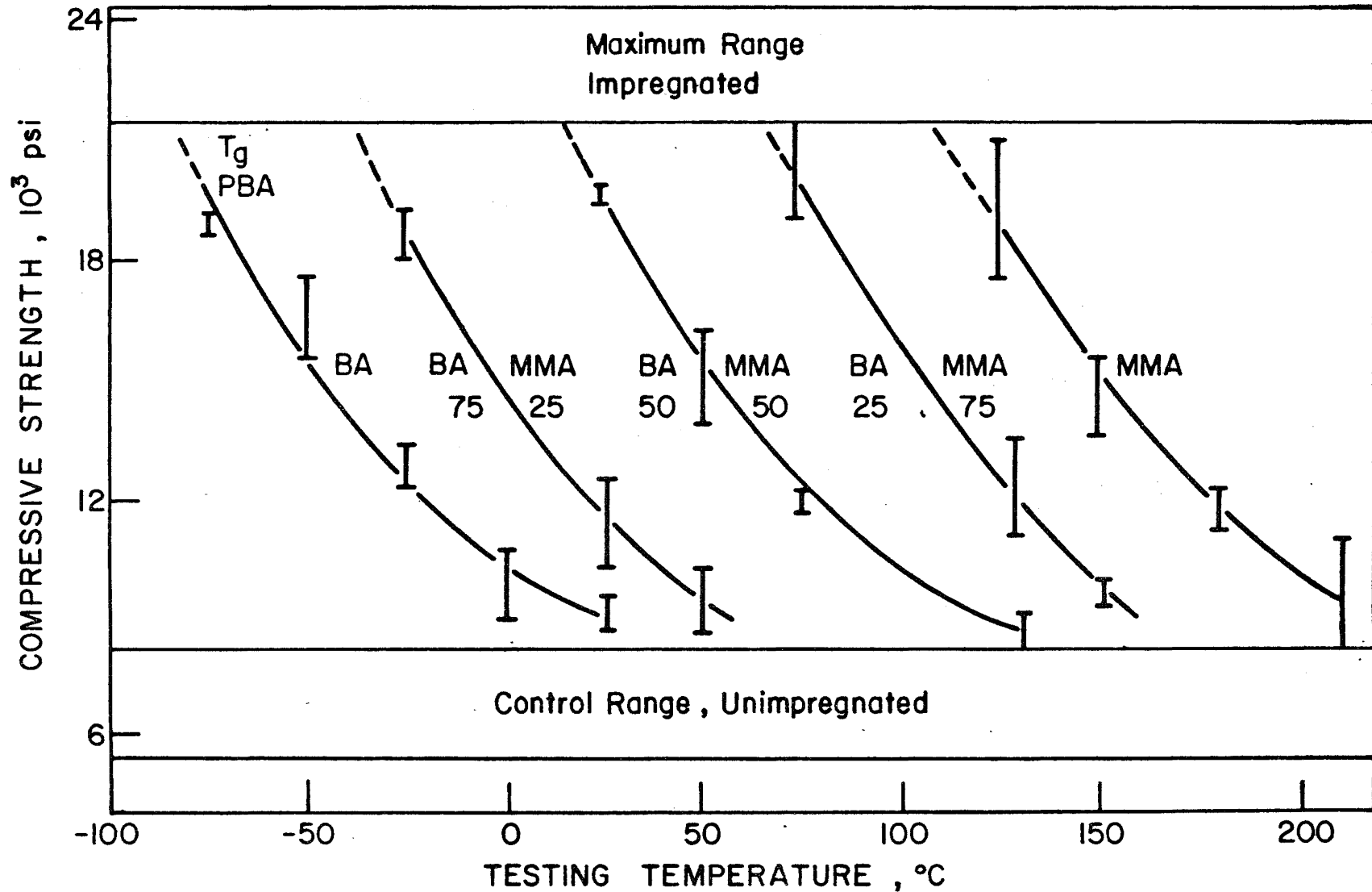
Fig. E-11 Effect of Temperature on Compressive Strength of Polymer-Impregnated Mortars Containing Polymers and Copolymers of n-Butyl Acrylate (BA) and Methyl Methacrylate (MMA)
(1 psi = 6.89 PN/m^2, $^\circ$F = 9/5°C + 32)
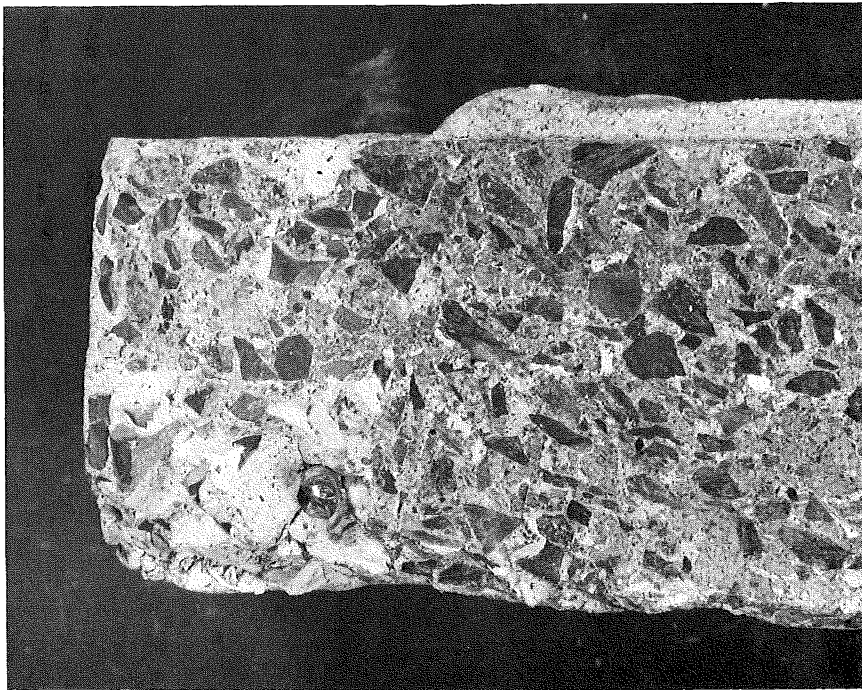
Fig. E-12 Fracture Cross Section of First Impregnated Slab (1A) Showing Polymer-Impregnated and Unimpregnated Regions (Note that Fracture Occurred through Aggregate Particles in Polymer-Impregnated Region and Around Particles in Unimpregnated Region)
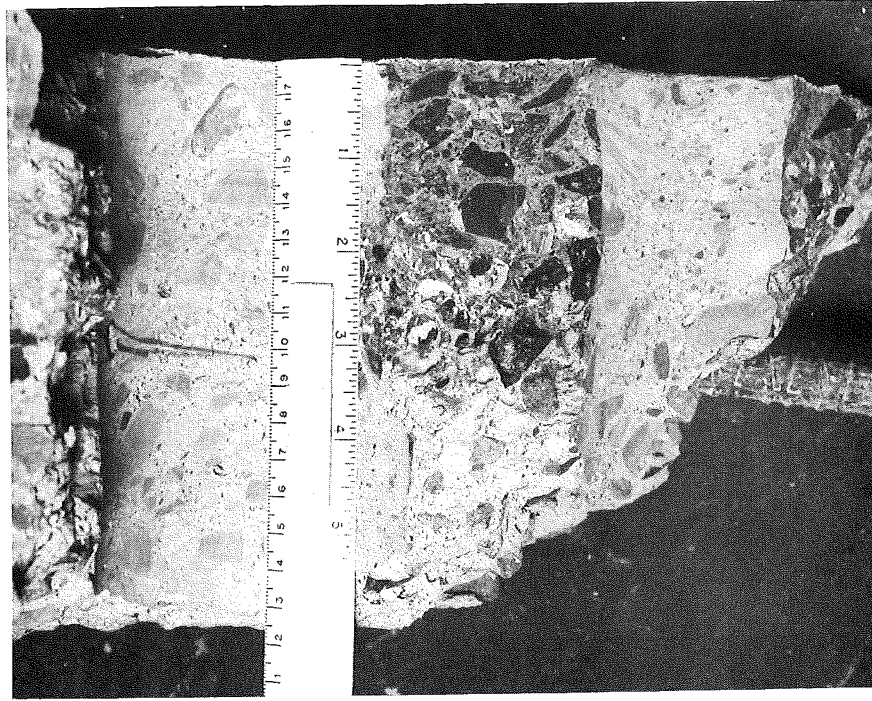
Fig. E-13   Closeup of IBMA Impregnated Slab Section,
            Note Uniformity of Coloration in Impregnated
            Portions
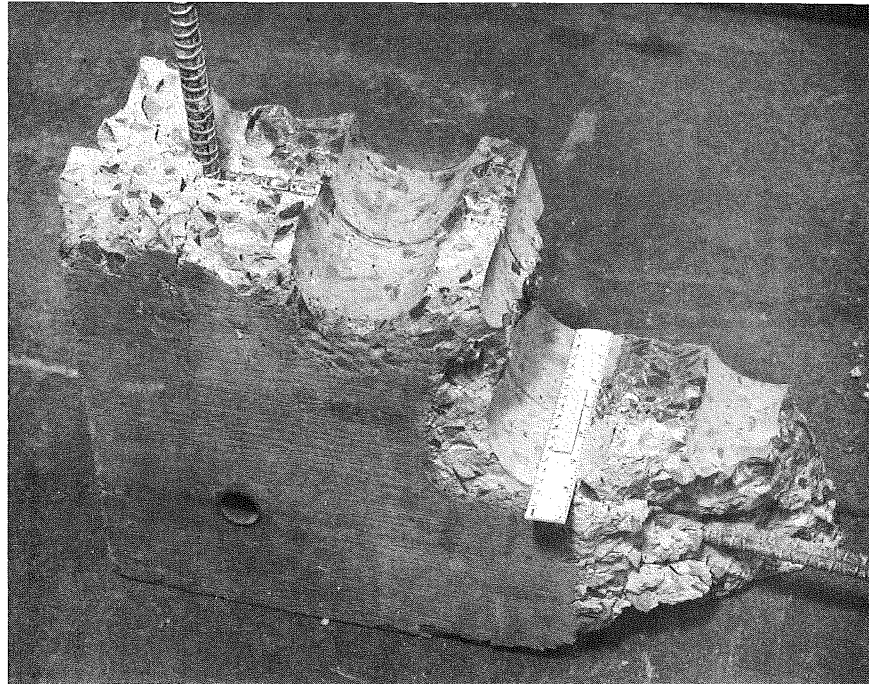
Fig. E-14   Overall View of Partially Impregnated Slab after
            Curing, Note the Evenness of Impregnation and Fracture
            of all Aggregates in the Impregnated Area
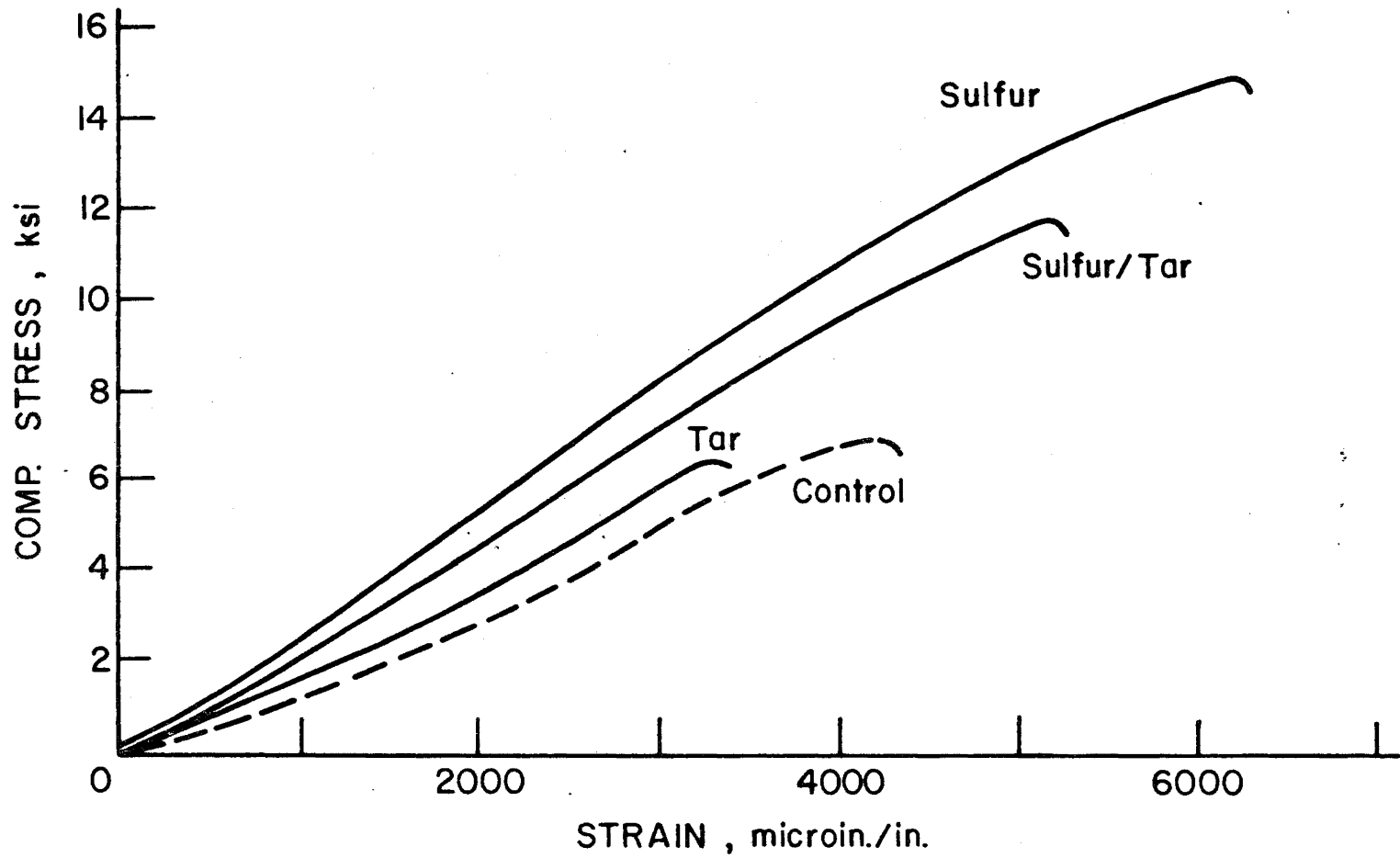
Fig. E-15 Stress-Strain Data for Impregnated Concretes (One psi = 6.89 kN/m², One Inch = 2.54 cm)
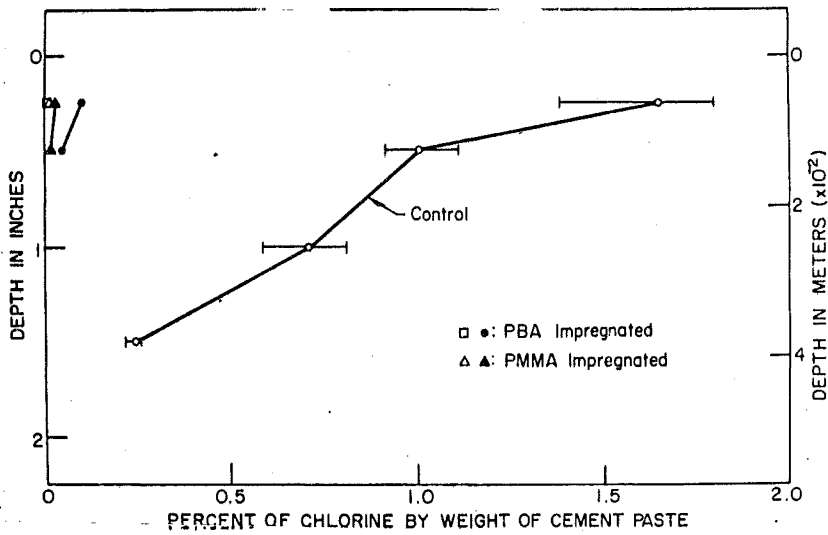
Fig. E-16   Effect of Polymer Impregnation on Chloride
            Penetration in Portland Cement Mortars
            (One Inch - 2.54 cm)
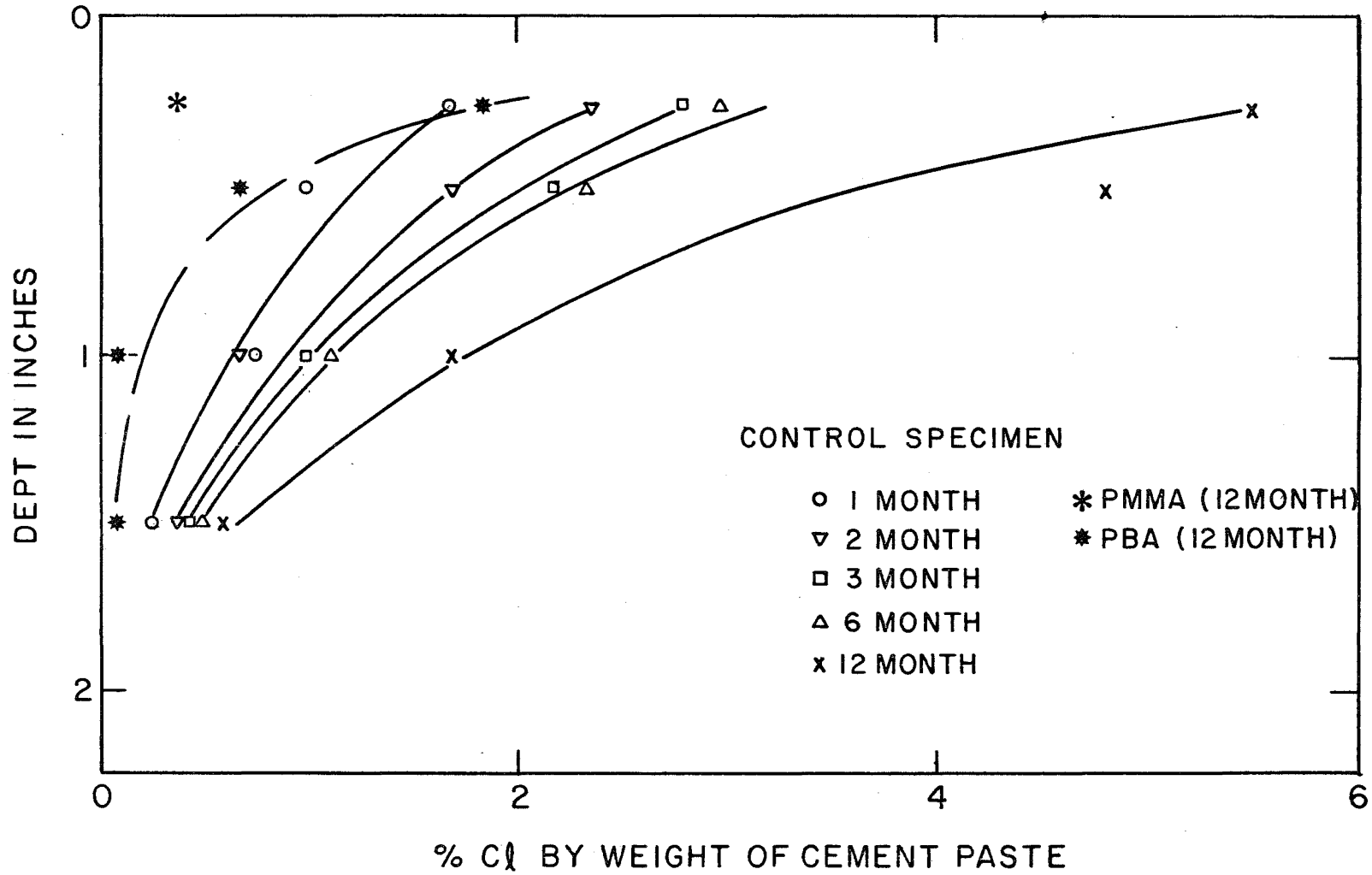
Fig. E-17 Effect of Polymer Impregnation on Absorption of Chlorides (One Inch = 2.54 cm)

A. |← 1 mm →|
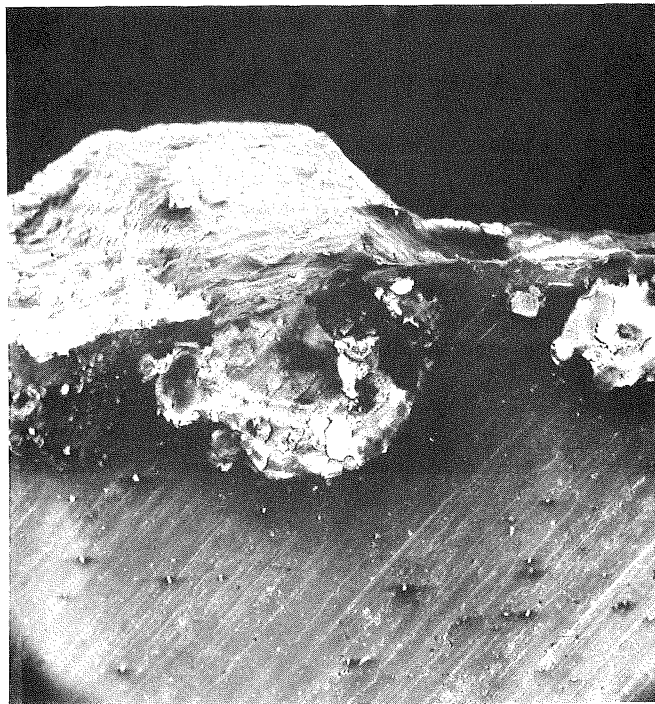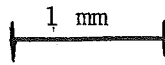
B.

Fig. E-18 Scanning Electron Photomicrographs of the Near End Sections of
Steel Reinforcing Rods in Salt-Contaminated Concrete Slabs After Freeze-
Thaw Testing: A. Polymer-Impregnated Core 2-1; B. Unimpregnated Core 5-3,
Polymer Loading, 5 wt. %
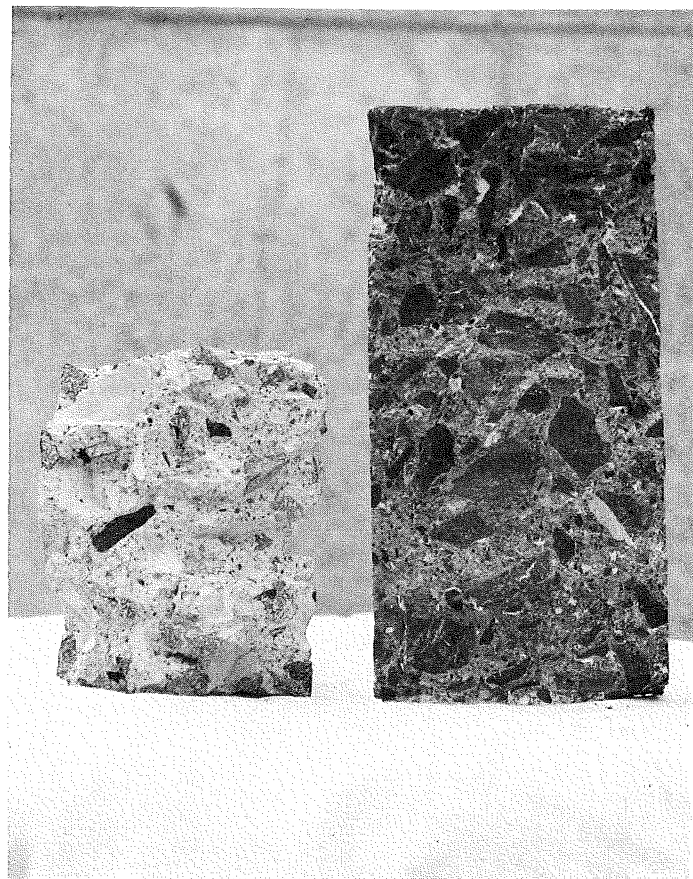
Fig. E- 19 Fracture Cross Sections of Cores from: (A) Salt-Contaminated
Unimpregnated Concrete Slab 5; (B) Polymer-Impregnated Concrete Slab 2
(Note Uniform Dark Coloration and Difference of Fracture Mode of Polymer-
Impregnated Core)
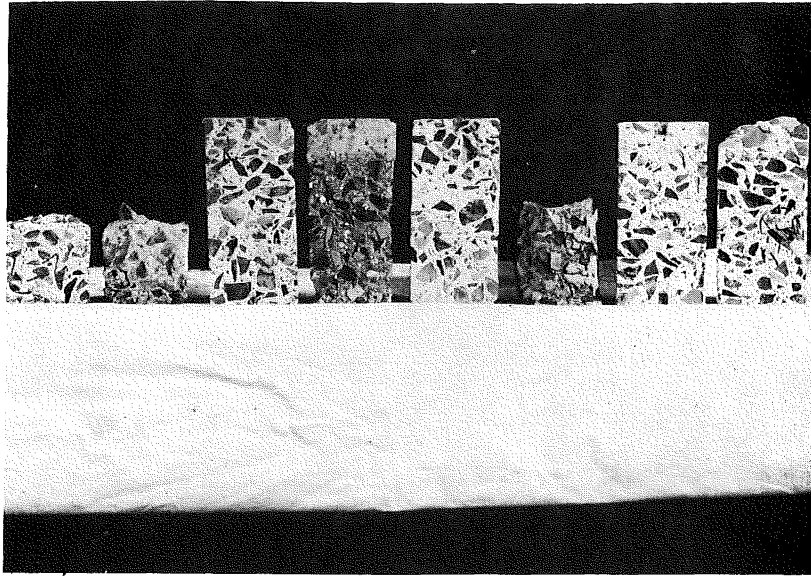
A.
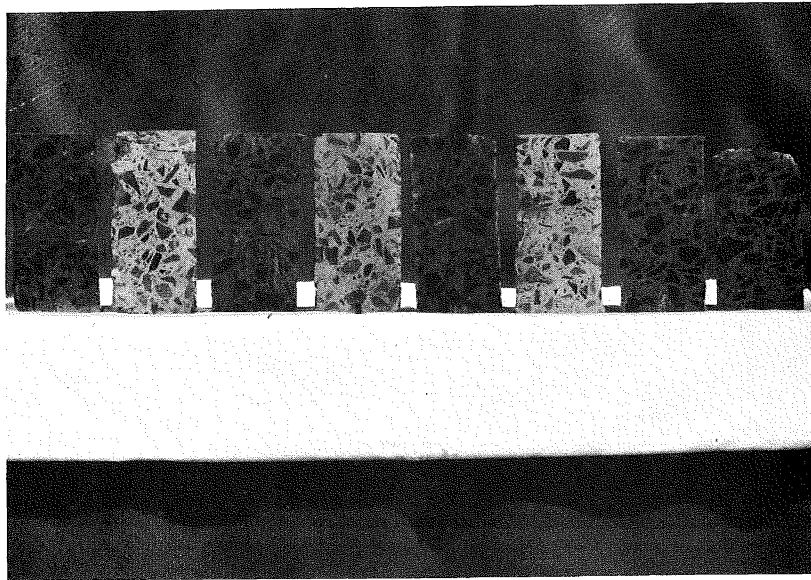
B.

Fig. E-20 Sawed Cross Sections of Cores Subjected to Freeze-Thaw Testing:
(A) Acid-Etched; (B) Polished (Note Virtually Complete Disintegration of
Cementitious Matrix and Aggregate Particles in Unimpregnated Cores)

BALL BEARING ABRASION TEST MACHINE
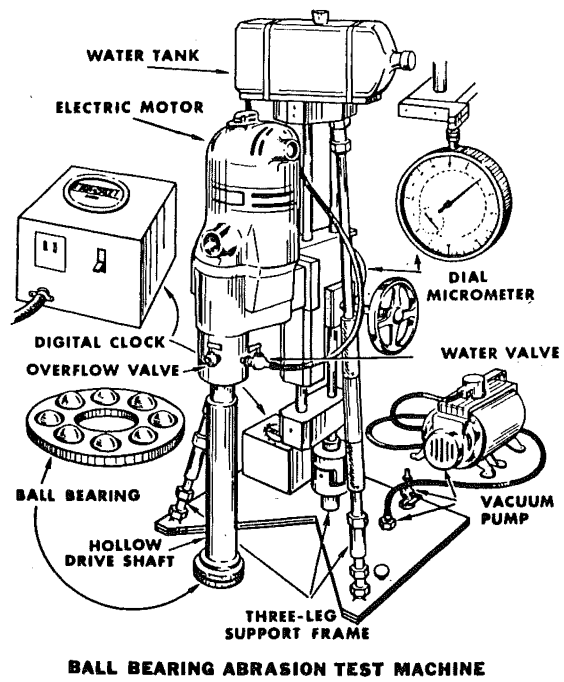
Fig. E-21 Abrasion Test Apparatus
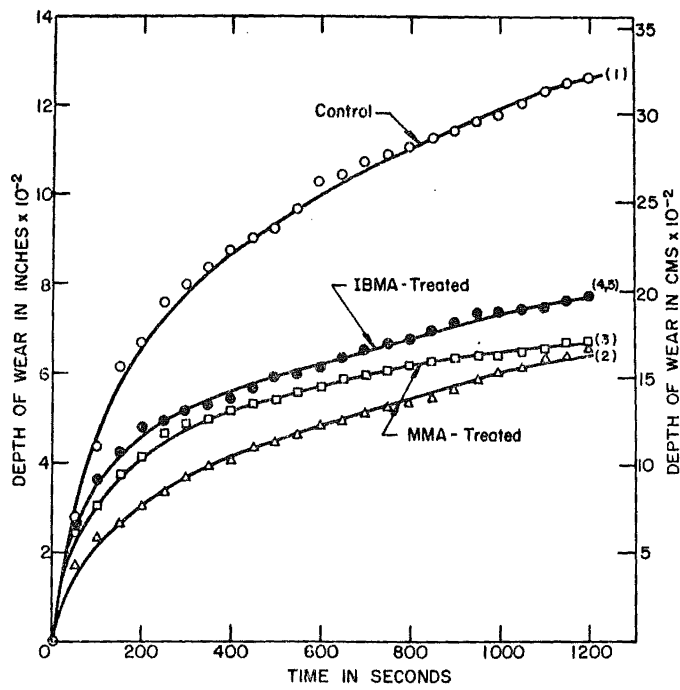
Fig. E-22   Variation of Depth of Wear with Time for Polymer-
Impregnated Concrete Slabs (One Inch = 2.54 cm)
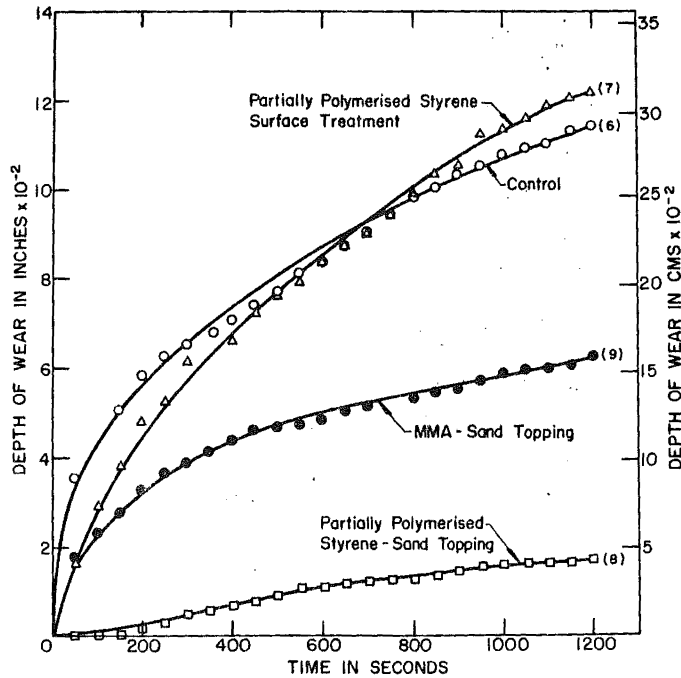
Fig. E-23   Variation of Depth of Wear with Time for Polymer-
Impregnated, Polymer-Sand Topped, and Unimpregnated
Concrete Slabs (One Inch = 2.54 cm)

APPENDIX F

EFFECTS OF CONTAMINANTS

INTRODUCTION

Experiments were carried out to examine the effects

of contamination of concrete with deicer salts and roadway deposits

(grease, oil, rubber) on the drying, impregnation, and polymerization

processes. The effects of the contaminants on the mechanical and

durability properties of polymer-impregnated concrete were also studied.

EFFECT ON DRYING

Laboratory studies on the effects of deicer salt contamination

on drying were carried out on concrete cylinders (1). The characteristics

of the concrete mixture are given in Table F-1.

Twenty-four 3-in. (7.6 -cm) diameter by 6-in. (15.2 -cm) high

concrete cylinders were made from the batch and were fog-cured for

28 days. All specimens were then dried at 260°F (125°C) for 24 hr.

The specimens were then divided into three groups of eight specimens

each. The first group, designated D, was submerged in water, and

the other two groups, DI and DII, were submerged in 3 percent (by

weight) sodium chloride solution for a period of 48 hr. All specimens

were then dried to constant weight in a circulating oven at 260°F (125°C).

The salt-contaminated specimens experienced weight losses that averaged

only about 87 percent of weight loss experienced by the non-salt-

contaminated ones at the time the latter had achieved constant weight

(17 hr). After an additional 49 hr of drying, the salt-contaminated

specimens showed an average weight loss that closely approached

Table F-1. Concrete Mixture Proportions and Properties

Water/Cement Ratio (by weight)	0.5
Water, lb (kg)	24.4 (11.1)
Cement, lb (kg)	48.8 (22.1)
Sand, lb (kg)	104.5 (47.4)
Coarse Aggregate, lb (kg)	113.5 (51.5)
Air Entraining Agent, cm^3	10
Air Content, %	7
Slump, in. (cm)	2.75 (7)

that of the noncontaminated specimens at 17 hr (98 percent).

Specimen set DII was subsequently resoaked in the salt solution for

another 48-hr period and dried to constant weight to produce a higher

level of salt-contaminated specimens for mechanical properties studies.

This experiment indicates that the presence of deicer salts

in the pore systems of concrete may require higher energy input or

longer drying time to obtain a given degree of drying, as compared

with noncontaminated concrete.

EFFECT ON IMPREGNATION RATE AND MONOMER LOADING

Laboratory Concrete

A series of polymer-impregnation tests using the pressure method

on slab specimens produced in the laboratory was carried out to evaluate

the effects of chloride contamination on impregnation rate and on

monomer loading (2). The 24-in. x 24-in. x 6-in. (61.0-cm x 61.0-cm x 15.2-cm)

concrete slab specimens were prepared from a conventional non-air-entrained

1.00:1.92:6.10:6.75 water-portland cement (type 1)-course sand-limestone

aggregate (1 in. [2.5 cm] maximum) mix with a cement factor of 485 lb/yd^3

(287 kg/m^3) and 28-days-average compressive strength of 4750 psi

(32800 Pa). The measured air content was 3 percent and the slump

was 2.5-3.0 in. (6.4-7.6 cm). The slabs were given a normal trowel

finish and were cured in the fog room (90-100 percent relative humidity)

for at least 28 days before use in drying and impregnation tests. All

slabs contained nominal steel reinforcement at a 4-in. (10-cm) depth

to simulate the structure of the bridge deck. The slabs were dried to

constant weight in an oven at 250°F (121°C). One slab was soaked in

salt solution to constant weight and redried in the same manner as

described above, resulting in a salt concentration in the concrete of 0.3 percent by weight. That slab and three noncontaminated ones were subjected to vacuum-pressure impregnation using the apparatus described in Appendix C. The monomer system used was 90:10 methyl methacrylate-trimethylolpropane trimethacrylate containing 0.5 percent azobisisobutyronitrile initiator. Various vacuum-pressure levels were used and the impregnation process was continued until the monomer penetrated the entire 6-in. (15.2 -cm) thickness of the slabs. The results are shown in Table F-2.

The predicted time for impregnation is based on the relationship discussed in Appendix D. Note that the salt-contaminated slab took longer to impregnate than predicted by the equation while the three noncontaminated slabs gave results that closely agreed with predicted values. Also, it can be seen in Table F-2 that the monomer loading in the salt-contaminated slab was less than in the noncontaminated slabs (5.0 vs. 5.5 percent). Therefore, it can be concluded that salt contamination does reduce the rate of impregnation and polymer loading, although not to an appreciable extent.

Field Concrete

For this study (3), concrete cores were taken from three 7-year-old bridge decks with an ADT (Average Daily Traffic) of 5160 in 1969. The three decks were in excellent condition and did not display the presence of large cracks, spalled areas, or potholes. The concrete used in the construction of the three decks was required to meet the Pennsylvania Department of Transportation specifications for Class AA reinforced vibrated concrete. Portland cement (type 1) was used,

and glacial sand and crushed limestone were the aggregates. The average slump, air content, and flexural strength for the concrete used in these decks are given in Table F-3.

The impregnation system consisted of methyl methacrylate (MMA), trimethylopropane trimethacrylate (TMPTMA), and azobisisobutyronitrile (AZO) mixed in the ratio of 100:10:0.5 parts by weight, respectively.

A total of 26 cores was taken from the three bridge decks. The coring positions represented the lateral range of the different usage areas on a bridge deck. Those areas are the water tables and the truck and passing lanes. Duplicate cores were taken from these areas in order that chloride determinations could be made. Figure F-1 shows the positions from which the cores were taken.

The bottoms of the cores were trimmed with a diamond saw to provide specimens that were 4 in. (10. · cm) in diameter by approximately 5 in. (13 cm) in height. The cores were then dried in a forced draft oven at 239°F (115°C) for 72 hr followed by 24 hr at 239°F (115°C) in a vacuum oven at 29 in. (98 kPa) Hg vacuum. After cooling under vacuum, the sides of the cores were painted with a coat of epoxy. A metal ring 1 in. (2.5 cm) in height, 4 in. (10. : cm) in diameter, was bonded to the top of each core with epoxy to provide a reservoir for ponding the monomer during the impregnation of the cores.

To determine the quantity of deicer salts present in the cores, the Berman (4) chloride titration procedure was employed. Chloride analyses were performed on cores 1-2, 1-4, 1-6, 2-2, 2-4, 2-6, 3-5, 3-6, and 3-8. To provide the cement paste sample used in the titrations,

Table F-2. Impregnation of 24-in. x 24-in. x 6-in.

(61.0 -cm x 61.0 -cm x 15.2 cm) Slabs

Slab No.	Salt Content %	Vacuum Treatment	Impregnation Pressure psi (kN/m^2)	Time hr	Predicted Time hr	Polymer Loading %
1A	0.0	None	30 (210)	17–24	18	5.5
1	0.0	2 hr @ 25 in. (63.5 cm) Hg	40 (280)	7.0–8.5	7–10	5.5
2	0.3	1.5 hr @ 28 in. (71 cm) Hg	60 (410)	5.0–7.5	4.0–5.5	5.0
8	0.0	1.5 hr @ 28 in. (71 cm) Hg	80 (550)	2.0–3.5	2–3	5.5

Unit Conversion: 1 kN/m^2 = 1 Pa

Table F-3. Average Concrete Control Parameters

Bridge Structure Number	Slump (in.)	Air Content (%)	Flexural Strength psi @ 7 days
6254NB	2.2	6.5	769
6254SB	2.2	6.5	641
6258NB	2.2	6.2	956

Unit Conversion: 1 in. = 2.54 cm.

the cores were first split using the tensile splitting method. The
cement paste was then extracted as a fine powder by drilling on the
split face with a 3/16-in. (0.48-cm) carbide drill bit. The positions
drilled were in the cement paste areas and care was taken to avoid any
large aggregate particles. Cement paste samples were obtained from
four areas on each core (0 to 1/4 in. [0.6 cm], 1/4 to 3/4 in.
[0.6 - 1.9 cm], 3/4 to 1-3/4 in. [1.9 - 4.5 cm], and 1-3/4 to 3-3/4
in [4.5 - 9.5 cm] in depth from the wearing surface).

The impregnation of the dried cores with the MMA system was
accomplished by allowing the monomer to soak through the cores from
the wearing surface only with an evaporation barrier provided above the
free monomer surface. The rate of impregnation was determined by
periodic weighing of the specimens during impregnation. Completion
of impregnation was assumed to occur when the monomer exuded uniformly
from the bottoms of the specimens.

It was assumed that the heaviest traveled areas would have the
greatest amount of surface contamination. Therefore, six cores
were taken from the truck lane, three from the right wheel path
and three from between the wheel paths. The surfaces
of these cores were cleaned by three methods (detergent, lye, and sand
blasting). Cores 1-7 and 2-7 were scrubbed for 5 min with a 20
percent by weight detergent (Biz) solution; cores 2-7 and 2-8 were
scrubbed for 5 min with a 20 percent by weight lye (NaOH) solution;
cores 1-9 and 2-9 were cleaned by sand blasting at a pressure of 75
psi (.0.66 MPa) for a period of 10 min.

Typical results of the chloride analyses for the nine bridge
deck cores are presented in Figure F-2. The concentrations of the
chlorides appear to decrease linearly as a function of depth. This
agrees with the results for sound concrete found in other research on
the durability of concrete bridge decks (5). In general, the degree
of contamination by chlorides was determined to be approximately the
same for the areas investigated except for the areas not used by
traffic where the concentrations were lower.

The lateral position of the cores on the decks was matched with
the closest lateral position of the cores used for chloride analyses.
The values of chlorides present in the top 1/4 in. (0.6 cm) were then
assigned to the respective impregnated cores. These chloride values
and the impregnation data are presented in Table F-4.

Correlation coefficients were calculated for the chlorides in the
top 1/4 in. (0.6 cm) versus the percent MMA at 96 hr and versus the
rate of impregnation (slope). Both correlation coefficients were
significant at the 95 percent confidence level.

Due to the small sample sizes of the cores subjected to the
various cleaning processes, no statistical analyses were performed.
However, by observing the percent MMA gained in 96 hr for the six cores
that were cleaned (1-7, 1-8, 1-9, 2-7, 2-8, and 2-9) with the remaining
cores from the same two bridge decks (presented in Table F-4), it
is concluded that contamination from materials considered here had no
significant effect on polymer loading. However, clearly the presence of deicer
salts in the concrete retards the impregnation rate, as shown earlier
for mortars (6).

Core No.	Slope $(g/hr^{1/2})$	Monomer gained in 96 hr (g)	Total Monomer gained[1] (g)	Percent at 96 hr	Percent Cl at 1/4 in. (.6 cm)	Total Soak Time (days)
1-1	7.4	81.5	98.5	82.7	0.074	7
1-3	6.7	71.1	87.6	81.2	0.333	7
1-5	5.6	54.8	87.9	62.3	0.319	11
1-7	5.0	54.0	81.7	66.1	0.319	11
1-8	4.7	50.4	68.9	73.1	0.319	9
1-9	5.9	58.8	84.0	70.0	0.319	9
2-1	5.0	53.0	74.6	71.0	0.163	9
2-3	5.0	52.7	81.8	64.4	0.355	11
2-5	5.1	56.1	84.2	66.6	0.377	11
2-7	5.9	65.2	86.8	75.1	0.355	9
2-8	5.1	50.0	81.2	61.6	0.355	11
2-9	5.8	68.1	93.9	67.2	0.355	11
3-1	8.7	87.5	87.5	100.0	0.020	4
3-2	7.7	78.2	93.7	83.5	0.020	6
3-3	7.6	76.0	82.7	91.9	0.298	5
3-4	5.6	60.9	76.5	79.6	0.192	7
3-7	5.4	58.8	72.5	81.1	0.020	7

Unit Conversion: 1 oz = 28.35 g.

1. At complete penetration.

EFFECT ON POLYMERIZATION

It has been reported in the literature (7) that 90 percent of
polymerization is achieved at the peak of the exotherm for the MMA-
TMPTMA monomer system. Therefore, it was decided to investigate the
effect of contaminants on polymerization by measuring the time
required to reach the exothermic peak. The need for the determination
of the warm-up time was eliminated by measuring the difference in
time to peak exotherm between a control and the contaminated specimens.

Since the exotherm of the polymerization reaction can be dependent
on specimen size, a constant volume was chosen. A specimen size of
0.88 oz (25 g) was used because the specimen had to be large
enough to overcome the effects of the temperature of the oil bath but
small enough so that the oil bath temperature remained essentially
constant during polymerization.

It has been shown that the rate of polymerization (3) is dependent
on the activation temperature. It was also expected that the level
of contamination would alter the polymerization time. Therefore,
polymerization time studies were conducted at 131°F (55°C), 149°F
(65°C), and 167°F (75°C) with contaminant levels of 0.5, 1.0, and
2.0 percent by weight. The exotherm of reaction was measured by
means of a copper-constantan thermocouple. The depth of the
thermocouple in the specimens was kept constant. The culture tubes
containing the specimens were placed in the oil bath; care was taken
to prevent the oil from the bath from entering the specimens. The
contaminants investigated were sodium chloride, calcium chloride,
linseed oil (used as a sealant on bridge decks), motor oil, automobile

lubricant (grease), and asphalt cement (used in patching and sealing cracks and joints).

The effects of the various contaminants on polymerization are presented in Table F-5. It can be seen that the effects of all contaminants decrease sharply with increasing polymerization temperature, becoming essentially nil at 167°F (75°C). In fact, at 149°F (65°C), only the asphalt cement significantly affected polymerization. At 131°F (55°C) all contaminants except sodium chloride significantly reduce the polymerization rate. This suggests that the activation temperature should be kept above 149°F (65°C) in order that polymerization be achieved. Also, asphalt cement should be removed to the extent practical from the surface prior to impregnation.

EFFECT ON MECHANICAL PROPERTIES

The same group of concrete specimens described at the beginning of the section entitled "Effect on Drying" earlier in this appendix was used to study the effect on mechanical properties (1). After the drying tests, half of the specimens(4) from each group were cooled down, placed in the impregnation vessel (Appendix D), and subjected to both vacuum and pressure. Air was removed from the specimens by a vacuum pump at 29 in. (100 KN/m^2) of mercury for 1-1/2 hr before MMA containing 0.5 percent by weight azobisisobutyronitrile was induced into the vessel. The vessel was then pressurized with nitrogen at 60 psi (0.41 MPa) for 1-1/2 hr to speed up the penetration of monomer. After removal from the vessel, the specimens were polymerized under hot water at 160°F to 175°F (70°C to 80°C) for 4 hr. The polymer loading of the specimens after polymerization was calculated as the

Table F-5. The Effects of Road Contaminants on the

Polymerization of MMA-TMPTMA-AZO System

Level of Contaminant (% of MMA System Wt.)	Type of Contaminant	Increase in Polymerization Time[1] (min)			Number of Exotherms		
		55°C	65°C	75°C	55°C	65°C	75°C
0.5	NaCl	7	2	0	1	1	1
1.0	NaCl	3	1	0	1	1	1
2.0	NaCl	5	7	0	1	1	1
0.5	CaCl$_2$	30	5	0	2	1	1
1.0	CaCl$_2$	26	3	0	2	1	1
2.0	CaCl$_2$	39	10	0	2	1	1
0.5	Linseed Oil	47	2	0	2	1	1
1.0	Linseed Oil	45	1	0	2	1	1
2.0	Linseed Oil	88	8	0	2	1	1
0.5	Motor Oil	44	3	0	2	1	1
1.0	Motor Oil	30	3	0	2	1	1
2.0	Motor Oil	68	13	2	2	1	1
0.5	Grease	52	4	0	2	1	1
1.0	Grease	56	6	0	2	1	1
2.0	Grease	81	15	2	2	1	1
0.4	Asphalt Cement	138	27	2	2	1	1
1.2	Asphalt Cement	273	81	2	2	1	1
2.0	Asphalt Cement	470	120	3	3	2	1

Table F-5. The Effects of Road Contaminants on the

Polymerization of MMA-TMPTMA-AZO System

(Continued)

Unit Conversion: $°F = (\frac{9}{5}) \, °C + 32.$

1. Polymerization time is 67 percent of the time (after the system

attains bath temperature) it takes the system to reach its peak

exotherm temperature. This time for the MMA system is only

108 $\pm$ 8 minutes at 55°C and 32 $\pm$ minutes at 65°C.

increase in weight after polymerization in percent of the initial dry weight.

The remaining one-half of the specimens from each group were used for controls in the mechanical properties determinations. A modification of the standard splitting tensile test (ASTM C496-66) was used. The set-up has the advantage that the lateral strain can be automatically recorded as a function of load. A strain gauge was glued to the bottom plane surface of each specimen, horizontally in the center of the specimen.

The specimens used for compression tests (ASTM C39-66) were capped with high-strength gypsum plaster to assure plane parallelism of the ends. Two clip-type extensometers were fixed on either side of the specimen between two rings. The load-strain relationships were recorded automatically on an X-Y plotter for both the tension and compression tests.

Essentially, uniform impregnation and complete conversion to polymer were achieved for all of the PIC specimens, as shown by visual and microscopic examination, and by the observation of at most a faint odor due to unreacted monomer (in only a few specimens on freshly broken surfaces). The results of the mechanical properties determinations are shown in Table F-6 and in Figures F-3 and F-4.

Looking at the differences between the control specimens and the impregnated specimens in Table F-6, it appears that tensile strength and Young's modulus do tend to decrease slightly with increasing salt content. The compressive strength, on the other hand, appears to give a minimum value at the intermediate salt-content value.

Table F-6. Effects of Salt Contamination on Mechanical Properties

Specimen Series	% Salt	Polymer Loading, %	Tensile Strength ksi	Compressive Strength ksi	Young's Modulus ksi x 10^3
D	0.0	7.7	1.45	19.6	6.7[a]
D Control	0.0	0.0	0.39	4.2	2.3[a]
Difference	0.0	7.7	1.06	15.4	4.4
DI	0.5	7.7	1.40	15.8	5.8
DI Control	0.5	0.0	0.42	4.5	2.9
Difference	0.0	7.7	0.98	14.3	2.9
DII	1.0	7.1	1.38	19.9	6.3
DII Control	1.0	0.0	0.47	4.8	3.6
Difference	0.0	7.1	0.91	15.1	2.7

[a]Tangent Modulus.

[b]Secant Modulus.

[1]Conversion Factor: 1 ksi = 6.89 kPa

However, for the salt contents used in this experiment (up to 1.0 percent), the effect on mechanical properties is relatively insignificant. The tendency of polymer impregnation to mask initial differences in different concretes by producing composites that have very nearly the same mechanical properties may imperil any meaningful comparison of differences between controls, impregnated specimens and salt content. In other words, the best comparison may be between the impregnated specimens and the salt content irrespective of the controls. This comparison yields no consistent evidence of a relationship between salt content and mechanical behavior, at least in well-dried specimens.

EFFECT ON FREEZE-THAW RESISTANCE

As described under "Freeze-Thaw Tests" in Appendix E, salt contamination reduced the freeze-thaw resistance of nonimpregnated concrete, but had no apparent effect on the durability of polymer-impregnated concrete. Both salt-contaminated and non-salt-contaminated polymer-impregnated specimens showed outstanding resistance to freeze-thaw action.

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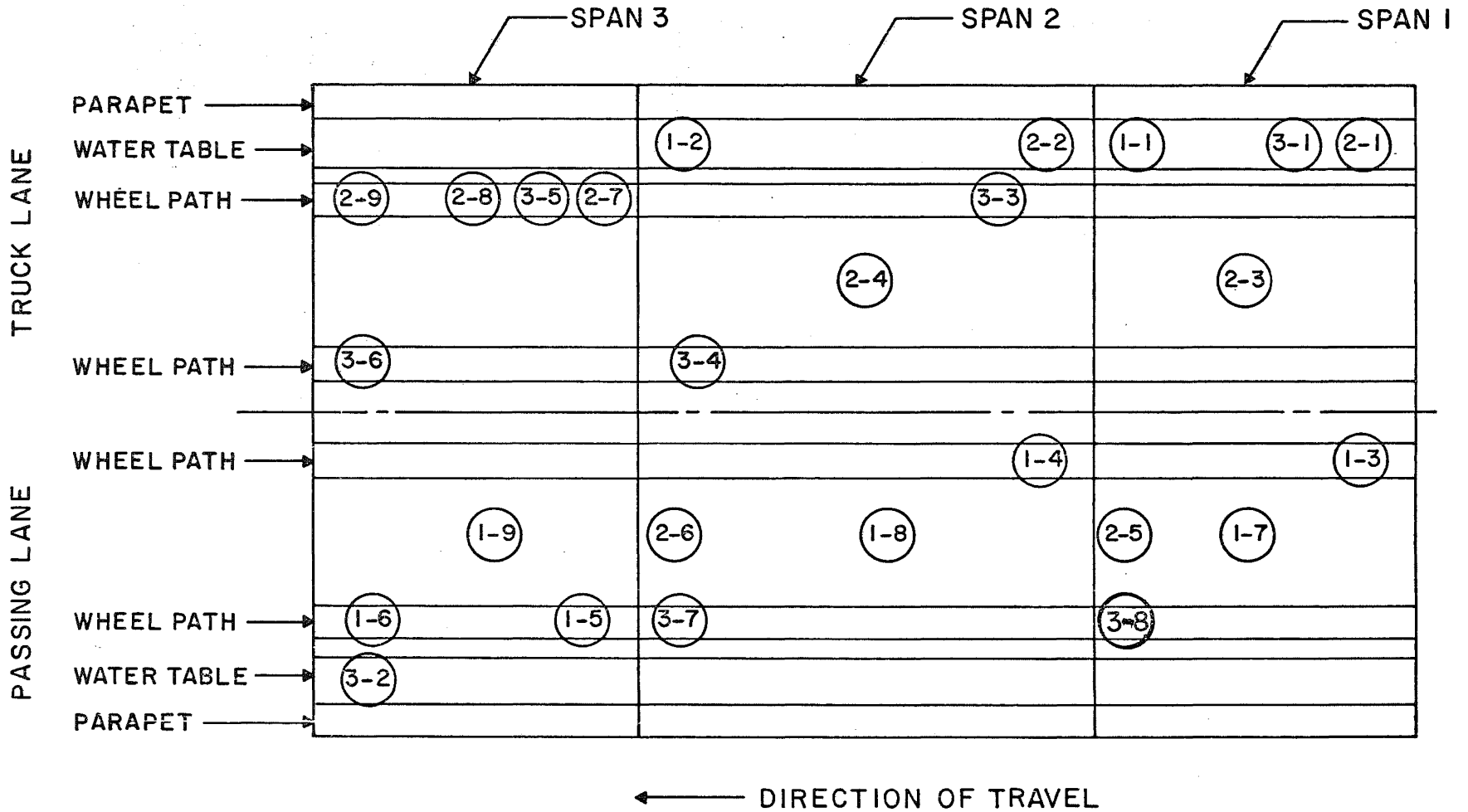   Vol. 4, No. 3, pp. 179-184, Fall 1972.

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FIGURE F-1 CORING POSITIONS OF BRIDGE DECK 6254 NB (I-I to I-9), 6254 SB (2-I to 2-9), AND 6258 NB (3-I to 3-8).
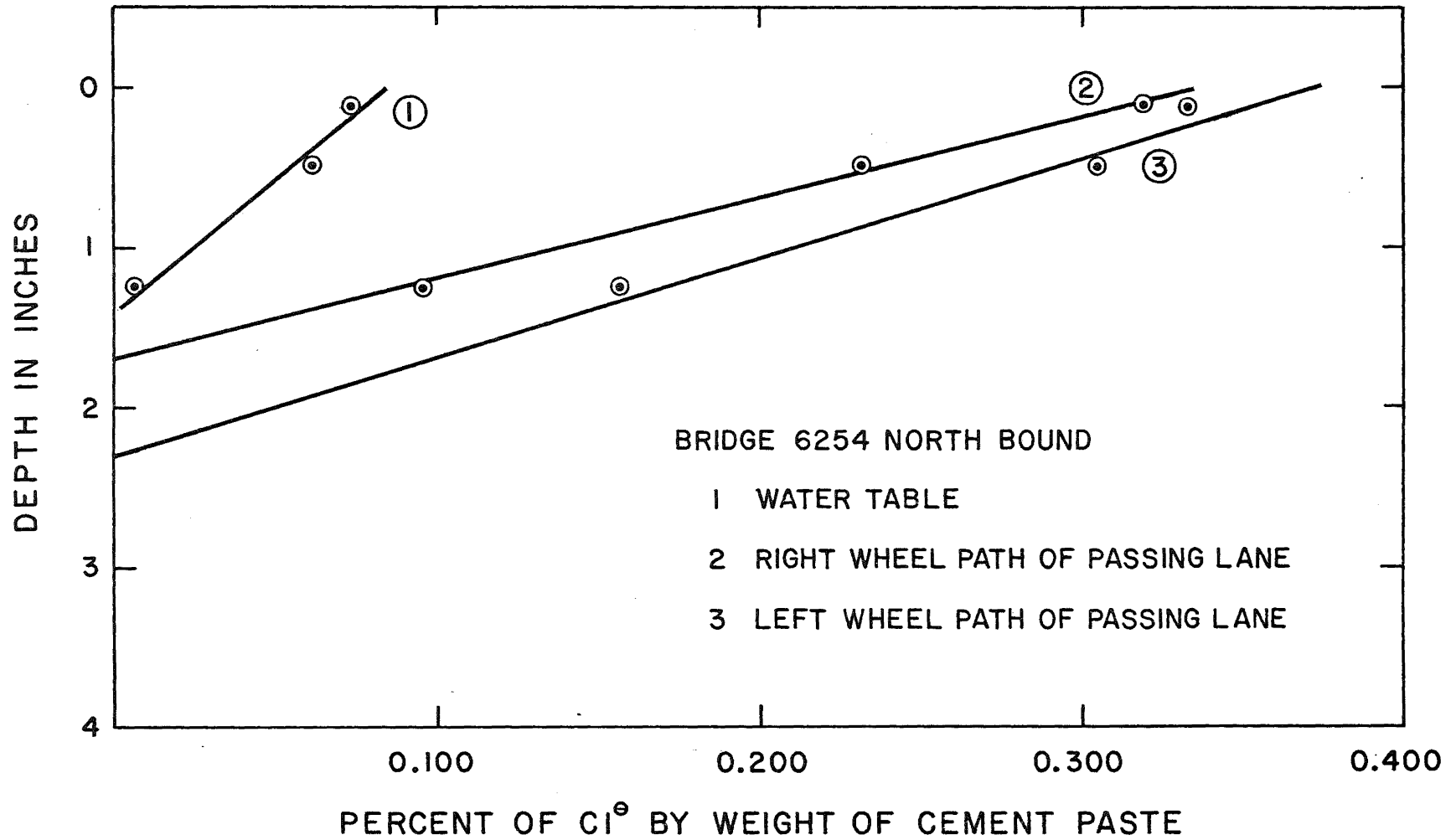
FIGURE F-2 CHLORIDE CONTENT OF BRIDGE 6254 NORTH BOUND
1 in. = 2.54 cm
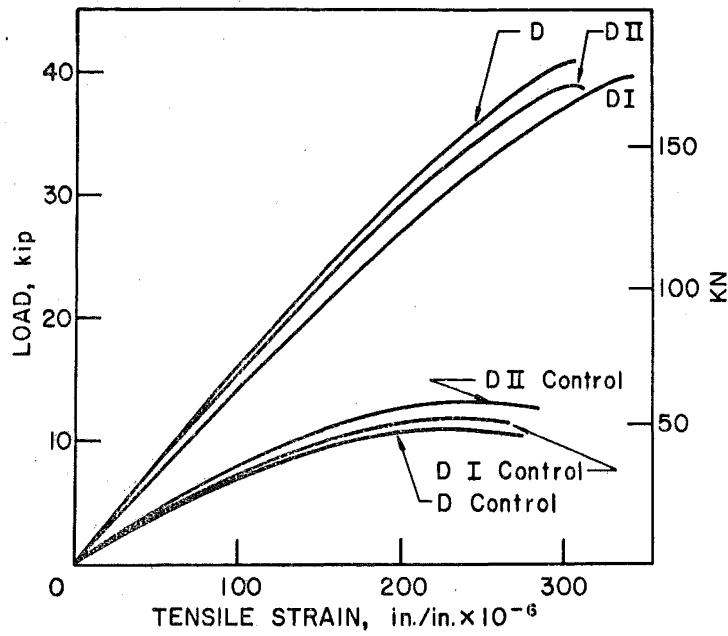
Fig. F-3 Tensile Load-Strain Curves for Salt-Contaminated Concrete
Impregnated with MMA
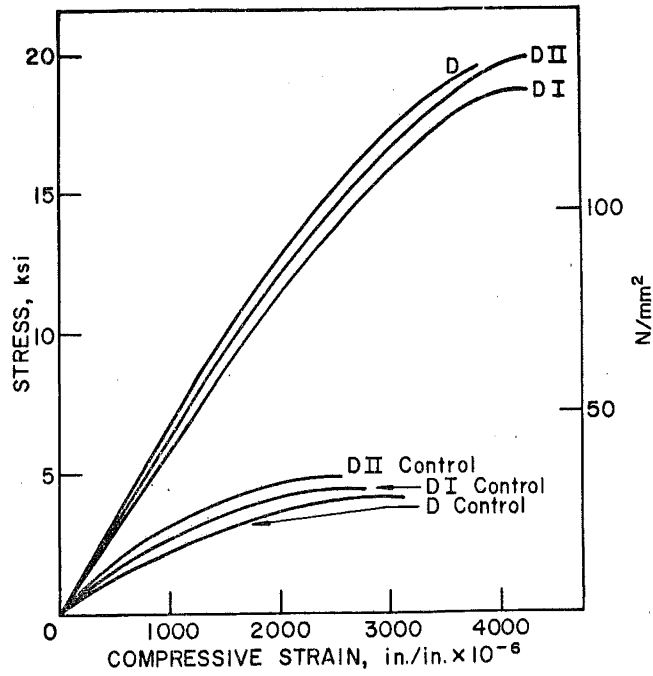
Fig. F-4 Compressive Stress-Strain Curves for Salt-Contaminated Concrete
Impregnated with MMA

APPENDIX G

METHODS FOR POLYMER IMPREGNATION

GENERAL

Prior to moving to preliminary small-scale field tests using the PTI test track bridge, experiments were conducted on large slabs in the laboratory (see also Appendix C). Two combinations of drying, impregnation, and polymerization were used: (1) gas-fired infrared drying, ponding, and hot-water-heated polymerization; and (2) torch-drying, pressure impregnation, and steam-heated polymerization.

For the preliminary field trials, a site in the water table area on span 2 of the PTI test track bridge (discussed earlier) was selected (Figure G-1). At this location, the deck was 7.5 in. (19 cm) thick with #5 reinforcing bars on 6-in. (15 cm) centers and #4 temperature steel on 12-in. (30-cm) centers. Both laboratory and field tests are discussed below.

IR DRYING - SOAK IMPREGNATION - HOT WATER POLYMERIZATION

Laboratory Studies

Large slabs were constructed in the laboratory to investigate infrared drying techniques, temperature distribution during drying and polymerization, soak-impregnation techniques, and polymerization using hot water bath. These slabs were constructed to simulate bridge decks in the laboratory and to evaluate laboratory data acquired on cores and cylinders (Appendices B, C, D, and F) on a larger scale.

A 6-ft x 6-ft x 6-in. (1.83 -m x 1.83 -m x 0.15 - m) slab with one layer of reinforcing steel was constructed to investigate the

temperature distribution during drying in a large slab. Copper-constantan thermocouples were placed in the slab at depths of 1/2 in. (1.3 cm), 1 in. (2.5 cm), 2-1/2 in. (6.4 cm), and 4 in. (10.2 cm) from the top at five different locations in the slab. Figure G-2 shows the general design of the large slabs. Numbers 1-5 in Figure G-2 are the thermocouple positions for the 6-ft x 6-ft x 6-in. (1.83-m x 1.83-m x 0.15-m) slab. Table G-1 gives the mix design for the 6-ft x 6-ft x 6-in. (1.83-m x 1.83-m x 0.15-m) slab.

A second slab 6-ft x 6-ft x 8-in (1.83-m x 1.83-m x 0.20-m) with two layers of reinforcing steel was constructed using the general design similar to the design of bridge decks constructed in Pennsylvania given in Figure G-2. Letters A and B (Figure G-2) indicate the thermocouple positions for this slab. The thermocouples in this slab were embedded at 2-1/2 in. (6.4 cm) and 4 in. (10.2 cm). Table G-1 gives the mix design.

After the slabs were hydrated for 28 days (wet burlap placed over the surfaces), each slab was subjected to a series of drying tests. These tests were performed to understand the drying technique beyond the overdrying used in cylinder studies. There are several methods being investigated for drying bridge decks in the field and infrared drying represents one of the more promising techniques.

Gas-fired infrared heaters were applied to the slabs over a surface area of 1-1/2 ft x 2-1/2 ft (4.57 m x 7.62 m). This simulates point drying on a bridge deck since at present it does not seem feasible to dry the whole bridge deck at once. Gas-fired infrared heaters were chosen for the drying experiments because of their relative efficiency and low

Table G-1. Concrete Mix Design (one cubic yard)[1]

Material	Amount		
			PSU Test
	6' x 6' x 6" Slab	6' x 6' x 8" Slab	Track Bridge
			Deck
Cement (Type 1) - lb	588	588	588
Fine aggregate (silica sand) - lb	1099	1099	1075
Coarse Aggregate (limestone) - lb	1920	1920	1986
Water/cement - gal/sack	5.3	5.3	5.0
Air entraining agent - oz	10	10	10.5
Air content - %	6.5	5.4	6.5
Slump - in.	2.5	2.0	2.5
Compressive strength - psi average 3 cylinders (28 days)	3519	4110	3980

Unit Conversions: 1 in. = 2.54 cm

1 ft = .305 m

1 psi = 6.89 kN/m^2 (Pa)

consumption of propane or natural gas. The infrared heater (Pavement
Reclaiming Corp., Buffalo, N.Y., Model TPRC JH2 Joint Heater) used
burned about 2.9 lb (1.32 kg) propane/hr and it produced 60,000 BTU
(63.3 MJ).

It became evident in the drying studies using infrared heat
(Appendix C) that one can either maintain a constant surface temperature
(as in oven drying) or maintain the heater at a constant distance above the
concrete. If a constant surface temperature is desired, the surface
temperature of the concrete must be continually monitored and the heater
distance above the surface adjusted accordingly. This method may decrease
the drying rate, and it was decided for these tests to maintain a constant
heater distance between the concrete and heater because of faster drying r
rates and less monitoring (1).

Temperature profiles obtained during IR drying of the 6-ft x 6-ft
x 6-in. (1.83 -m x 1.83 -m x 0.15 -cm) and 6-ft x 6-ft x 8-in.
(1.83 -m x 1.83 -m x 0.20 -cm) slabs were presented in Appendix C.
There were many drying tests conducted and the temperature profiles
reported are considered to be typical. During some of the slab drying
tests, severe cracking was observed. The drying curve profiles agree
with a discussion of moisture movement in concrete presented by Harmathy
(2), as mentioned in Appendix C. In the first period (constant rate
period), the average moisture content decreases fairly fast and the
temperature in the concrete rises, after which it remains fairly constant.
Capillary flow is believed to be the principal mechanism of migration
in this period. This period ends when the concrete temperature begins to
increase. The second period is called the falling rate period and

moisture movement is mainly by an evaporation-condensation mechanism.
During this period, the rate of temperature rise throughout the concrete
steadily decreases until equilibrium with the surroundings is reached.
The data presented agree with this discussion.

As previously discussed in Appendix C, in order to predict if the
concrete is dry enough for impregnation at 4 in. (10.2 cm), using the
temperature as an indication, one can insert a thermocouple to a depth
of 4 in. (10.2 cm) and read the temperature, or one can use the surface
temperature as an indication of the temperature at 4 in. (10.2 cm).
It was found that the best indication is to observe the rate of surface
temperature change once per hour, and when the rate of increase per
hour was 10°F (5.5°C) or less, the temperature at 4 in. (10.2 cm) was
approaching equilibrium. In all drying tests, including some on the
bridge decks, this rate ($\leq$ 10°F/hr [$\leq$ 5.5°C]) occurred about 2 hr
after the temperature at 4 in. (10.2 cm) reached about 212°F (100°C).
Hence there appear to be two ways of expressing the same criteria:
(1) when the rate of temperature change at the surface is 10°F (5.5°C)/hr
or less, drying equilibrium is nearly attained at 4 in. (10.2 cm); or
(2) when the temperature at 4 in. (10.2 cm) is above 230°F (110°C),
drying equilibrium is practically attained.

After drying the concrete slabs until the temperature at 4 in.
(10.2 cm) was above 230°F (110°C), a metal impregnation box (2-1/2
ft x 1-1/2 ft x 1 ft [0.76 m x 0.46 m x 0.31 m]) was immediately
secured over the dried area. This box was secured to the concrete surface
using a silastic rubber compound. The concrete was allowed to cool to
ambient conditions ($\sim$ 12 hr) and the monomer (MMA-TMPTMA-AZO, 100:10:0.5
by weight) system was placed in the box. The top of the box was enclosed

with a clear polyethylene sheet completely taped around the sides of the box. This totally contained system helps to keep the evaporation of the monomer system to a minimum. The monomer system was allowed to soak for 4 days based on results from cores and cylinders discussed in Appendix F. There is some indication at present (Appendix B) that the ponding time could be reduced to 1 to 2 days.

At the end of the impregnation time, the excess monomer was removed from the surface. At the same time, water $\geq$ 185°F (85°C) was placed in the impregnation box. This water was at a minimum depth of 7 in. (17. 8 cm). Immersion heaters (1000-2500 watts [3600-9000 kJ/hr]) and a stirrer were placed in the water to maintain the bath temperature at $\geq$ 185°F (85°C). The immersion heater wattage was varied in order to maintain the desired bath temperature. During the polymerization the impregnation box was completely surrounded by insulation. This helped in maintaining a high bath temperature. The immediate application of hot water ($\geq$ 185°F [85°C]) to the concrete also helps to decrease surface depletion by polymerization of the surface. The steady state polymerization temperature at 4 in. (10. 2 cm) was about 130°F (54 °C) and it was maintained for 10 hr. While immersion heaters were used during these tests, it may be impractical to generate enough electricity for them on a bridge deck. Other means of heating water, such as steam, may have to be employed.

The depths of impregnation achieved during slab tests were from 3-1/8 in.(7.9 cm) to 4-1/4 in.(10.8 cm). The results are given in Table G-2 under the bridge deck field trials later in this appendix.

PRELIMINARY FIELD TRIALS: PENNSYLVANIA TRANSPORTATION RESEARCH FACILITY BRIDGE DECK

In order to verify results obtained on the large slabs in the laboratory, field drying, impregnation, and polymerization trials were performed on the Pennsylvania Transportation Research Facility bridge deck. The concrete mix design for this bridge deck and a description of the bridge can be found in Reference 3. The drying data are presented in Appendix C.

Figure G-3 shows the infrared heater with a metal box enclosure during the bridge deck impregnation trial. The metal box enclosure was used to protect the heater from the wind and to act as a reflector. The other box is the impregnation box which was placed around the dried area.

After drying the bridge deck until the temperature at 4 in. (10.2 cm) was above 230°F (110°C), a metal impregnation box (2-1/2 ft x 1-1/2 ft x 1-ft [0.76 m x 0.45 m . x 0.31 m]) was immediately secured over the dried area. This box was secured to the concrete surface using a Silastic rubber compound. The concrete was allowed to cool to ambient conditions (~12 hours), and the MMA system (MMA-TMPTMA-AZO),100:10:0.5 by weight) was placed in the box. The top of the box was enclosed with a clear polyethylene sheet completely taped around the sides of the box (Figure G-4) as in the large-scale laboratory studies.

After an impregnation (soak) time of 4 days, the excess monomer was removed and hot water ($\geq$ 185°F [$\geq$ 85°C]) was placed in the impregnation box. Immersion heaters and a stirrer were placed in the hot water and insulation was placed around the bath. A steady state temperature of 130°F (54.4°C) at 4 in. (10.2 cm) was achieved. Figure G-5 shows some of the investigators adjusting the hot water bath during polymerization on the bridge deck trial.

A summary of the drying, impregnation, polymerization, and results of
some of the slab and bridge deck tests conducted are given in Table G-2.
Cores cut from the impregnated areas show heavy loadings from 3-1/2 in. (8.9 cm)
to 4 in. (10.2 cm) from the top. These heavy loadings (based on monomer
density) are estimated to be between 7.3 - 9.8 percent of the concrete
volume (4). In addition to the heavily loaded area, a depth below that
area of 1 in. (2.5 cm) to 1-1/2 in. (3.8 cm) is also impregnated.
This area became evident during acid-etch studies of part of the slab
and bridge deck cores and may be a result of a monomer evaporation-
condensation mechanism. This is reasonable since the MMA vapor pressure
at room temperature is about double that of water. Figure G-6 shows
part of a core from the bridge deck field trial. One section was placed in
HCl; the HCl was changed until the reaction was complete. The total
penetration was over 4 in. (10.2 cm) deep on the bridge deck; exposed
limestone aggregate has been destroyed, but the polymer-impregnated
areas remain intact.

In summary, criteria for drying concrete slabs and bridge decks to
a 4-in. (10.2 -cm) depth using infrared heaters can be proposed. These
criteria are either to measure the temperature at 4 in. (10.2 cm) and to
stop drying when it reached $\geq$ 230°F (110°C) or to stop drying when the rate
of temperature rise on the surface is less then 10°F (5.5°C)/hr. Impregnation
by ponding to achieve a depth of 4 in. (10.2 cm) required about 4
days. This time may possibly be reduced to 1 to 2 days if a depth of
3 in. (7.6 cm) to 3-1/2 in. (8.9 cm) instead of 4 in. (10.2 cm) is required.
Polymerization using a hot water bath was successfully completed at 4 in.
(10.2 cm) when the temperature at 4 in. (10.2 cm) was maintained at
$\geq$ 130°F (54 °C).

Table G-2. Summary of Soak Impregnation Tests (1)

A. Drying and Impregnating

Test	Ambient Temp (°F)	Temp (°F) at End of Drying[1]			Monomer[2] Soak Time
		Surface	2.5"	4"	
6 ' x 6' x 6" Position 3	70	623	325	251	4 days
6' x 6' x 8" Position A	69	630	317	267	4 days
PSU Test Track Bridge	31	671	280	231	4 days; 10 hr

B. Polymerization and Penetration

Test	Steady State Polymerization Temp (°F)			Time (hr) at Steady State Polymerization Temp		Depth of Penetration[3] (in.)
	Bath	2.5"	4"	2.5"	4"	
6' x 6' x 6" Position 3	185	145	129	21	20	3-1/4 - 4-1/4
6' x 6' x 8" Position A	202	156	141	10	10	3-1/8 - 4
PSU Test Track Bridge	203	140	131	10	10	3-3/8 - 4-1/2

Table G-2.   Summary of Soak Impregnation Tests

(Continued)

Unit Conversions: 1 ft = .305 cm

1 in. = 2.54 cm

$$°F = (\frac{9}{5}) \; °C + 32.$$

1. The distance between the gas-fired infrared heater (60,000 BTU) and the concrete surface was about 11 in.

2. The monomer system used was 100 parts MMA, 10 parts TMPTMA, and 0.5 parts AZO.

3. The first depth is the depth of the heaviest loading (7.3-9.8% by volume [4]). The second number is the total depth including depth of the lesser loaded area (<10% by volume).

FLAME DRYING - PRESSURE IMPREGNATION - STEAM POLYMERIZATION

Laboratory Studies

A test of this combination of processes was conducted using a 6-ft x 6-ft x 8-in. (1.83 -m x 1.83 -m x 0.20 -cm) slab of the type described above (5, 6). As before, the slab was fitted with thermocouples to permit the measurement of temperatures at various depths. Drying was effected using the propane torch assembly described in Appendix C and shown on Figure G-7. A 1/2-in. (1.3 -cm) layer of sand was used to minimize thermal stresses at the surface. Temperature profiles were similar to those obtained with the IR heater (see Appendix C). No serious problem with cracking was encountered.

Impregnation was effected using the pressure impregnation unit used in small-scale test (Figure G-8 and G-9). Polymerization was effected using steam provided by a pressure cooker (10 psi [70 kPa] to 13 psi [90 kPa]) for 10 hr.

As shown in Figures G-10 and G-11, examinations of a core revealed a dense impregnation to a depth of 3 in. (7.6 cm) (excluding the sand cover) with a less dense impregnation for an additional 1 in. (2.5 cm) to 1.5 in. (3.8 cm).

Preliminary Field Trial: Pennsylvania Transportation Research Facility Bridge Deck

The drying, impregnation, and polymerization were carried out in the following sequence: (1) an area of the bridge deck was dried for 10 hr using the propane torch assembly (Figure G-7); (2) the pressure impregnator (Figures G-8 and G-9) was used to impregnate an area 16 in. (0.41 m) in diameter for 8 hr at a pressure of 15 psi to 20 psi (100 Pa 140 kN/m^2); (3) the impregnated concrete was polymerized by feeding steam

from a pressure cooker (10 psi to 13 psi or 70 Pa   - 90 Pa   ) into

the impregnation chamber and also over the surface of the deck for 10 hr.

Thermocouples were installed in the bridge deck to monitor the temperature

during drying. The monomer used was the 90:10 methyl methacrylate-

trimethylolpropane trimethacrylate mixture containing 0.5 percent

azobisisobutyronitrile initiator.

The deck was dried thoroughly in 10 hr using the propane torch

assembly. During this time the temperature at the 4-in. to 5-in.

(10-cm to 13-cm) depth reached 250°F (121°C). No cracking of the

surface was observed, even though the surface temperature was about 700°F

(372°C). Unexpectedly, the ambient temperature dropped to subffeezing

levels during the impregnation (Figure G-12); this hindered proper

sealing of the gasket and resulted in leakage of monomer. Nevertheless,

the impregnation and subsequent polymerization were successful.

Examination of a 4-in. (10-cm) core taken from the polymer-impregnated

area followed by etching in a 18.5 percent hydrochloric acid showed that the

impregnation was complete to a depth of at least 5 in. (13 cm) (Figure

G-13). In some areas, the impregnation was complete throughout the

whole 7.5-in. (19-cm) depth of the deck, as indicated by the appearance

of a dark spreading patch of monomer on the underside, which eventually

covered an area equal to one-half of the area impregnated from the

upper surface. A slight odor of monomer was detected when the core was

removed; however, the polymer loading at the 5-in. (13-cm) depth was

sufficient to give fracture through rather than around the aggregate

particles. Also,the large air voids were completely filled with polymer to

the 4-in. (10-cm) depth. Thus, this first field trial demonstrated

that practical impregnations can be attained within a reasonable

time by pressure impregnation at 15 psi to 20 psi (100 $_{Pa}$ to 140 Pa).

It may also be noted that preliminary tests of skid resistance after 13

months of service indicated no significant effect of impregnation (see

p. E-43).

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   7-8, 1975.
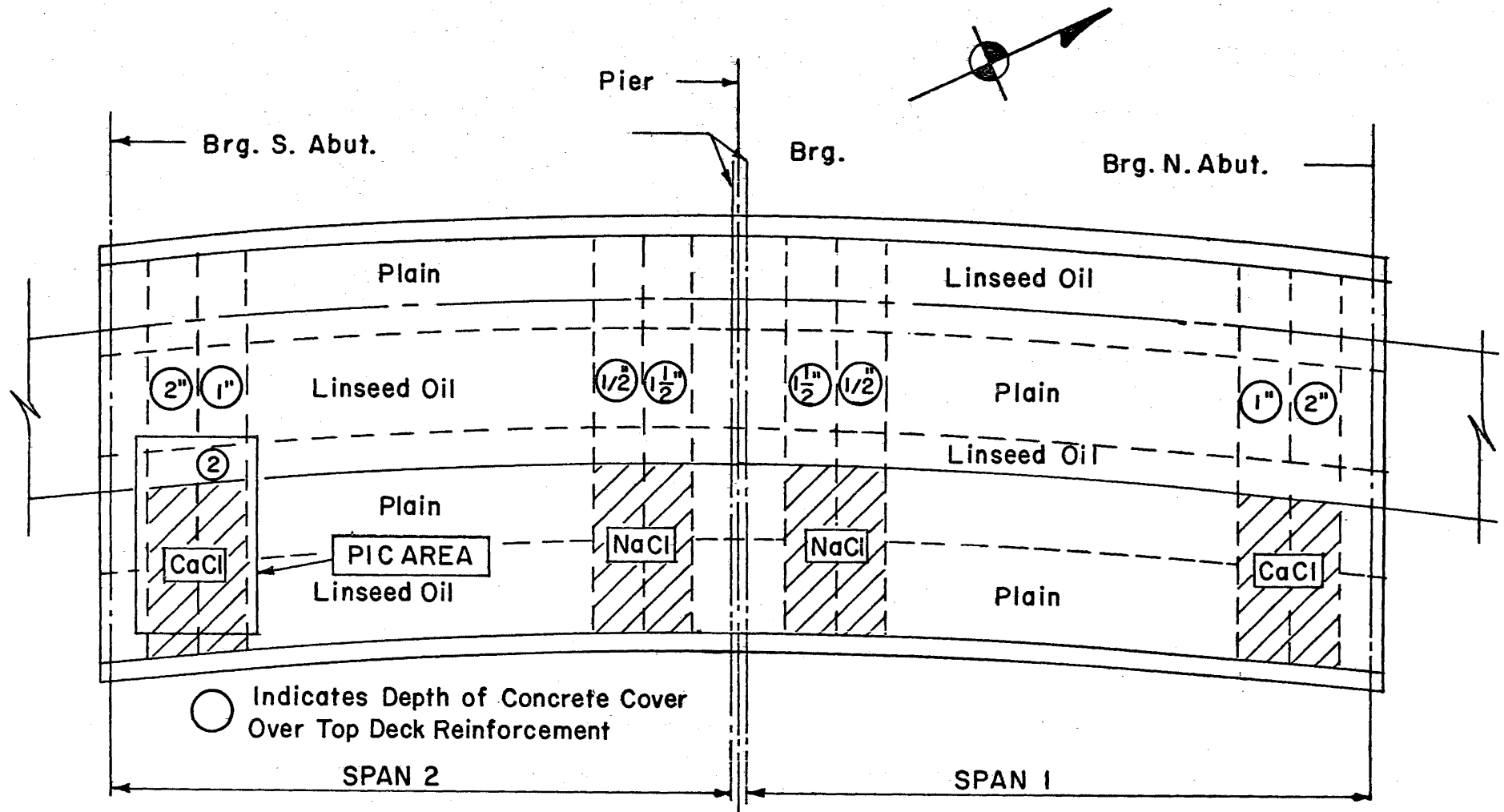
Fig. G-1 Location of Field Trials on PTI Test Tower Deck. Preliminary test: infrared drying-ponding method ; torch-drying-pressure impregnation . Large-scale tests, shaded area.

11 BARS (No. 4) ON 6" CENTERS

9 BARS (No. 5)
ON 8" CENTERS

1
A

2'

4   5   2

6'

3'   B
           3

1.5'

6'
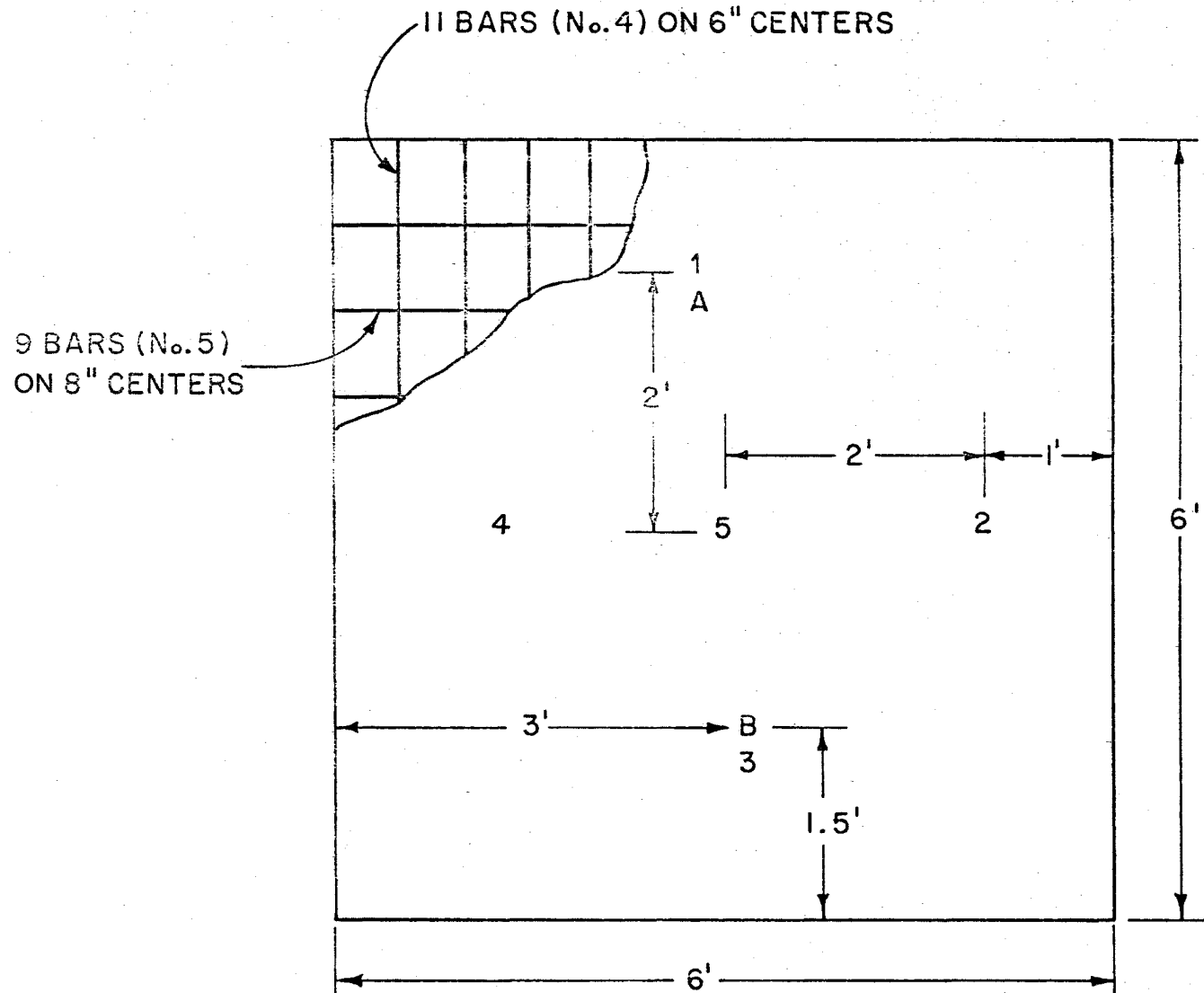
Fig. G-2 LARGE SLAB DESIGN. 1 m = 2.54 cm
Ref. PRB etc. ASCE paper Ref. 1
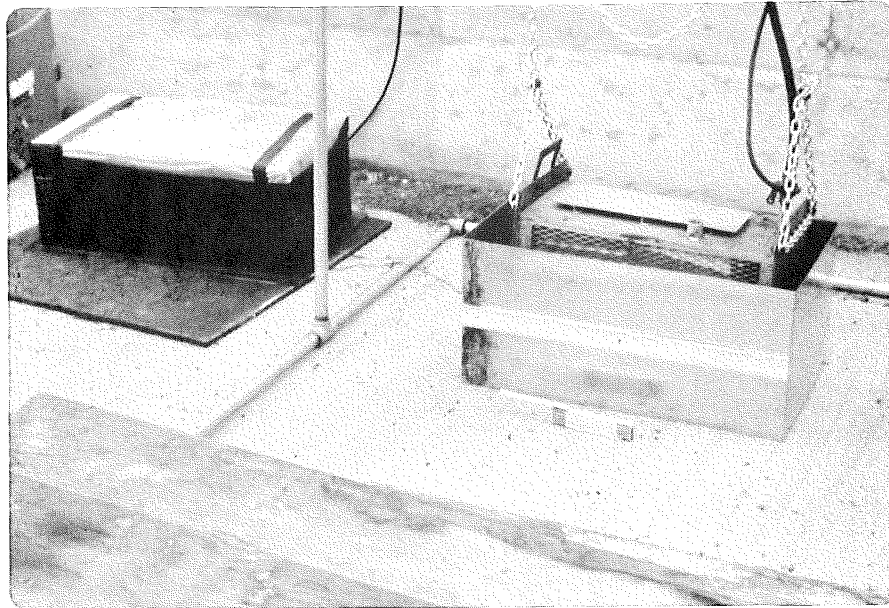
Fig. G-3   Infrared Heater Setup During a Bridge Deck
Impregnation Trial (1)
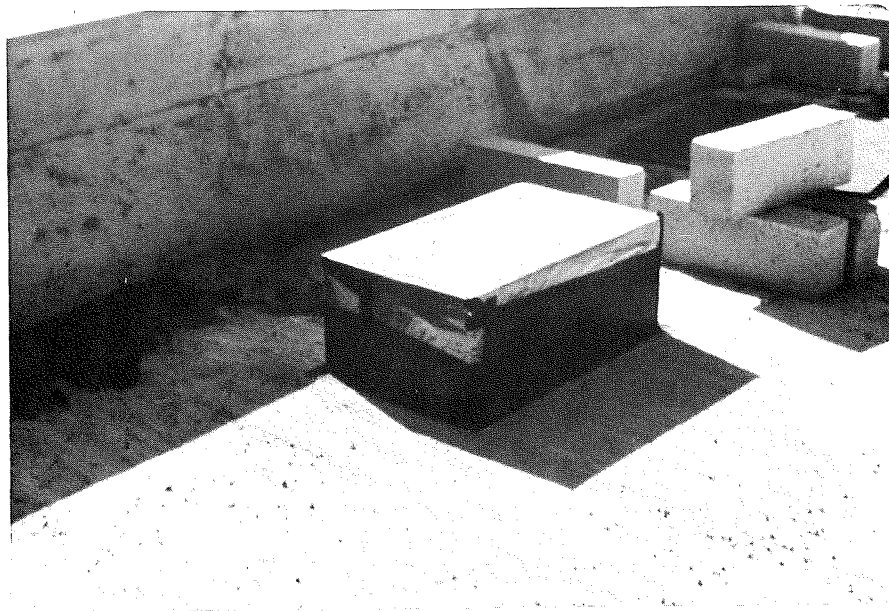
Fig. G-4   Impregnation Box Placement During a Bridge Deck
Impregnation Trial (1)

Fig. G-5   Investigators Checking the Polymerization Bath During a Bridge
Deck Impregnation Trial (1)

Road Surface

Etched With
HCl

1" = 2.54 cm
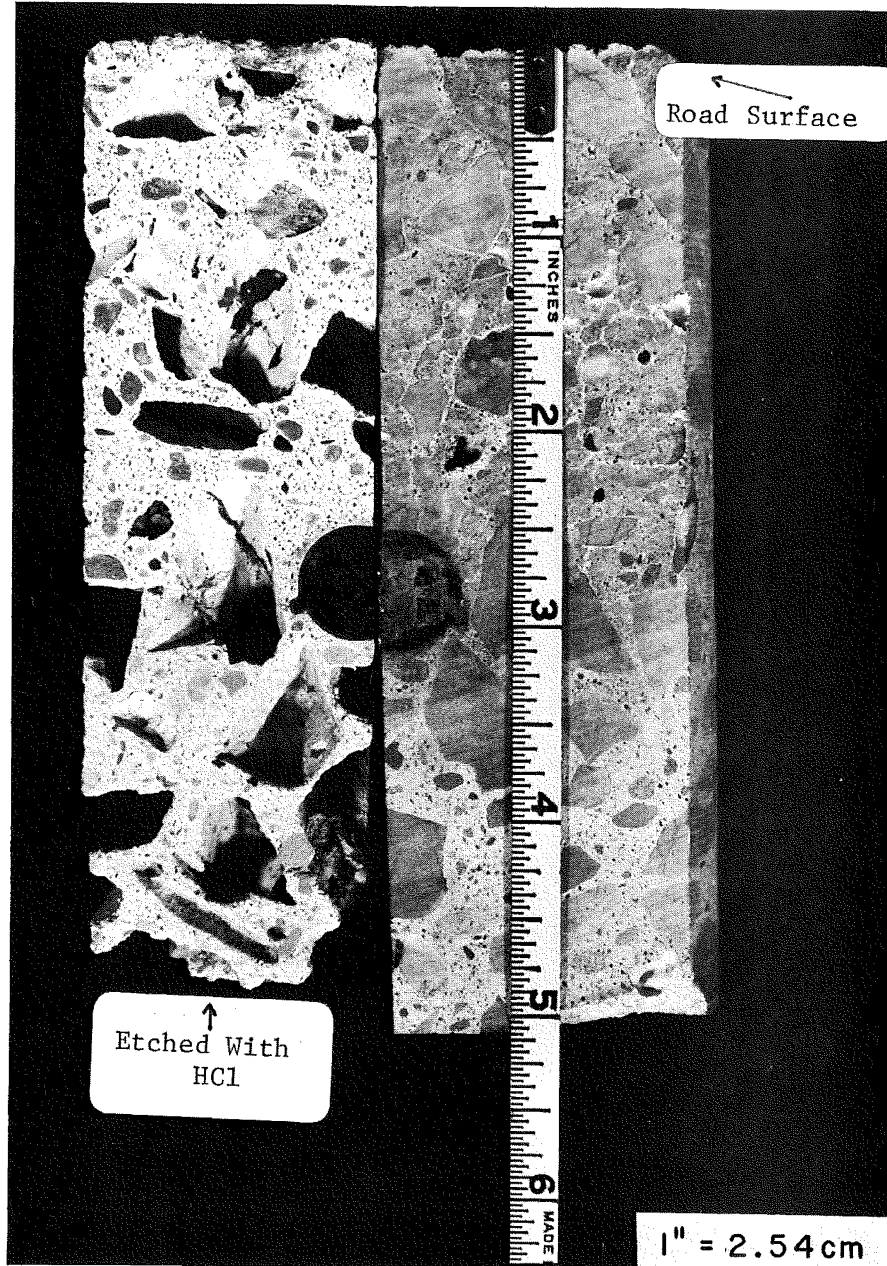
Fig. G-6 A Core from One of the Impregnated Areas of Bridge
Deck Using Soak Technique (1)
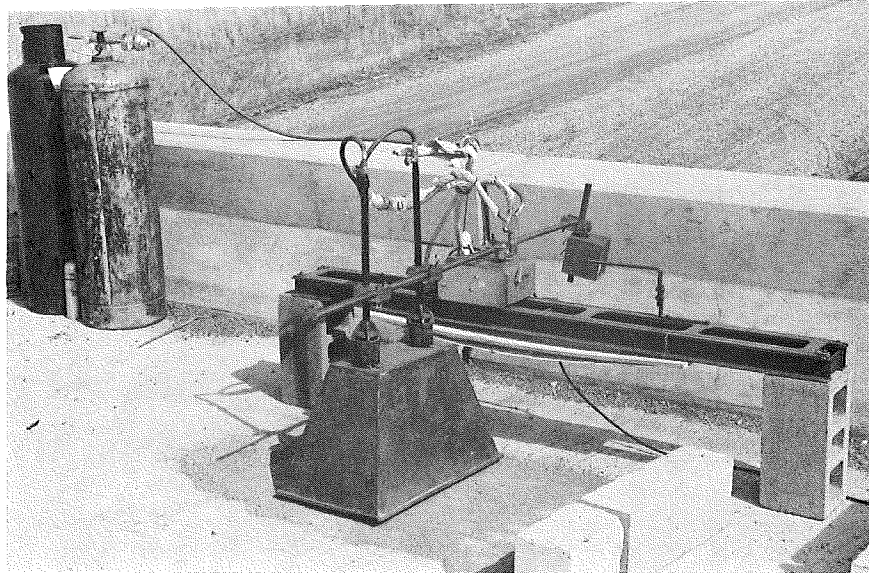
Fig. G-7 Propane Torch Assembly Used in Fast Drying of Concrete
Slaba and Bridge Deck
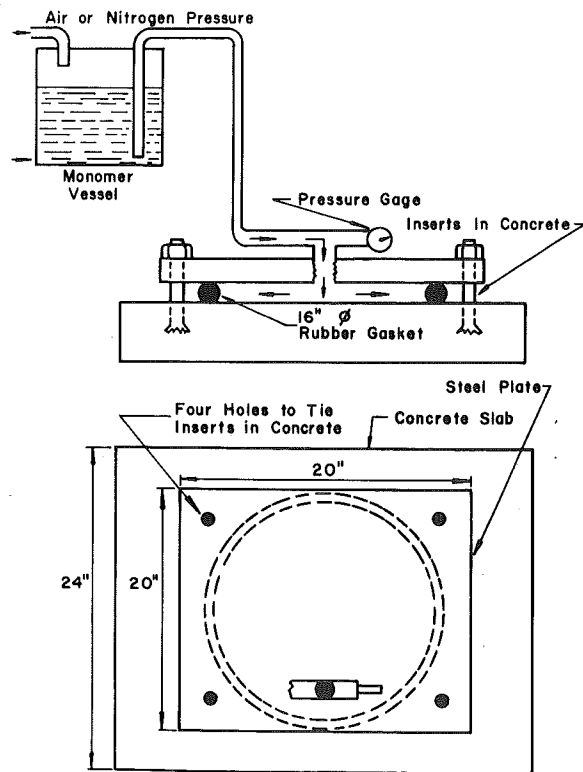
Fig. G-8 Schematic Representation of Pressure Impregnation
Device
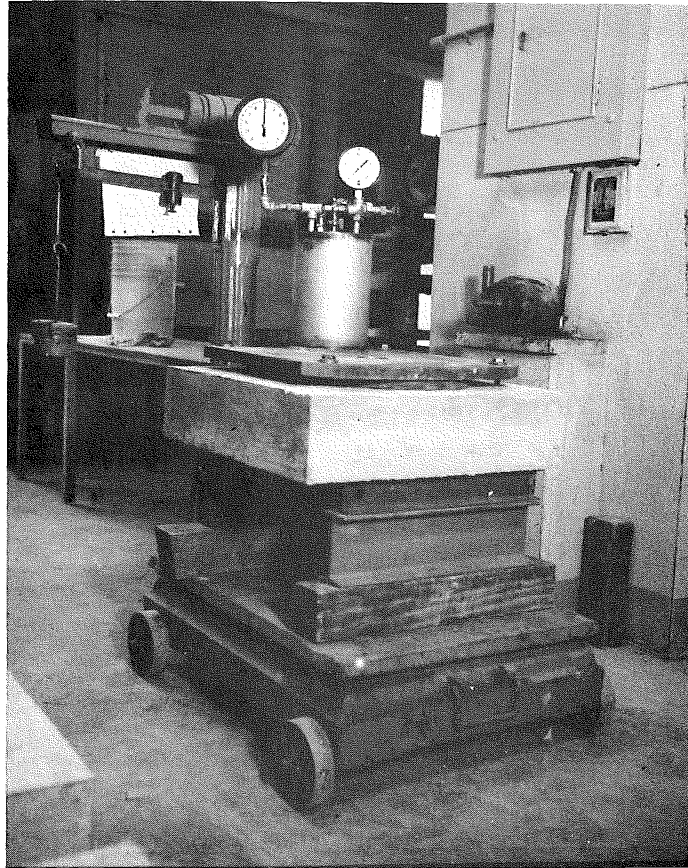
Fig. G-9   Prototype Pressure Impregnation Device
           Bolted to Concrete Slab and Mounted on
           Supports
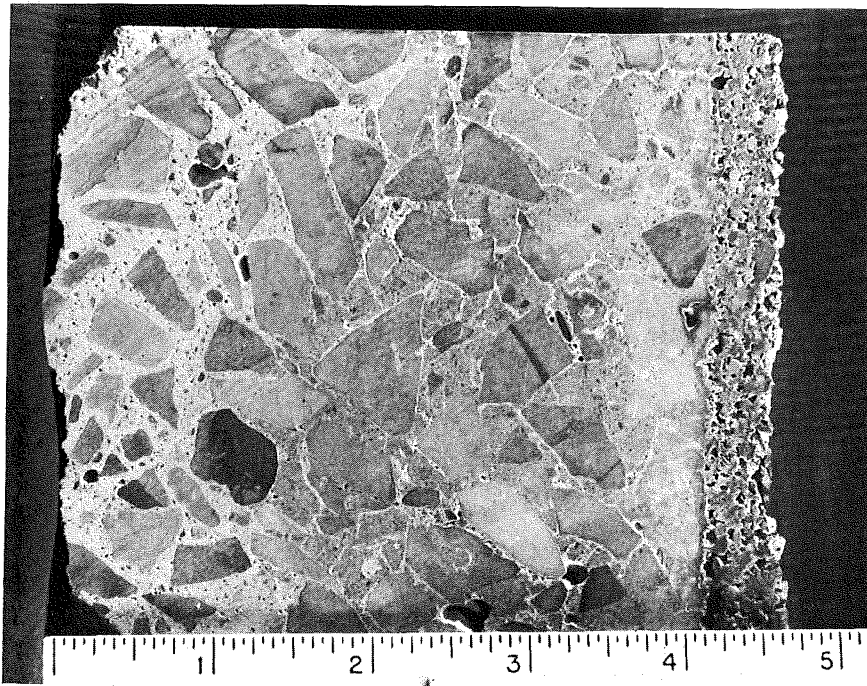
Fig. G-10 Slab Core Pressure-Impregnated with MMA
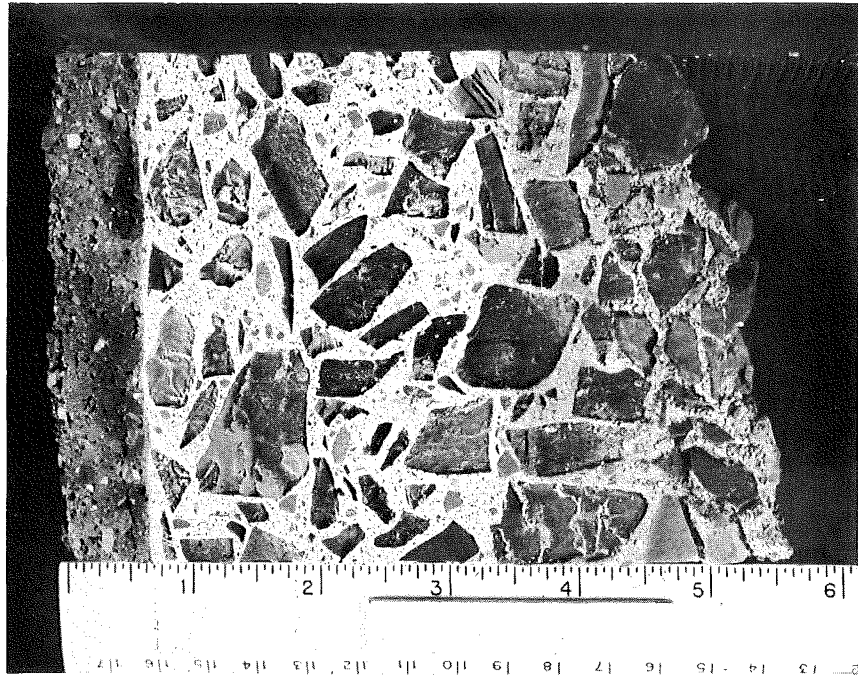
Fig. G-11 Slab Core Pressure-Impregnated with MMA and Etched with Dilute HCl
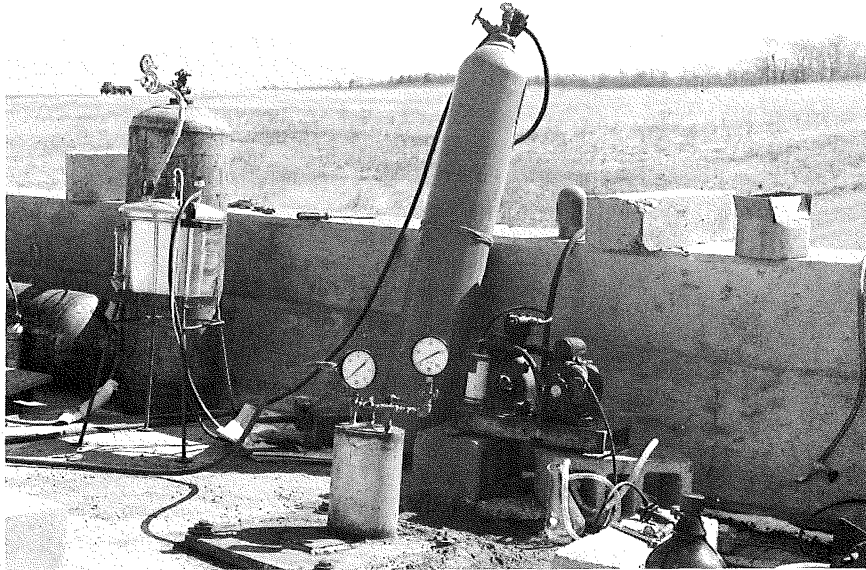
Fig. G-12 Pressure Impregnation Unit in Operation on Bridge Deck
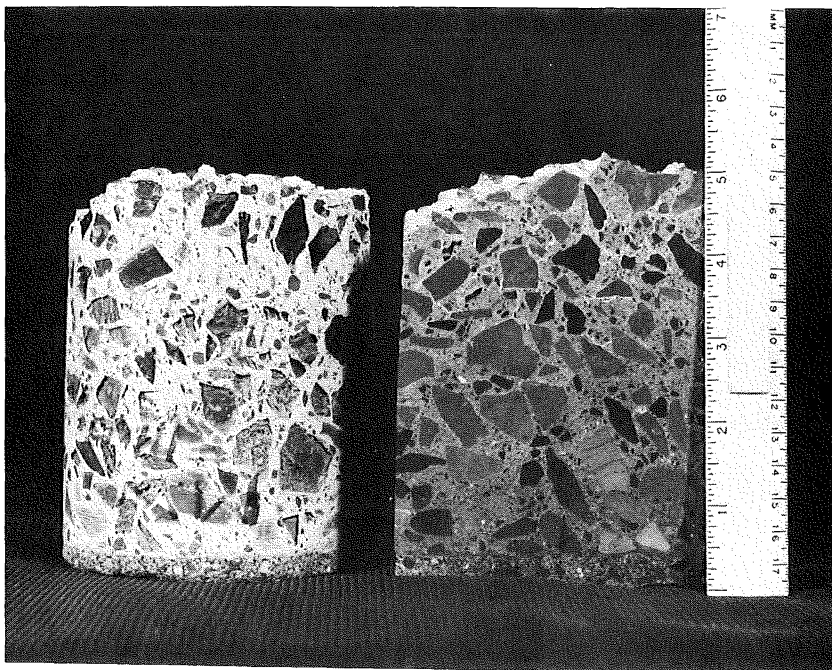
Fig. G-13 4-inch Core from Polymer-Impregnated Bridge Deck
(pressure process): A. Acid-etched; B. Polished
Section (Note: limestone aggregate particles are
eaten away, but cementitious matrix is unaffected).

APPENDIX H

LARGE-SCALE FIELD TRIALS

PENNSYLVANIA TRANSPORTATION RESEARCH FACILITY

Description of Site and Bridge

Field impregnations were conducted using a bridge deck at the transportation research facility constructed by PennDOT near the campus of The Pennsylvania State University. This facility provides,for research purposes,a pavement surface subject to controlled wear from traffic (nonpublic) with full exposure to weather, and consists of a track approximately 1 mi (1.61 km) in length and one lane in width. The configuration of the track is that of a lopsided oval, with one curve larger than the other, and with two straight sections connecting the curves. This arrangement allows test vehicles to traverse all but the small curve at a speed of 50 mph (80 km/hr). The entire track is designed at zero grade. Each of the straight sections, one in cut, the other in fill, is divided into three structural test sections, each test section being approximately 400 ft (122 m) in length. The large-radius curve contains special study sections, the majority of which will deal with environmental factors. Loading is applied through conventional truck axles.

The research facility bridge (Figures H-1 and H-2) consists of a two-span, two-lane structure with span lengths of 60 ft (18.3 m) center-to-center of bearings for each of the simple spans. The width of the bridge comprises two 15-ft (4.57-m) traffic lanes and a 6-ft (1.83-m) shoulder. The bridge is on a 547.67-ft (166.9-m) radius curve and has a uniform superelevation of 10.40 percent from gutter to gutter. One span of the

structure is decked with precast, prestressed concrete planks with a composite cast-in-place concrete topping. The other span has a conventional cast-in-place deck formed on removable wood forms in one half (including the area selected for impregnation in span 2) and on stay-in-place forms in the other half. Concrete mix data are given in Appendix C. Safety curbs and parapets without railings are used on both spans. Stringers for the bridge are precast, prestressed composite I-beams. Further details of the bridge are presented in one of the reports of the Commonwealth of Pennsylvania Research Project No. 71-8 (1).

The following studies have been conducted by others on the bridge:

1. The behavior of two types of bridge decks under controlled loading conditions

2. The effect of different environmental and maintenance variables on the deterioration of the bridge deck surface

3. The behavior of the superstructure components under dynamic and static loading conditions

4. Design, fabrication, and construction as related to behavior under load.

The structure was loaded with one million cycles of variable axle loads equivalent to one million cycles of an 18 kip (80 kN) axle. At various locations in the bridge deck, the top reinforcement was placed at depths varying from 1/2 in. (1 cm) to 2 in. (5 cm) and deicers (NaCl and $CaCl_2$) were applied during the winter months to study the modes of deck deterioration. The bridge was instrumented with strain gages and deflectometers to determine load responses. In addition to repetitive dynamic loadings, the bridge was also subjected to static loadings,

including a load to failure at the end of the bridge test project.

Impregnation Area

The trial itself was conducted on a 12-ft x 6-ft (3.7-m x 1.8-m) area of the facility's bridge deck (Figure H-1), using two adjacent 12-ft x 3-ft (3.7-m x 0.9-m) sections. At this site (water table area on span 2) the deck was 7-1/2 in. (19 cm) thick with reinforcing bars (#5) on 6-in. (15.-cm) centers and temperature steel (#4) on 12-in. (30-cm) centers.

Chloride Distribution

The total application of $CaCl_2$ deicing agent to the impregnation area during the 2-year bridge deck testing period amounted to about 0.4 lb/sq. ft (2 kg/m^2). Chloride determinations were made on a test core using the Berman (FHWA) method (2).

As shown in Table H-1, chloride ion concentrations by weight in the paste phase ranged from about 0.05 percent near the surface to about 0.002 percent at a depth of from 1 in. (2.5 cm) to 2 in. (5.1 cm). These values correspond to about 0.67 lb/yd^3 (0.40 kg/m^3) and 0.03 lb/ yd^3 (0.02 kg/m^3), respectively. These values are less than the concentrations believed to represent potential problems with respect to the onset of corrosion in the steel (2).

Drying

The impregnation area was dried with gas-fired infrared heaters. In order to dry a 12-ft x 6-ft (3.7-m x 1.8-m) area with the heater capacity presently available three different heater positions were required. The infrared heater was shut down in each position when the temperature at 4 in. (10 cm) was $\geq$ 230°F (110°C). Curves for one of

Table H-1. Chloride Distribution in Impregnation Area of Bridge Deck
at Pennsylvania Transportation Research Facility

Depth from Surface	Percent Chloride (by Weight) in Mortar
0 – ½"	0.047
½" – 1"	0.008
1" – 2"	0.002

Unit Conversion: 1 in. = 2.54 cm.

the three drying areas are shown in Figure H-3; these curves are typical of those obtained for the other two adjacent positions.

Impregnation Unit

A special impregnator (4 ft x 12 ft [1.22 m x 3.66 m] in area) was designed and constructed of 3/8 in. (0.95cm) aluminum sheet to permit the impregnation of a 3-ft x 12-ft (0.9 -m x 3. 7-m) section, using either a soak technique or an applied pressure of 20 psi (140 kPa) (Figure H-4). The area was selected to be of a scale reasonably compatible with potential practice. For use under pressure, the unit was provided with 24, 1-inch (2.5 -cm) holes to accommodate 3/4-in. (1.9 -cm) self-drilling tie-down inserts in holes drilled in the deck (Figure H-5); for use at various slopes, the long walls were trapezium-shaped (Figure H-6).

Impregnation of First Area

Thermocouple Insertion. To monitor temperatures during polymerization, thermocouples were inserted at depths of 2.5 in. (6. 4 cm) and 4.0 in. (10. 2 cm) at three different locations. The placement is shown in Figure H-7.

Attachment of Impregnation Unit. After location of the rebars using a pachometer, the insert holes were drilled (Figures H-5 and H-8). In spite of considerable care, one rebar was struck; drilling through it widened the hole sufficiently to cause some difficulty later with the impregnation. Epoxy resin was used to bond the insert concerned. The vessel was then placed over a dual set of silicone rubber gaskets and bolted to the deck (Figures H-6 and H-9)--a procedure necessary only when pressurized impregnation is desired.

Impregnation. Following placement of the impregnation unit, a total

of 120 lb (54 kg) of monomer (90 parts MMA + 10 parts TMPTA + 0.5 parts

AZO catalyst) was fed into the chamber and the pressure raised to 15 psi

(100 kPa) over a period of 10 min. No leaks were observed through the

gaskets, though some leakage was observed on the underside of the deck

(Figure H-10). The latter leakage was ascribed to small cracks formed

at the unconstrained edge of the deck section; no such cracks were ob-

served in the next section, which was away from the edge. Since the

insert in the epoxy-filled hole then worked loose, thus causing exces-

sive leakage at 15 psi (100 kPa), the pressure was reduced to 5 psi

(35 kPa) and the impregnation continued for about 7.5 hr, during which

period the monomer supply was replenished twice. The residual monomer

was then pumped out.

Polymerization. After covering of the adjacent, dried 3-ft x

12-ft (0.9 -m x 3.7 -m) area, 300 gal (1 m^3) of hot water (195°F

[91 °C]) was introduced into the chamber; the water, which had been pre-

viously heated in oil drums using propane torches, was circulated

through a heated 55-gal (0.2-m^3) drum (Figures H-11 and H-12). Unfor-

tunately, the water apparently picked up some residual monomer for when

some water spilled, vapors were ignited, requiring the use of the fire

extinguisher that had been brought along in case of such events. (This

illustrates the hazards implicit in the use of MMA as a monomer and the

need for extreme caution in handling). To avoid possible further prob-

lems, circulation was stopped, 165 more gal (0.6 m^3) hot water added,

and heating provided by a combination of three 2500-watt (2500 Joules/sec)

immersion heaters and steam produced in a pressure cooker. (Thus in one trial,

experience was gained with several heating systems.) To minimize heat losses, the chamber was covered with a fiberglass insulating layer and a tarpaulin (Figure H-13); it was possible to maintain a mean water temperature of 169 ± 9°F (76 ± 5°C) throughout the 12-hr polymerization period. Using the thermocouple pattern shown in Figure H-7, it was found that internal temperatures at the edge of the treated area ranged from 120°F (49°C) to 135°F (57°C), depending on the depth and location (see Figure H-14).

In order to verify whether or not polymerization had been attained at the desired depth, a core was taken the next day from the area which had shown the lower polymerization temperature. As is discussed below, satisfactory impregnation was in fact achieved.

It may be concluded that ponded water, heated electically or with steam, should be adequate for polymerization.

Impregnation of Second Area

Preparation. After removal of the water used with the first area, the impregnator was unbolted, 16 more inserts fitted, and the impregnator bolted down again. In spite of care taken to avoid doing so, two rebars had been struck during drilling, and the holes filled with epoxy resin before bolting. It was also noted that the gaskets (made of Dow-Corning Silastic E rubber) showed some signs of deterioration in the form of hardening and edge cracking. Since the asperities in the surface of the deck were 1/4 in. (0.6 cm) deep, the gaskets were placed very carefully and the bolts tightened using a torque wrench (to 150 ft-lb [200 J] torque) in order to balance the stresses.

Impregnation. Although a pressure test indicated that leakage was

occurring through the inner gaskets, it was necessary to either proceed or cancel the trial, since the site had to be cleared by the following morning for other experimental work on the deck. It was decided to proceed. After feeding in 120 lb (54 kg) of monomer, 15 psi (100 kPa) pressure was applied gradually, in the hope that the second gasket would hold. In fact, the leakage stopped, apparently because the monomer reswelled the stiffened inner gasket. However, slight leakage was noted from a small crack on the underside of the deck. After 3 hr the valve became clogged with polymer and remained so for 4 hr, at which time another valve was used and pressurization continued for an additional 5 hr. In the latter case, the pressure was reduced to 5 psi (35 kPa) due to loosening of the two epoxy-mounted bolts. Thus the schedule for the 12-hr period was: 3 hr at 15 psi (100 kPa), 4 hr at ambient pressure, and 5 hr at 5 psi (35 kPa).

Polymerization. In this case the same general procedure was used as in the first area, except that hotter water (210°F [99 °C]) was introduced into the chambers, and the water temperature maintained at 180°F (82°C) (for 12 hr). On completion, it was found that the bottom of the heated area was 15°F (8°C) hotter than the surrounding area.

Due to resumption of the PennDOT testing program on the deck after completion of the trial, it was not possible at that time to take a core in the section.

Observations and Discussion

As shown in Figure H-15, on removing the chamber from the surface after polymerization, a froth of polymer was found on the surface, but was easily washed away. On close examination the surface was

found to be speckled with conical beads of hard polymer, showing that effective polymerization had taken place at least on top (Figure H-16). A 4-in. (10-cm) diameter core taken from the first area (Figure H-17) showed that full impregnation was obtained up to a depth of 3-1/2 in. (8.9 cm) with an additional 1 in. (2 cm) or more of partial impregnation, thus demonstrating that the stated objective of up to 4-in. (10 -cm) impregnation was essentially achieved. The results in the second area may be expected to be even better since pressurization was done at higher pressure for a longer time. Interestingly, tests of skid resistance after 13 months of service indicated no significant effect of impregnation (see p. E-43).

It may also be noted that both the drying and impregnation experience shows that it is just as easy to treat a larger area as a smaller one; indeed heat losses, cracking, and total impregnation time are thus minimized.

Even though this was the first large-scale trial (with several minor problems), the treatment of two adjacent 3-ft x 12-ft (0.9 -m x 3.7 -m) sections (previously dried) was successfully accomplished during one weekend, starting at 4 p.m. on August 23 and ending at 7 a.m. on August 25. Clearly, in practice, these times should be reduced significantly.

PennDOT BRIDGE

Selection of Deck for Field Trial

With the cooperation of PennDOT (Messrs. L. Sandvig, W. Gramling, R. M. Tirpak, and A. V. Cesare), several bridge decks were considered for our final field trial to demonstrate the impregnation of a section of a salt-laden but structurally sound deck in actual service. The best candidate was the bridge over Union Blvd. on Pa. Route 378 (formerly I-378), the spur route linking Bethlehem to U.S. Route 22 and I-78. The

concrete in the deck contained slag aggregate rather than limestone.

The nominal mix (type AA) was water-cement-sand-crushed slag 10.46:1:
1.89:3.37, with a cement factor of 1.562 and a 2-1/4" slump. Salt analyses
were received from Mr. R. M. Tirpak (District Office 5-0, PennDOT) for
cores shown in Figure H-18. Chloride contents (Table H-3) ranged from
0.8 lb/yd^3 (0.47 kg/m^3) to 4.6 lb/yd^3 (2.7 kg/m^3) for core No. 10. It
was decided to impregnate area including core No. 10, as soon as arrange-
ments for traffic control and logistics could be made, and as weather would
permit in the early spring of 1975. Since the bridge receives heavy traf-
fic, careful planning was especially necessary.

General Preparations

Because of considerable wear in the wheeltrack (about 5/8 in.
[1.6 cm] in the area selected), and the fact that salt content was high
in the track area, the impregnation was conducted longitudinally along
the outer wheeltrack of the northbound traveling lane. This also per-
mitted safer operation as it minimized working in the open lane.

Traffic control and coring were provided through the courtesy of
PennDOT. Mr. R. Brunner served as an observer for PennDOT, and Mr. J.
Hoegg supervised the activities of other PennDOT personnel from District
5-0. Additional sampling for salt content was also made by Mr. Hoegg
in two locations within the impregnation area; concentrations of 3.4 and
2.8 lb/yd^3 (2.0 and 1.7 kg/m^3) were reported.

The trial was conducted over the weekend from Friday, March 21, 1975,
to Sunday, March 23, 1975, with clean-up on Monday, March 24, and coring
on Tuesday, March 25. During the trial the weather was spotty, with brisk winds
temperatures ranging between 35°F (18°C) and 55°F (30°C) and with showers on
March 22 and 24.

Table H-2   Chloride Content in Union Blvd. Bridge (L.R. 1007, Station 26 + 18) on Bethlehem Spur Route[1]

Core No.	% Chloride (wt. % of Concrete)	Salt Content lb/yd^3
10	0.121	4.60
11	0.021	0.80
12	0.071	2.70
13	0.053	2.01
14	0.127	4.83
15	0.041	1.56
16	0.047	1.79
17	0.083	3.15

Unit Conversion: 1 lb/yd^3 = 0.593 kg/m^3.

1. Courtesy of Bureau of Materials, Testing & Research, PennDOT.

Drying

Drying of the 3-ft x 12-ft (0.9 -m x 3.7 -m) test area was done in
two successive segments covering 4-ft x 6-ft (1.2 -m x 1.8 -m) areas each
on March 21, 1975. A 4-ft x 5-ft (1.21-m x 1.52-m) trailer mounted
propane-fired infrared unit and a 1-ft x 4-ft (0.31-m x 1.21-m) portable
unit were used at each setup. This is the same equipment that was used
on the Transportation Research Facility bridge trial. Drying of the first sec-
tion was started at 0955 a.m. and completed at 1600 p.m. The second section was
started at 1620 p.m. and finished at 2300 p.m. Table H-4 provides the
drying schedule, and the time-temperature data are plotted in Figure
H-19. A photograph of the drying operation in progress is shown in
Figure H-20.

Drying control was achieved by monitoring surface temperatures and
temperatures at 4 in. (10 cm) deep in the centers of each of the
areas. Surface temperatures were constantly recorded on a strip-chart
recorder using a chromel-alumel thermocouple. Temperatures at the 4-in.
(10-cm) depth were measured periodically using a portable pyrometer
and a chromel-constantan thermocouple inserted into 1/4-in. (0.6-cm)
diameter, 4-in. (10 cm) deep thermowells drilled into the concrete
from the top surface. The temperatures measured at 4 in. (10 cm) are
subject to an unknown error due to the high ambient temperatures in the
vicinity of the pyrometer indicator. In previous work, the temperatures
within the concrete were measured from the underside to avoid the com-
plications of having the thermowell and the instrument in the hot zone.
This was not possible in this case because of the inaccessibility of the
bottom of the deck. Therefore, the surface temperatures and past

Table H-3.   Drying Data--Bridge Deck Impregnation

Test at Bethlehem--March 21, 1975

Time	4-ft x 6-ft Section	Amb. Temp.,°F	Surface Temp.,°F	Temp. @ 4-in. Depth,°F	Remarks
9:55	1st				Start: Heater @ 11"
10:15	1st	46			
11:20	1st		513	105	
12:00	1st				Raised Heater to 16"
12:15	1st		536	150	
12:50	1st	52	540	185	
13:10	1st		572	183	
13:30	1st		572	195	
14:00	1st			210	
14:30	1st	57		205	
15:07	1st		608	200	
15:15	1st				Lowered Heater to 13½"
15:17	1st			200	

Table H-3. Drying Data--Bridge Deck Impregnation Test

at Bethlehem--March 21, 1975 (Continued)

Time	4-ft x 6-ft Section	Amb. Temp.,°F	Surface Temp.,°F	Temp. @ 4-in. Depth,°F	Remarks
15:34	1st		658		Raised Heater to 15½"
15:42	1st		649	200	
16:00	1st	62	662	210	Shut Down Heaters
17:20	1st			210	
18:10	1st			200	
18:35	1st			195	
19:30	1st			182	
20:25	1st			172	
23:23	1st			131	
16:20	2nd	56			Start: Heater @ 16"
17:20	2nd		446	93	
18:10	2nd	43	536	135	

Table H-3. Drying Data--Bridge Deck Impregnation Test

at Bethlehem--March 21, 1975 (Continued)

Time	4-ft x 6-ft Section	Amb. Temp.,°F	Surface Temp.,°F	Temp. @ 4-in. Depth,°F	Remarks
18:35	2nd			175	
19:30	2nd	43	536	175	Lowered Heater to 15½"
20:22	2nd		608	190	
21:00	2nd				Changed Gas Cylinders
21:35	2nd	50	622	195	
22:19	2nd		666	198	Lowered Heater to 14¼"
23:00	2nd		686	200	Shut Down Heaters

Unit Conversions: 1 in. = 2.54 cm

$$°F = \frac{9}{5}°C + 32$$

1 ft = 0.305 m.

securely caulked with a butyl rubber sealant.

Impregnation

To prevent runoff of any leaked monomer, a dike was constructed from lumber around the impregnation area and caulked to the concrete using caulking compound or Hydrostone, depending on the size of the joint needed (Figure H-24). The dike also served as a support for a polyethylene cover which was used for protection of the exposed surface during periods of intermittent rain (Figure H-25).

As mentioned above, when holes were drilled (Figure H-26) to fasten the impregnation chamber to the deck, small surface cracks appeared to open up; however, they appeared to be mostly superficial crazes (Figure H-21), which did not extend much below the surface. To provide a flat surface for the two 3/4-in. (1.9-cm) Silastic-E gaskets, a mixture of 50/50 Hydrostone/portland cement was brushed onto the flat areas of the roadway, and troweled and screened in the worn wheeltrack.

After mounting of the chamber over the dual gaskets (Figures H-27 and H-28), the gaskets were noted to be compressed to a thickness of 3/8 in. (0.9 cm). The chamber was first evacuated (to 27 in. of mercury [91 kPa]) for 1/2 hr, and then pressurized at 5 psi (35 kPa) at 1630 hr on March 21. Since at this pressure considerable leakage was observed on the underside (Figure H-29), the pressure was cut back to 2 psi (14 kPa) for 7-1/4 hr. At the end of this time is was possible to increase the pressure to 3 psi (21 kPa) for 1 hr and 8 psi (55 kPa) for 1/2 hr, at which time the impregnation was terminated (at 0230 hr, March 22). It was estimated that based on previous experience, a 4-in. (10-cm) penetration should have been achieved.

experience were used to judge when drying was complete to a 4-in.
(10-cm) depth. The heating rate used here was somewhat lower than
that used in previous work because of the unknown characteristics of the
slag-aggregate concrete used in this bridge deck.

No cracking of the slabs occurred during the heating process. How-
ever, after cooling, surface crazing developed where holes were drilled
for chloride samples, thermowells, and hold-down bolts for the impreg-
nator (see Fig. H-21). Subsequent coring revealed these cracks to be usually
less than ¼ in. (0.6 cm) deep, though one crack 1 in (2.5 cm) deep was noted.

As was the case in previous work, water was observed to exude from
the cold faces of the deck during the heating process. The test area
was located near an expansion joint and an appreciable amount of water
appeared at the top surface at this location (see Figure H-22). This
would indicate considerable horizontal movement of the water and might
suggest the presence of a fracture plane associated, perhaps, with cor-
rosion of the top reinforcing bars. As mentioned below, however, sub-
sequent coring failed to verify the existence of such a fracture plane.
Water also exuded from the underside of the deck (see Figure H-23),
though it was not possible to ascertain quantities or exact locations
of moisture exit from the concrete because of the presence of permanent
steel bridge forms.

It was estimated that the total amount of propane fuel used to dry
the 4-ft x 12-ft (1.2 -m x 3.7 -m) area (3 ft x 12 ft [0.9 m x 3.7 m]
used for impregnation) was about 220 lb (100 kg).

For protection against a light rain during the night of March 21,
the dried area was covered with overlapping galvanized sheets and

During the impregnation, the inner gasket leaked, but not the outer one; the monomer concerned was recycled. The odor of monomer was only detectable when transfer was taking place, and then only slightly.

Polymerization

Polymerization was begun at 0315 hr, March 22, using 120 gal (0.45 m^3) of water preheated to 205°F (96.1°C). The temperature dropped to 140-150°F (60°C-65.6°C) in the chamber due to heat transfer to the chamber and concrete. Steam was therefore fed in at atmospheric pressure to three locations in the chamber for agitation, circulation, and heating. Electrical heaters (5 in number, total wattage of 2800 J/sec were immersed in the water at 0600 hr, and 80 gal (0.30m^3) of additional water fed in. The temperature of water gradually increased from 140-150°F (60°C-6.6 °C) to 160-165°F (71°C-74°C) by 0800 hr, and to 170°F (7.7 °C) by 1000 hr. Heating was continued until 2000 hr (total time, 17-1/2 hr) at which time the temperature was in the range of 175-180°F (79°C-82°C). During the whole process, the chamber was well insulated (Figures H-30 and H-31). The hot water was left overnight in the chamber and discarded at 0700 hr, March 23, at which time the temperature of water had dropped to 110-120°F (43°C-50°C).

No odor of monomer was observed at any time during the polymerization. As noted in previous field work, the deck surface was covered with a light loose froth and small nodules of polymer, and, while wet, appeared similar to the untreated area with respect to traction.

Cores

Seven cores were taken, two outside the impregnation area (2 ft [0.6 m] away) and five within; two were drilled through the deck (8 in.

[20.3 cm]), and five to a depth of 5 in. (12.7 cm) (Figure H-32). One core which contained a surface crack (but no rebar) was subjected to the split-tensile test and found to have a strength of 610 psi (4.2 MPa). All cores were etched with 15 percent HCl to reveal the impregnation pattern (Figures H-33 and H-34).

Examination of the cores revealed the following:

1. No evidence for significant corrosion of the rebars in the control and other specimens (Figure H-35).

2. No evidence for delamination along any fracture planes generated by thermal stresses during drying or by corrosion at the rebars (Figure H-35)

3. No evidence for significant effects due to the surface crazing. For example, in the tensile test, a craze was lined up at right angles to the platens; fracture, however, tended to occur a few millimeters away from the craze.

4. Dense impregnation to at least 3 in. (7.6 cm), and less dense impregnation to 4 in. (10 cm) or more in some regions, but in most cases to below the top layer of reinforcing steel.

Conclusions

The trial was clearly successful in demonstrating the deep impregnation of a section of a deck in service under adverse weather conditions, without adversely affecting the deck by the stringent drying used. Further work is needed to define the maximum area that could be so treated at one time. Also, the impregnation procedure must be matched to the deck; this deck behaved quite differently from the test track bridge deck. Leaks, possibly around a rebar somewhere, limited the pressure which

could be applied.

SCALE-UP PROCEDURES AND COSTS

General

The feasibility of deep (up to 4 in. [10. cm]) impregnation of bridge deck concrete with methyl methacrylate in the field was demonstrated in this project. Equipment and procedures commensurate with the objective of demonstrating field practicability, including equipment scale-up, were developed. However, this project did not, nor was it intended to, possess the resources to build equipment of the magnitude required for economical impregnation of bridge decks on a commercial scale.

Scale-up

The equipment and procedures used were developed with an eye toward adaptability to commercial scale through scale-up procedures. Basically, this will require only direct dimensional scale-up to units capable of handling much larger areas per setup. A number of small units, of the size used on this project, could be employed at one time on a bridge deck, but the efficiency would be low and labor costs would be prohibitive. For example, the time requirements using the equipment developed in this research will be about 2 hr/sq.ft (21 hr/m^2) of deck surface for 4 in. (10. cm) of impregnation at 0 to 5 psig (0 to 35 kPa). Thus, a single unit of this scale would require 70 weeks, not including downtime for equipment repair and inclement weather, to impregnate two 12-ft (3.66-m) traffic lanes on a 200-ft (60.9-m) long bridge. The time will be reduced in proportion to the number of units used simultaneously. However, each unit will require, on the average, one to two full-time

workmen. Large units, say 12 ft x 40 ft (3.66 m x 12.20m), on the other hand, would require only about 0.16 hr/sq.ft (1.8 hr/m²) (see below for details), and could impregnate a bridge of the size mentioned above in about 5 to 6 weeks. Note that, in both instances, it is assumed that the operation proceeds around the clock, 6 days a week; the feasibility of such round-the-clock operation, even in inclement weather, was demonstrated. There do not appear to be any technical impediments to scaling the equipment up to the 12-ft x 40-ft (3.7-m x 12.20m) size, mentioned above. The cost estimates, presented below, are based on an assumed scale-up to 12 ft x 40 ft (3.66 m x 12.20m).

Cost Estimates

General. The cost estimates presented herein do not include amortization of capital equipment nor costs for equipment maintenance, weather delays, and traffic control. Basically, they consist of direct materials and labor costs only. The costs are computed for four specified impregnation depths (1, 2, 3, and 4 in. [2.5, 5.1, 7.6, and 10.2 cm]) and two impregnation pressures (0 and 15 psig [0 and 100 kPa]).

Drying. The costs for drying are based on an assumed average ambient temperature of 70°F (21 °C). Obviously, drying costs will vary inversely with ambient temperature. Other assumptions include a rated capacity of the heater of 9000 BTU/sq ft/hr (100 MJ/m²/hr), use of propane gas (heating value 20,000 BTU/lb [47 MJ/kg]; cost $0.20/lb [$0.44/kg]), an average manpower requirement of two men full-time at $10.00/hr each, and one half-hour needed for setting up the equipment. The results are shown in Table H-5.

Table H-4   Drying Costs

| Specified Impregnation Depth, in. | Est. Time, hr | Propane Requirements | | Labor | Total Cost |
		lb/sq ft	$/sq ft	$/sq ft	$/sq ft
1	0.8	0.36	0.072	0.054	0.126
2	1.8	0.81	0.162	0.096	0.258
3	3.0	1.35	0.270	0.146	0.416
4	4.5	2.03	0.406	0.208	0.614

Unit Conversions: 1 ft^2 = .0929 m^2

1 cm = 2.54 in.

Impregnation. Costs for impregnation are computed for both pressure impregnation (15 psig [100 kPa]) and ponding (0 psig). An average manpower requirement of two men full-time at $10.00/hr each has been assumed. Setup and take-down time is assumed to be 2 hr. Unit monomer consumption and cost figures (for 100:10 MMA:TMPTMA + 0.5% AZO) used are 0.75 lb/sq ft/hr (3.66 kg/m^2/hr) and $1.00/lb ($2.20/kg), respectively. The results are presented in Table H-6.

Polymerization. The polymerization costs are based on hot water polymerization with estimated heating costs of $0.033/sq ft/hr (0.355/m^2/hr) and manpower requirements of two full-time men at $10.00/hour each. Two hours total time for setup and take-down of equipment is included in the calculations. Notice that the heating cost is an average value and may be expected to vary with atmospheric chill factor (ambient temperature and wind velocity) and with the amount of insulation used. The results are presented in Table H-7.

Total Cost. Summing the drying, impregnation, and polymerization costs, the total estimated costs are presented in Table H-7 for each combination of four impregnation depths (1, 2, 3, and 4 in. [2.5, 5.1, 7.6, and 10.2 cm]) and two impregnation pressures of (0 and 15 psig [0 and 100 kPa]). Notice again that these estimated costs are based on drying and impregnating units capable of covering a 12-ft x 40-ft (3.66-m x 12.20m) area at each setup. Also, the above costs do not include amortization of capital equipment, maintenance, weather delays, or traffic control.

Table H-5. Impregnation Costs

Specified Impregnation Depth, in.	Pressure psig	Time hr	Labor $/sq ft	Monomer $/sq ft	Total Cost $/sq ft
1	0	4	0.250	0.750	1.000
2	0	15	0.708	1.500	2.208
3	0	30	1.333	2.250	3.583
4	0	49	2.125	3.000	5.125
1	15	1	0.125	0.750	0.875
2	15	5	0.292	1.500	1.792
3	15	10	0.500	2.250	2.750
4	15	17	0.792	3.000	3.792

Unit Conversions: 1 sq ft = .0929 m^2

1 psig = 6.895 kPa

1 in. = 2.54 cm.

Table H-6. Polymerization Costs

Specified Impregnation Depth, in.	Time hr	Labor $/sq ft	Heating $/sq ft	Total Cost $/sq ft
1	1.25	0.135	0.041	0.176
2	5.00	0.292	0.165	0.457
3	11.25	0.552	0.371	0.923
4	20.00	0.917	0.660	1.577

Unit Conversions: 1 sq ft = .0929 m^2

1 in. = 2.54 cm.

Table H-7.   Total Costs

Specified Impregnation Depth, in.	Drying Cost $/sq ft	Impregnation Cost $/sq. ft.		Polymerization Cost $/sq ft	Total Cost $/sq ft	
		@0 psig	@15 psig		@0 psig	@15 psig
1	0.126	1.000	0.875	0.176	1.302	1.177
2	0.258	2.208	1.792	0.457	2.923	2.507
3	0.416	3.583	2.758	0.923	4.922	4.089
4	0.614	5.125	3.792	1.577	7.316	5.983

Unit Conversions: 1 sq ft = .0929 m^2

1 psig = 6.895 kPa

1 in. = 2.54 cm.

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   of an Experimental Prestressed Concrete. Report to PennDOT on
   Project 71-8, Report PTI 7407, The Pennsylvania Transportation
   Institute, The Pennsylvania State University, Mar. 15, 1974.

2. Clear, K. C. Evaluation of Portland Cement Concrete for Permanent
   Bridge Deck Repair. Report No. FHWA-RD-74-5, Federal Highway
   Administration, Feb. 1974.
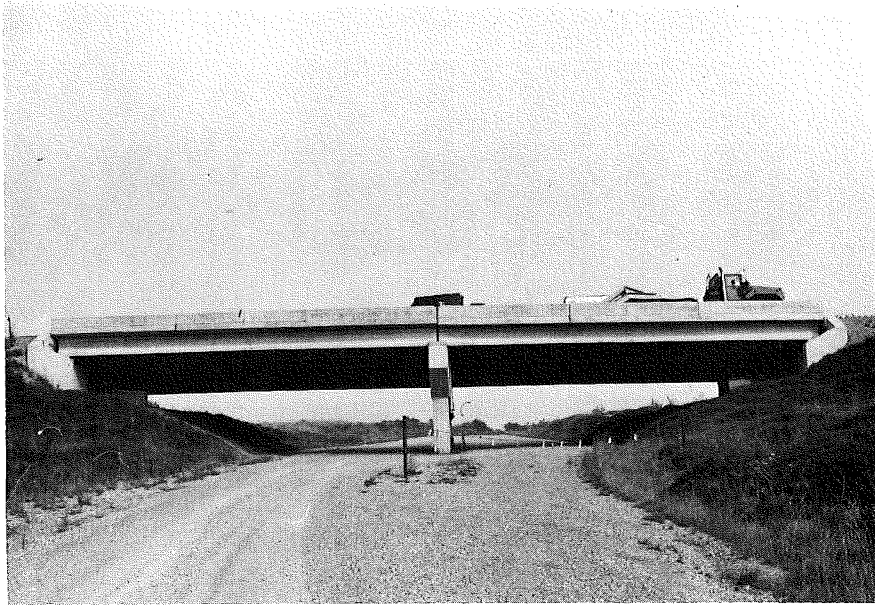
Fig. H-1   General View of PTI Test Track Bridge

Fig. H-2   Close-Up View of PTI Test Track Bridge

H-28
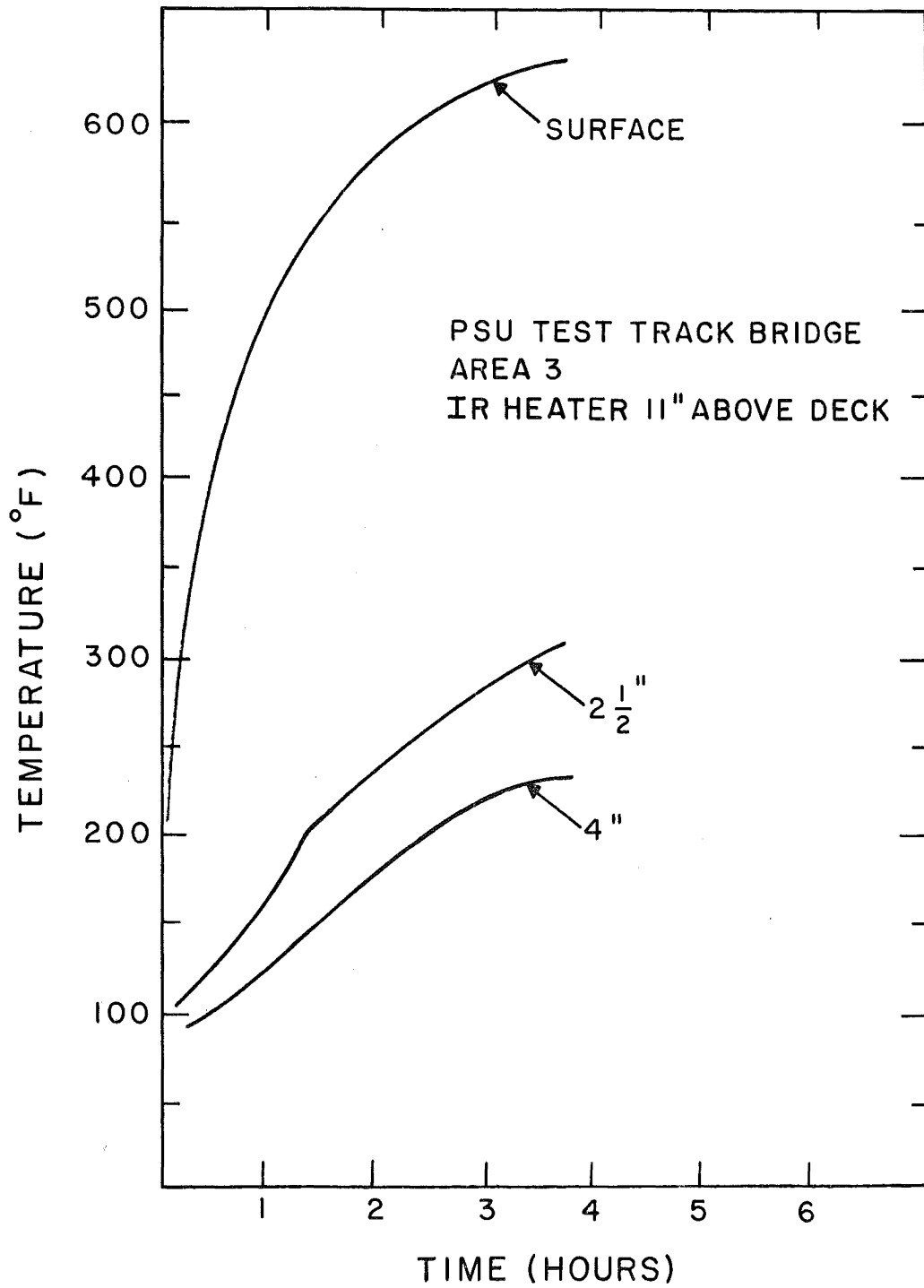
Fig. H-3   Temperature Profile vs. Time for 12'x6' Bridge Deck Drying Trial.

Sec.-A-A

Details Of Connection With Concrete Surface

Fig. H-4 Design of 3/x12' Pressure Impregnator

Inlet/Outlet Valve

Lifting Brackets

Intermittent Weld

24, 1" Ø Holes

Fully Welded At All Corners And Junctions

(1) All Aluminum Vessel
   (A) Aluminum Type: 60-61T651
   (B) Welding Process: MIG., 4043 Filler Wire
(2) Gaskets (Dual) Type: Silastic 'E' Rubber
(3) Weight = 450 lbs.
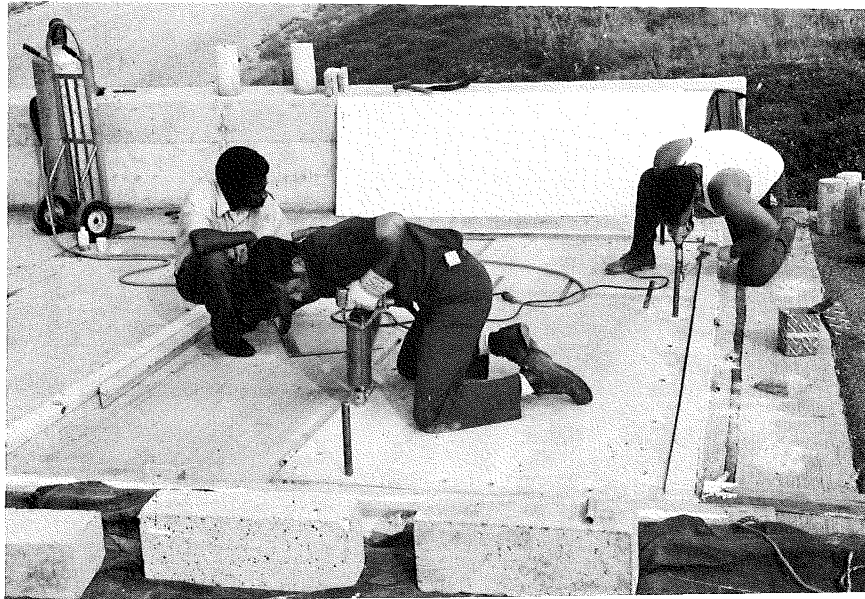
Fig. H-5 Drilling of Inserts in the Concrete Deck
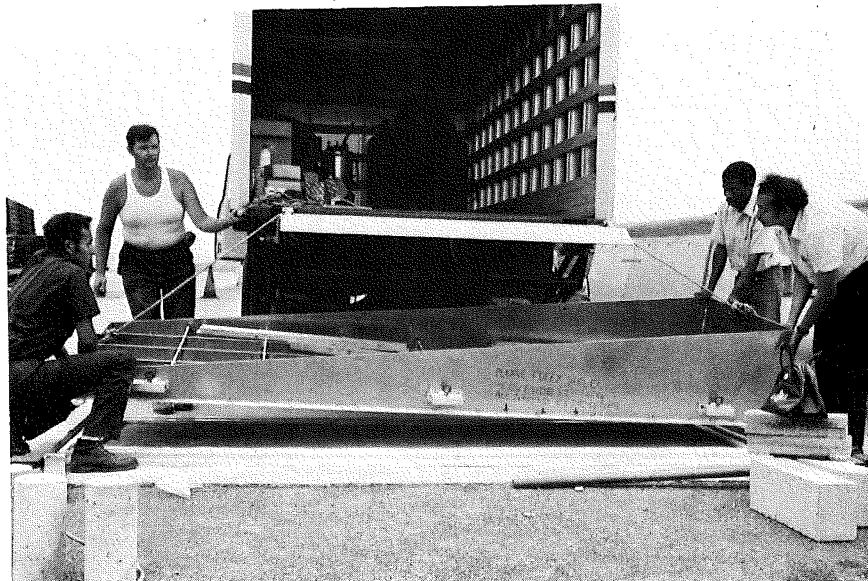
Fig. H-6 Positioning the Vessel on the Area of Treatment
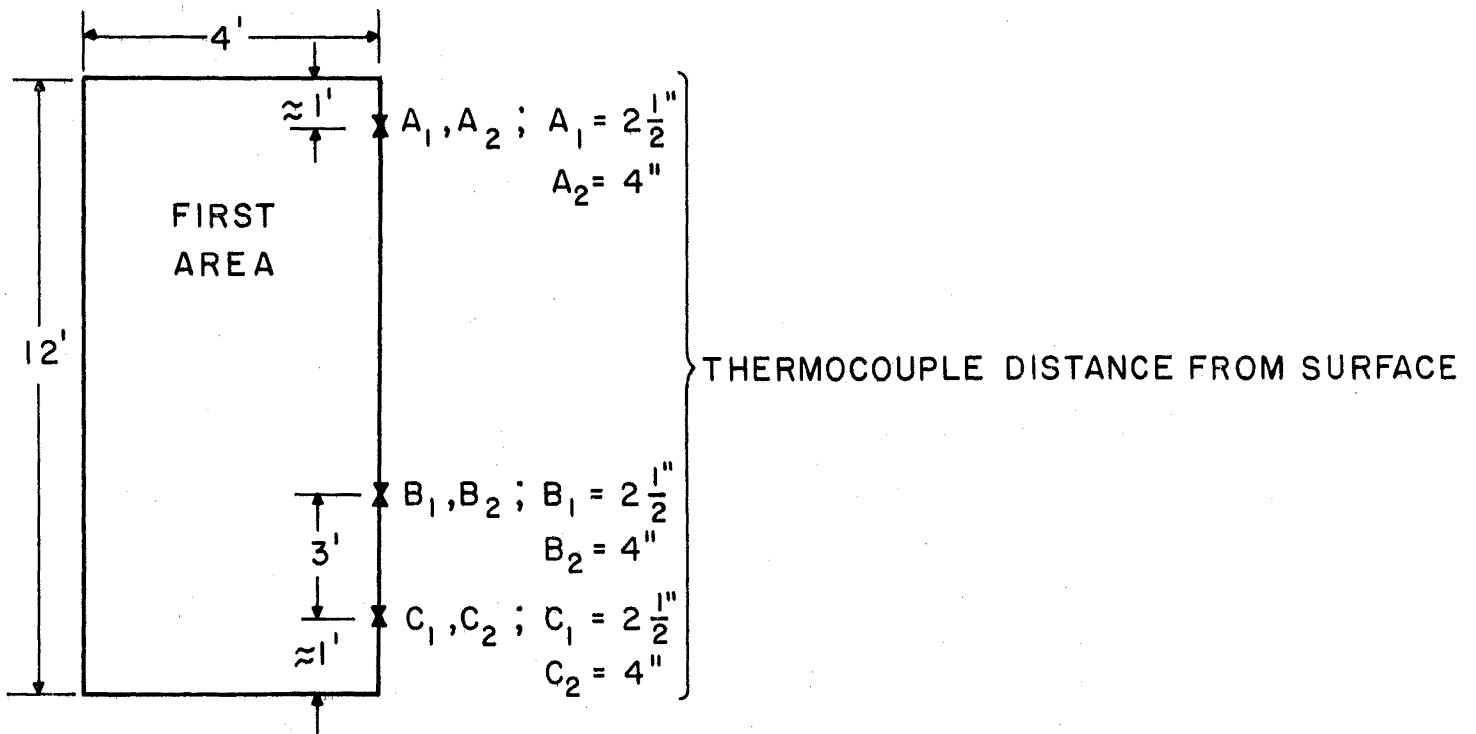
Fig. H-7 Sketch Showing the Location and Depth of Thermocouples to
Monitor Temperatures During Polymerization
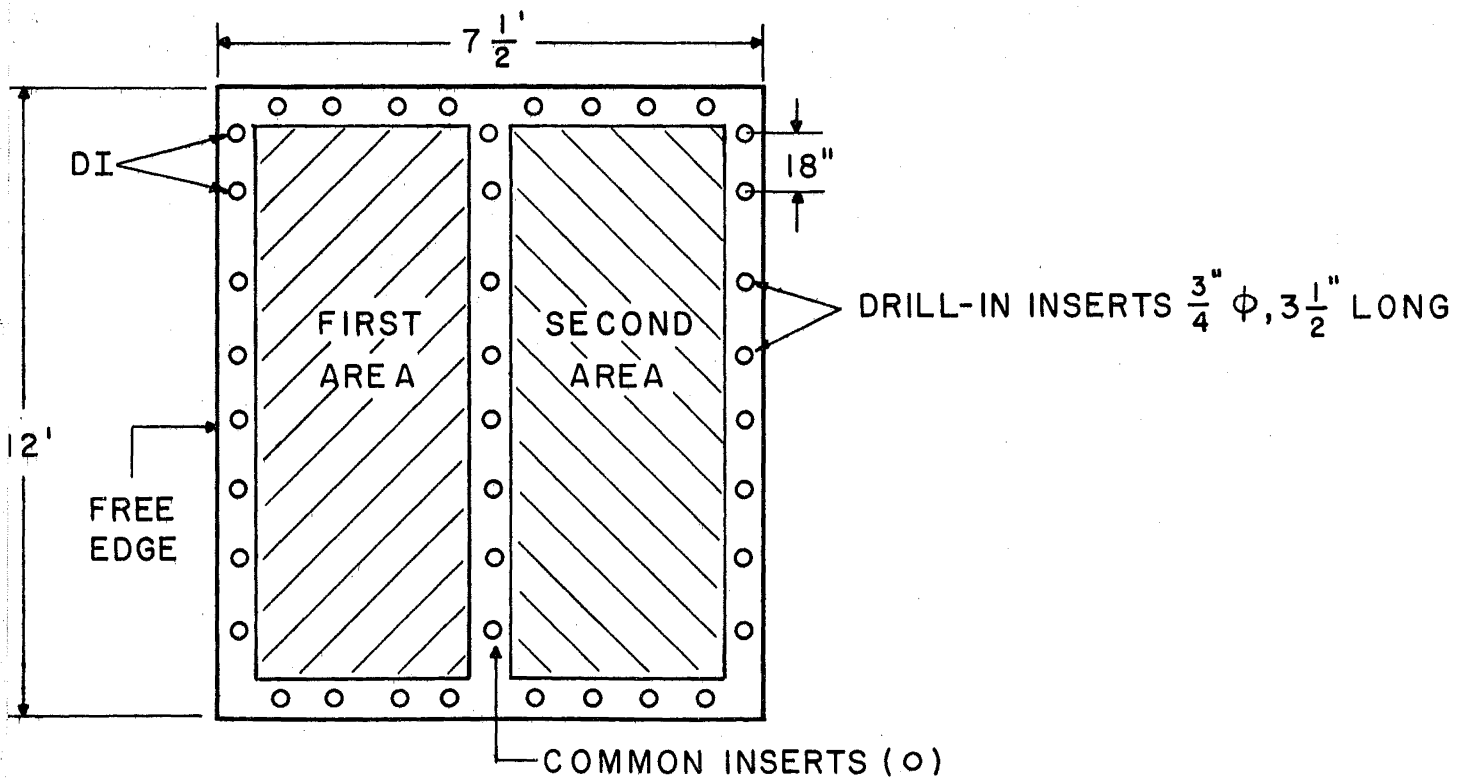
Fig. H-8 Sketch Showing the Adjacent Areas for Treatment and Location of
Inserts
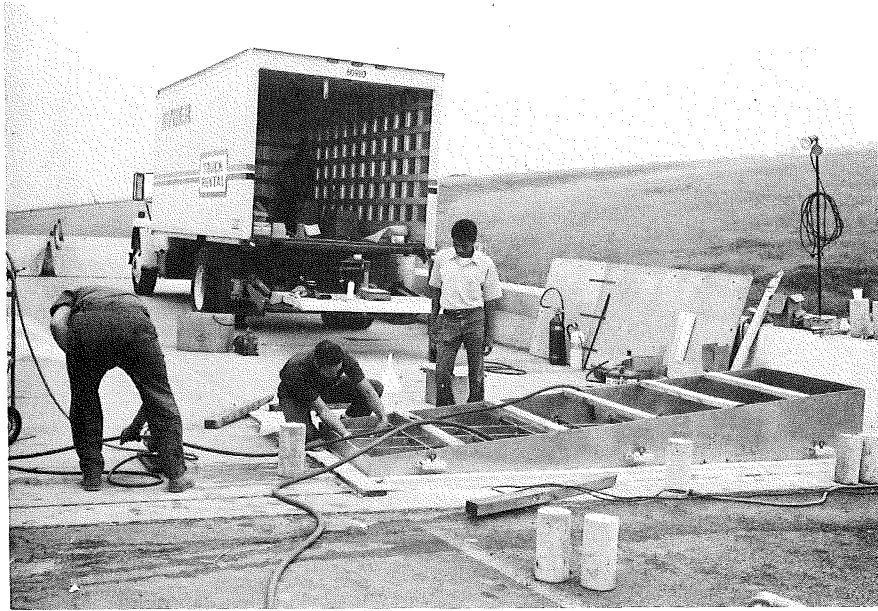
Fig. H-9   Tying Down the Vessel Over the Gaskets with Bolts

Fig. H-10   Monomer Leakage from Underneath the Slab
at the Free Edge

H-33

Fig. H-11   Circulation of Heated Water from Drums to Impregnation Chamber
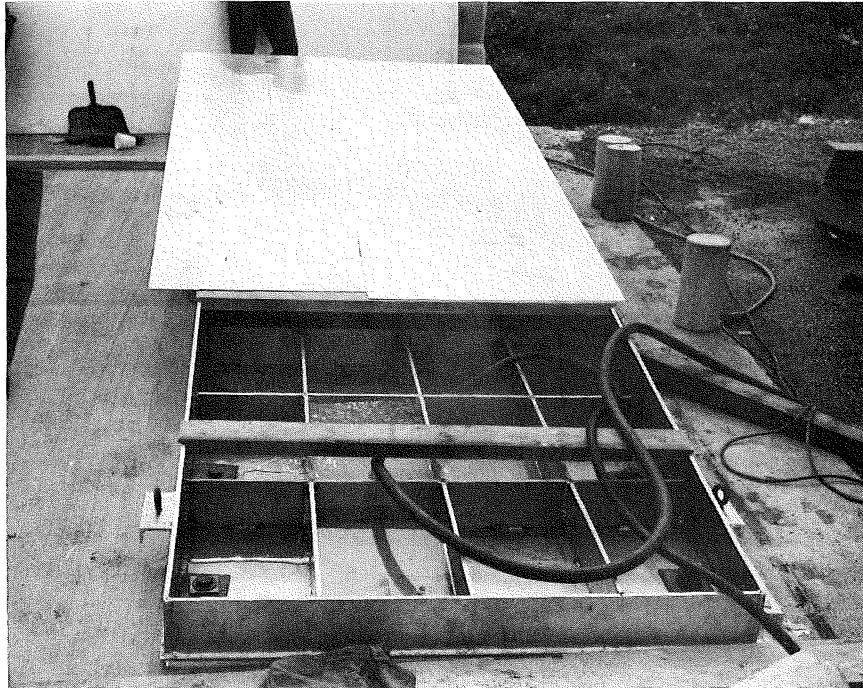
Fig. H-12   Close-Up View of the Impregnation Chamber Filled with Hot Water
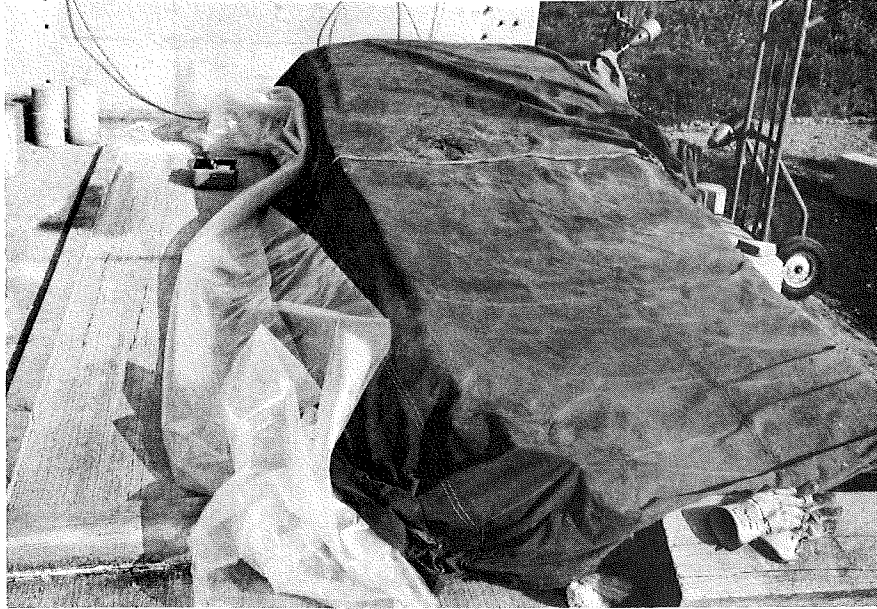
Fig. H-13   View of the Chamber Cover with Insulation During Hot Water
Polymerization
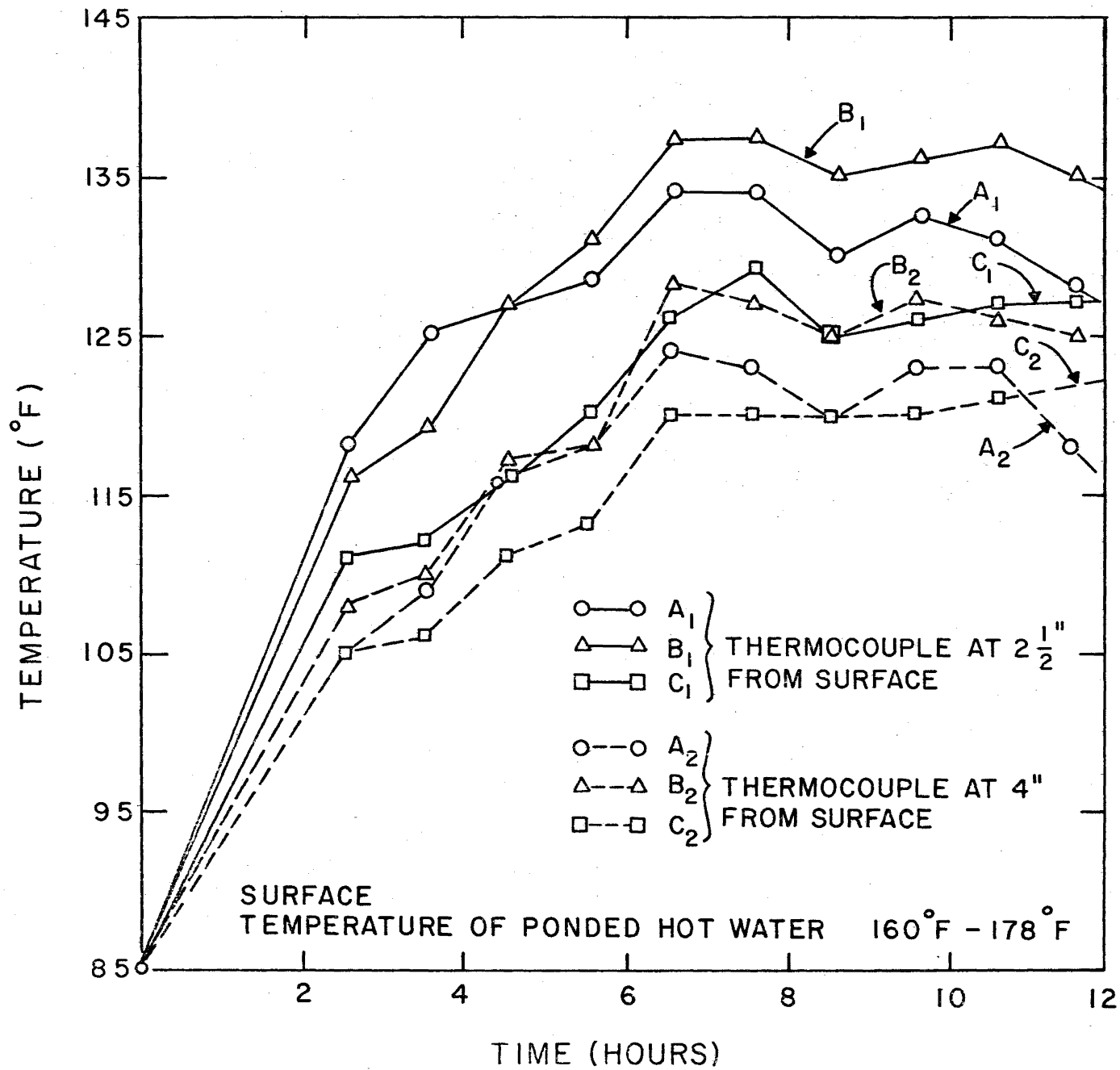
Fig. H-14 Temperature Distribution Curves for Hot-Water Polymerization
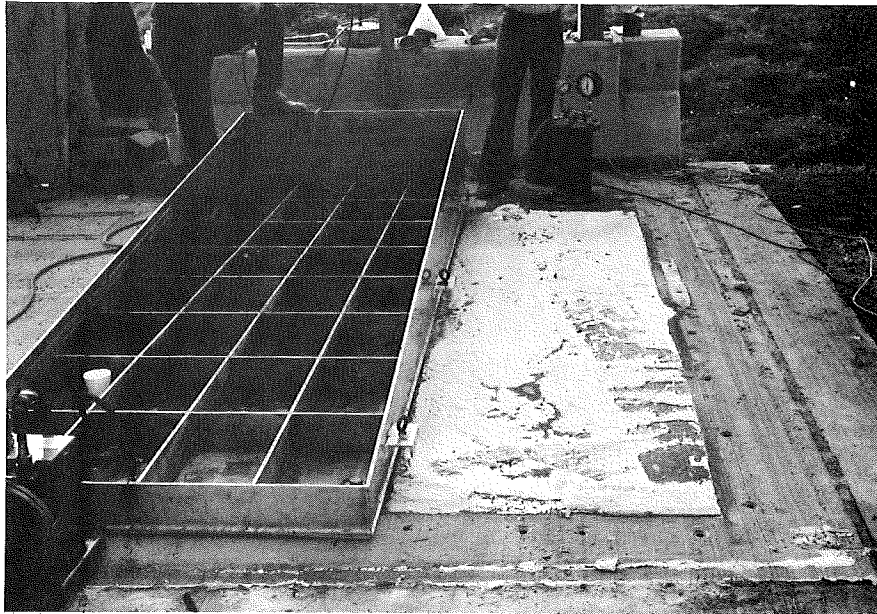
Fig. H-15 Polymer Froth on the Surface in First Area.
          Impregnation Vessel on the Second Area.
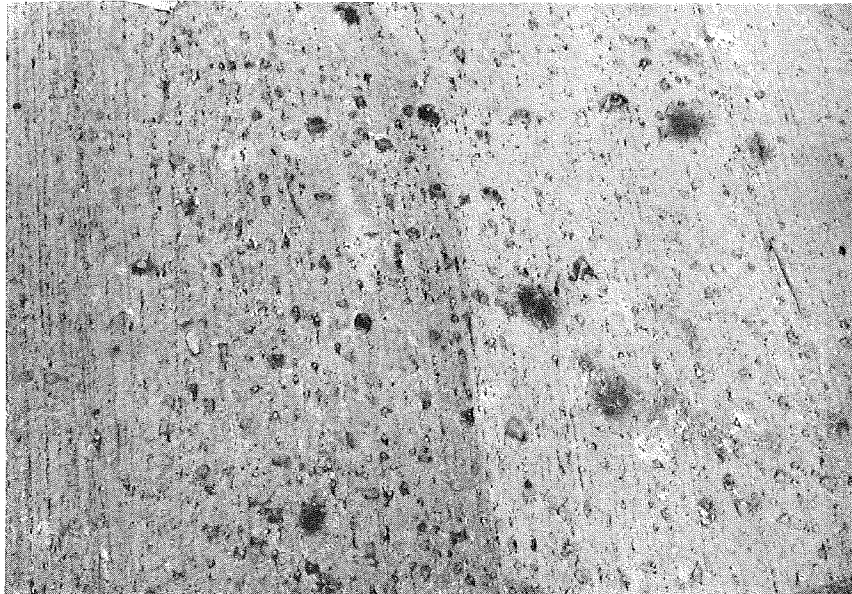
Fig. H-16 Closeup View of the Impregnated Surface. Note Polymer
          Beads on Surface
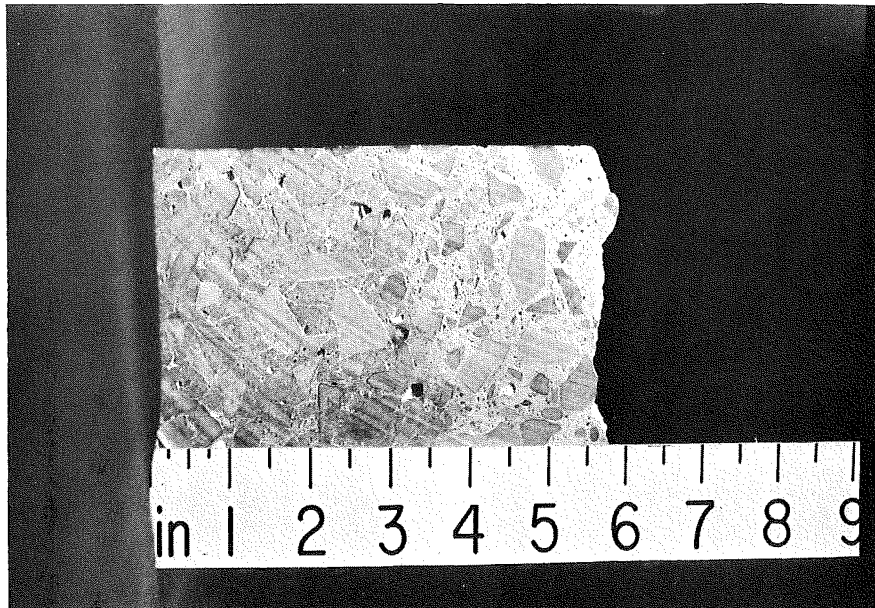
Fig. H-17 Cross-Section Through a 4" Diameter Core from the First Area.
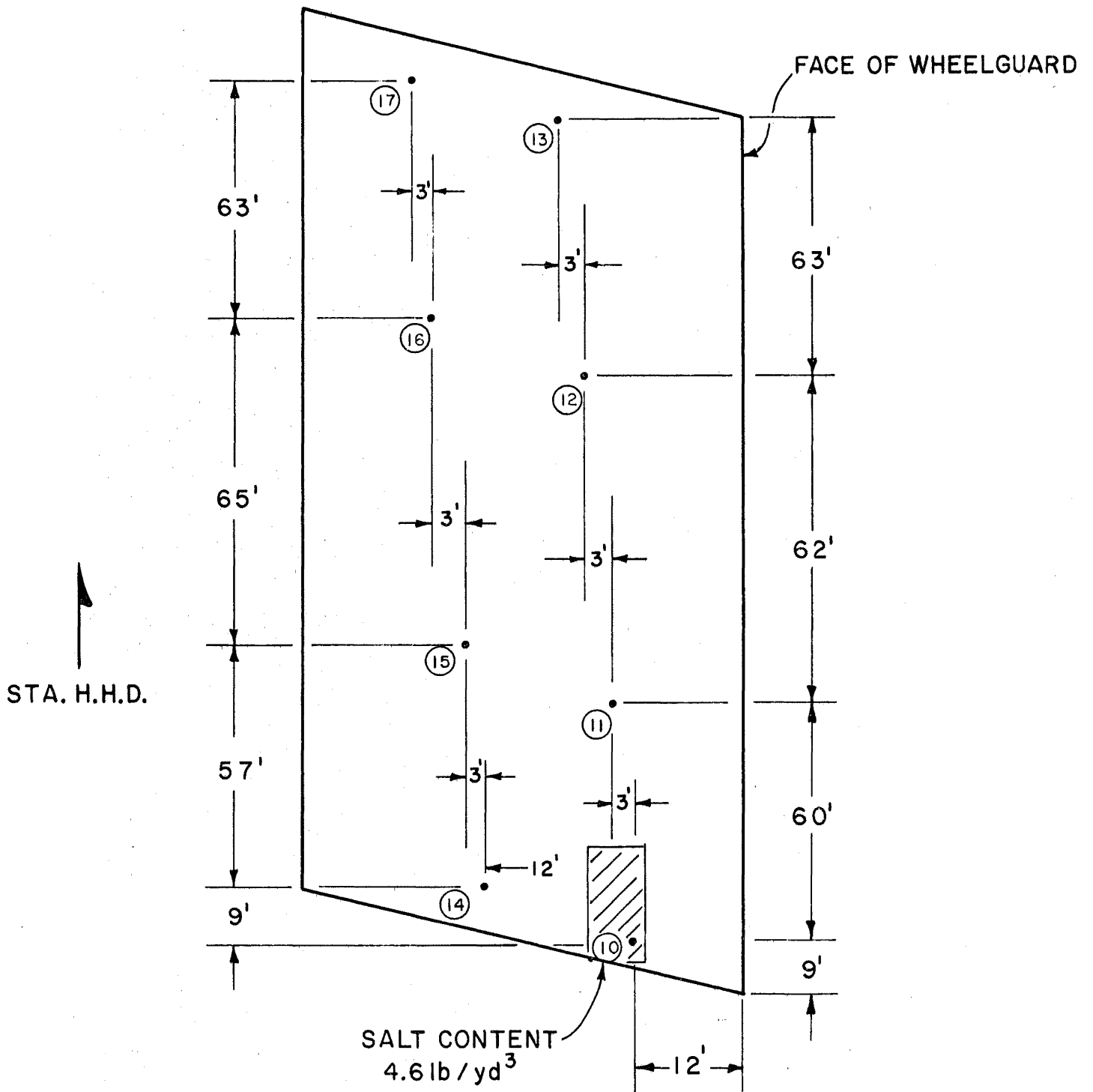Note 3½" of Full Impregnation with 1½" Band of Partial Impregnation.
(One Inch = 2.54 cm)

Fig. H-18
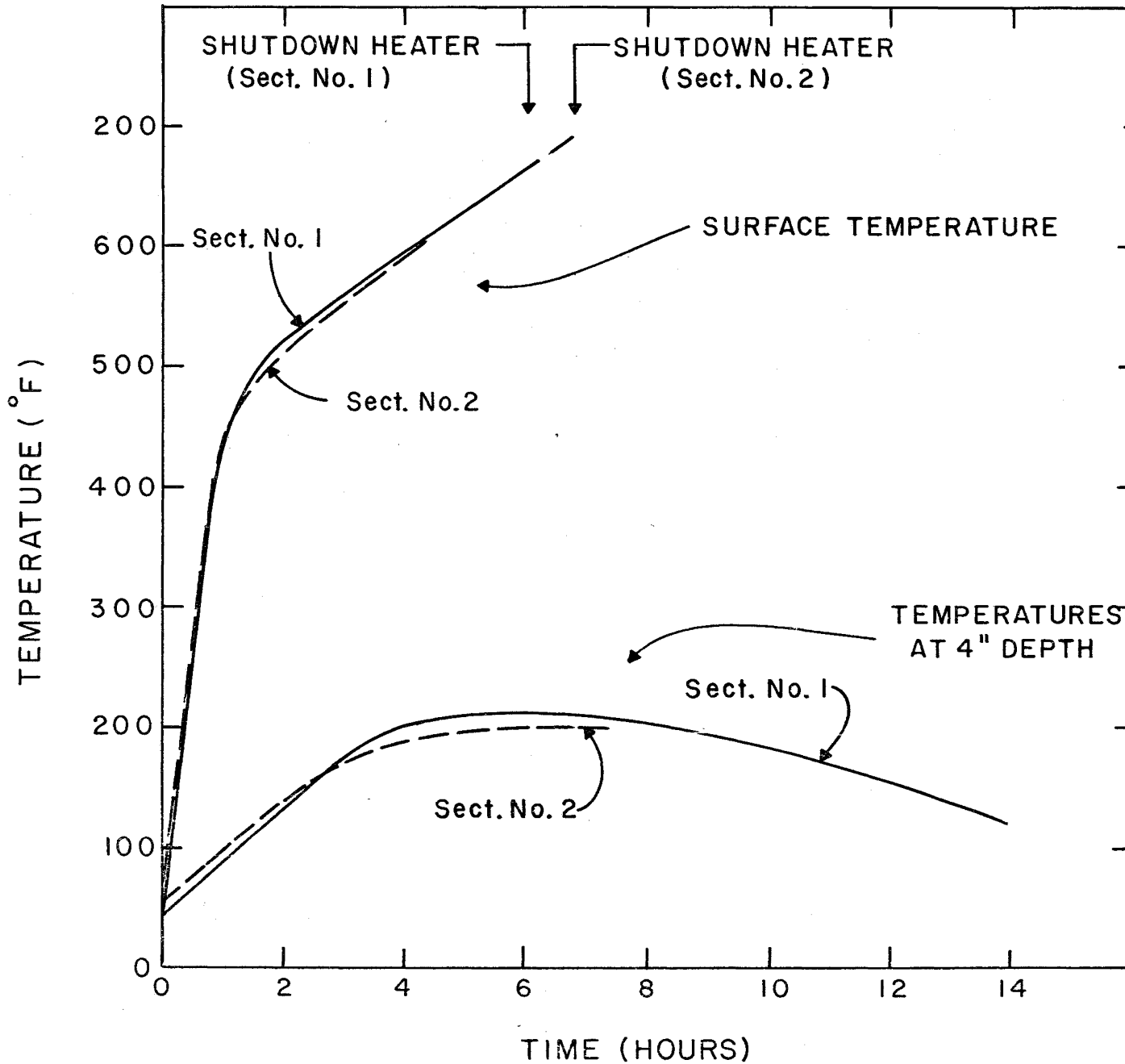
Fig. H-19 Drying Curves on Bethlehem Spur Route Bridge Deck. ($^{o}F = \frac{9}{5}{}^{o}C + 32$, One Inch = 2.54 cm)
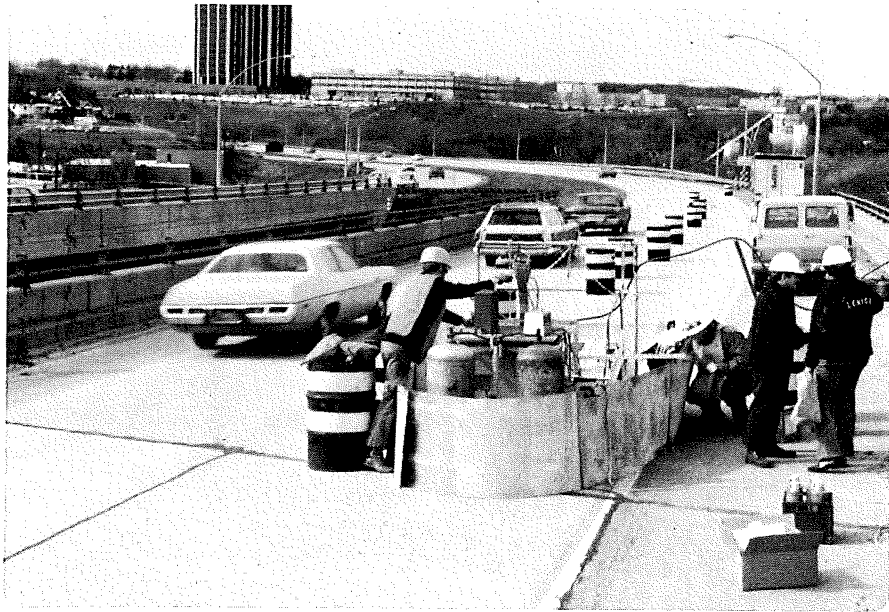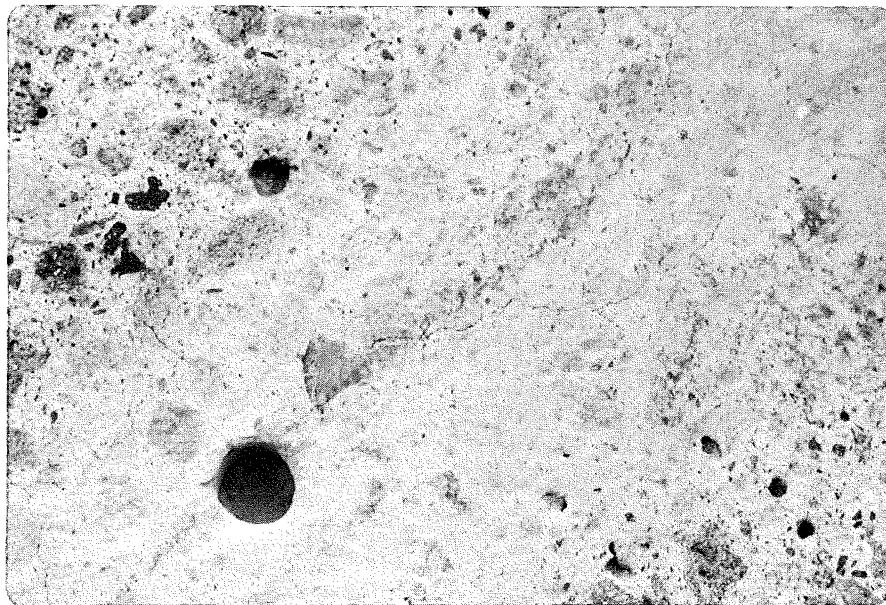
Fig. H-20   Drying in Progress

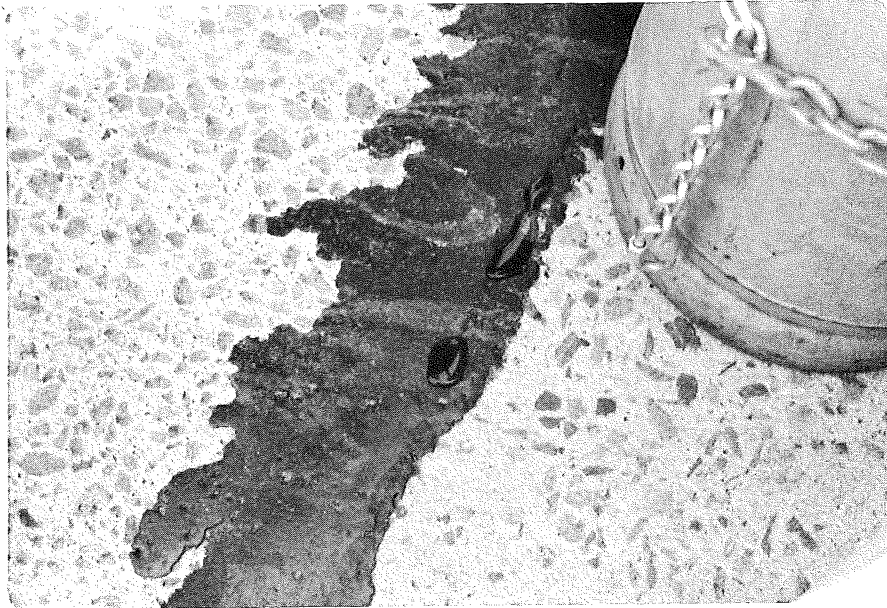Fig. H-21   Surface Crazing Induced by Drying

Fig. H-22   Water Exuding from Expansion Joint
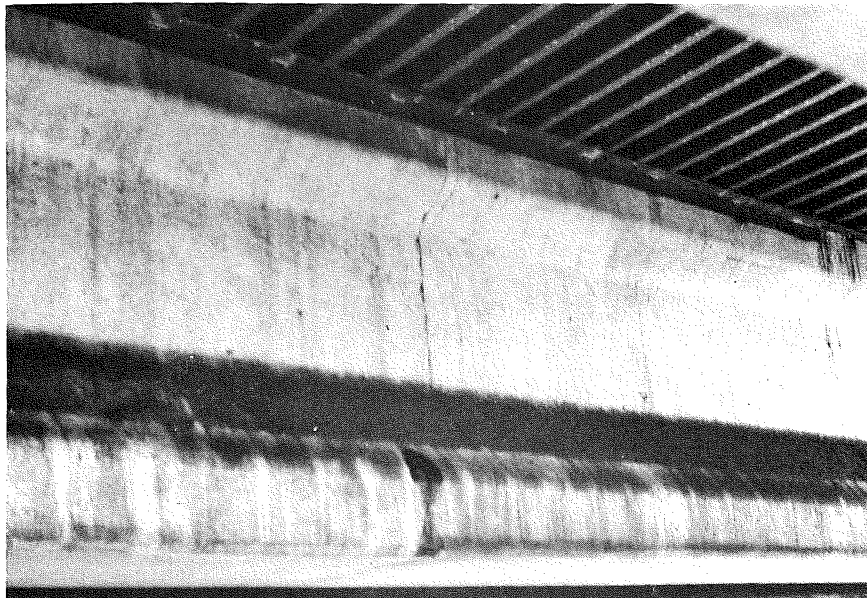

Fig. H-23   Water Dripping from Underside of Deck

Fig. H-24   Sealing the Dike.   Note the Prior Sealing of the Area Already Dried at Left.

Fig. H-25   Covering of Working Area Against Rain

Fig. H-26 Drilling Bolt Holes for Impregnation Unit
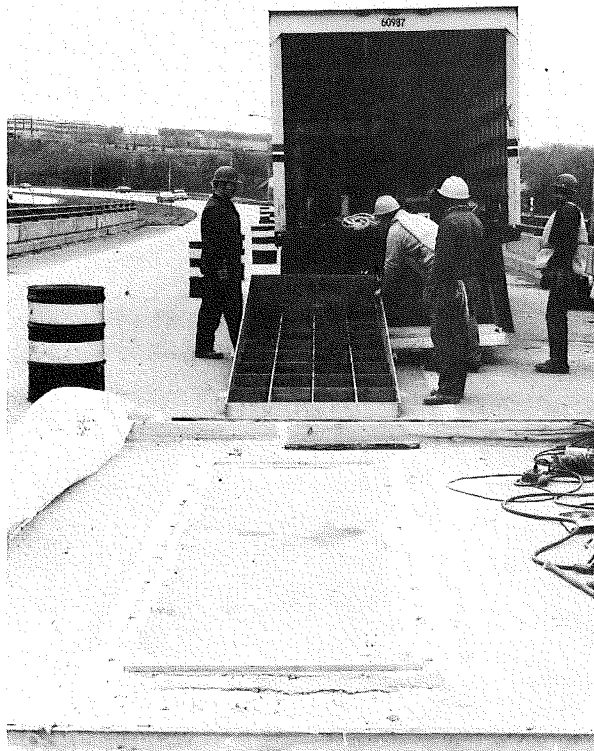
Fig. H-27 Unloading Impregnation Chamber. Note Gaskets in Place
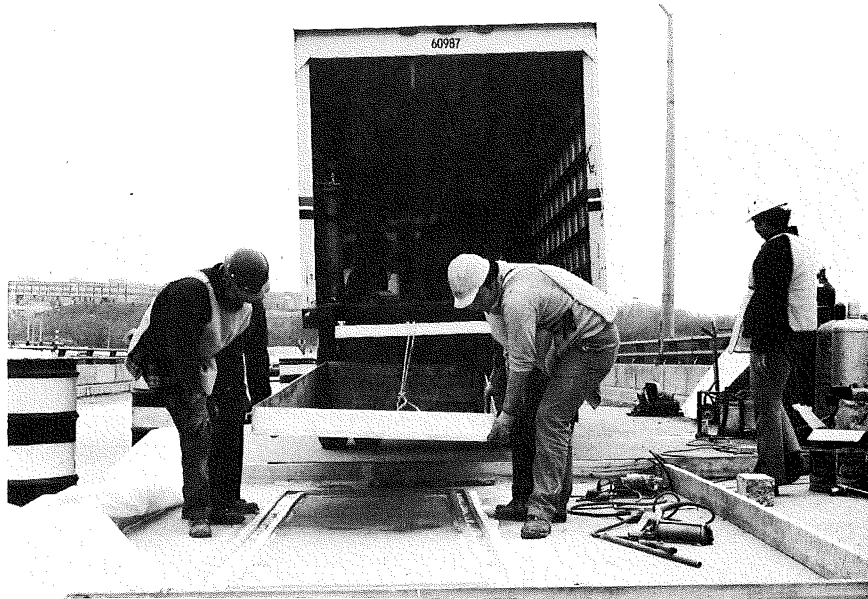
Fig. H-28   Placement of Chamber Over Gaskets

Fig. H-29   Dripping of Monomer on Underside of Deck

Fig. H-30   Polymerization Step.   Note Insulation.

Fig. H-31   Close-Up of Insulated Chamber
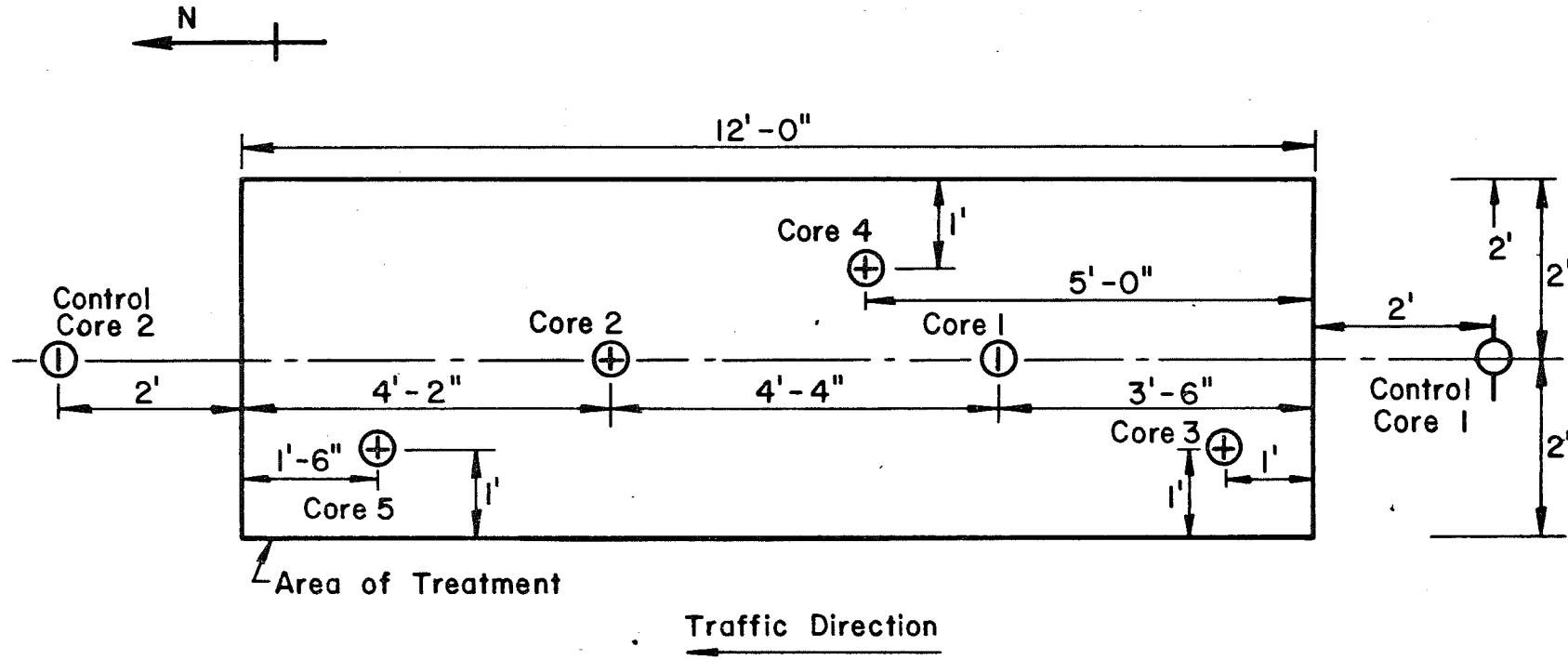
Fig. H-32 Coring Pattern for Impregnated Area of Bethlehem Spur Route Bridge Deck

Fig. H-33 Appearance of Acid-Etched Core From Bridge Deck; Note Dense
Impregnation to a Depth of 3 Inches (7.6 cm) and Less Dense Impregnation
Below

Core #2

Core #3

Fig. H-34   Cores Taken From Impregnated Area of Bethlehem Spur Route Bridge
Deck; Photographs Taken After Etching with 15% HCl

Core #4

Core #5

Fig. H-34   Cores Taken from Impregnated Area of Bethlehem Spur Route Bridge
Deck; Photographs Taken After Etching with 15% HCl

Impregnated Core #1

Control Core #1

Fig. H-35   Closeup of Cores from Bethlehem Spur Route Bridge
Deck (After Fracture During Split-Tensile Test)

APPENDIX I

FIELD MANUAL FOR POLYMER IMPREGNATION OF CONCRETE BRIDGE DECKS

INTRODUCTION

Purpose

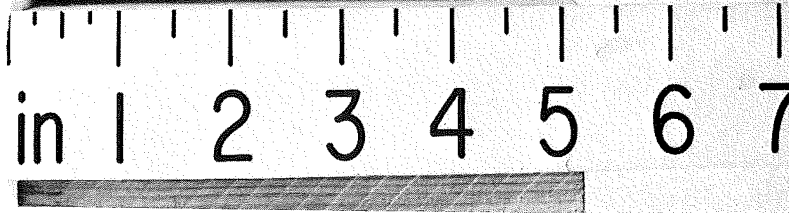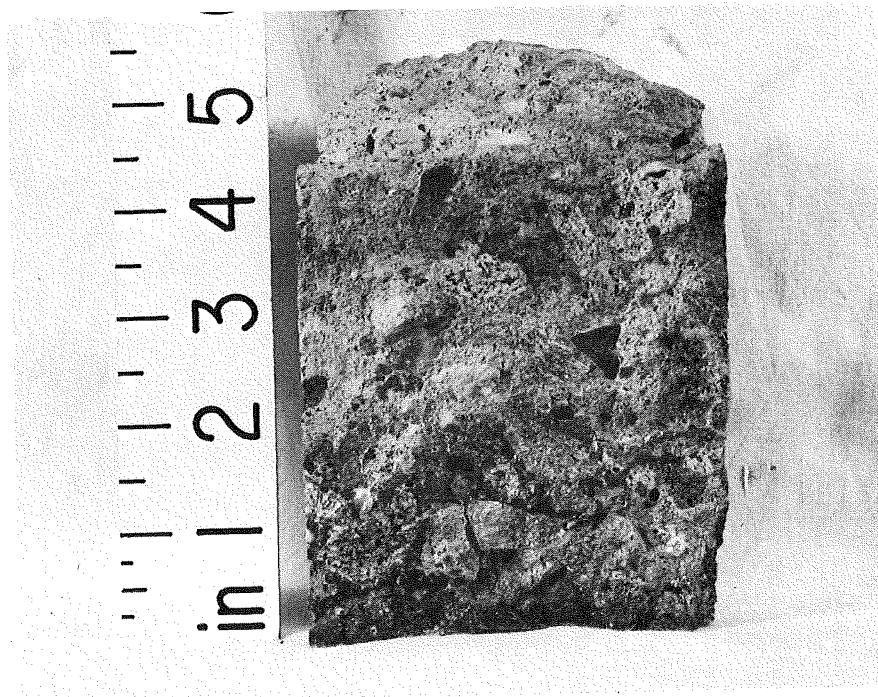The term "polymer impregnation," as used in this manual, refers to the process of saturating the top (traffic) surface of a concrete bridge deck to a specified depth with a liquid monomer, followed by subsequent polymerization (solidification) of the monomer in the pores of the concrete. Polymer impregnation increases the strength of the concrete and improves its resistance to wear. Most importantly, however, it blocks the pores of the concrete preventing water and deicing salts from reaching and inducing corrosion of the steel reinforcement. Before the concrete can be impregnated with a monomer, it must be dried. The monomer will not enter pores that are already filled with water. After drying and impregnation, the monomer must be converted to the polymer by the process of polymerization. The basic steps then are: (1) drying, (2) impregnation and (3) polymerization.

The purpose of this manual, then, is to provide basic guidelines, data, and procedural instructions for the execution of these three steps in the polymer impregnation of concrete highway bridge decks. Criteria for acceptability of the completed job and safety requirements are also presented.

Scope'

While several possible techniques are available for carrying out each of the three major tasks involved, this manual will cover the

only method that has been successful, to date, for deep impregnation of sound bridge deck concrete in the field. That method involves drying by means of infrared radiation, low pressure or atmospheric pressure impregnation, and hot water polymerization. The sampling plan, acceptance criteria, and basis of payment presented in this manual may be varied in accordance with the practices and customs of the highway agency. involved. The safety considerations cited in this manual relate only to special hazards associated with the materials and processes used in polymer impregnation of concrete bridge decks. These are intended to supplement, not to supersede, existing OSHA, state, and local safety codes.

MONOMER

Type

The monomer system should consist of a 100:10 mixture of methyl methacrylate (MMA): trimethylolpropane trimethacrylate (TMPTMA) with 0.5 percent azobisisobutyronitrile (AZO) initiator.

Handling and Storing

The three components of the monomer should be stored separately (i.e., not mixed) under security consistent with their fire hazard potentials, in an area where storage conditions will comply with suppliers' recommendations. If any transfer of materials that may allow vapors to escape is to take place in the storage area, adequate ventilation must be afforded and electrical facilities must be explosion-proof. Mechanical equipment, as necessary, should be furnished by the contractor for safe handling of the materials.

Quantities Required

The quantity of monomer mixture required will vary with the porosity of the concrete. However, for estimating purposes, it can be assumed that the typical bridge deck concrete will require approximately 3/4 lb (0.34 kg) of monomer mixture per sq ft (.093 m^2) of deck area per 1 in. (2.5 cm) of required penetration depth. An average porosity for the concrete to be impregnated should be ascertained from representative core specimens in order to provide more accurate determinations of monomer requirements. The rate of penetration should also be determined.

Mixing

Mixing of the monomer components should be carried out in a closed container in a well-ventilated area. Only the quantity of monomer required for the area to be impregnated at a given time should be batched and mixed. Batching and mixing should be carried out immediately prior to the impregnation step and in units not exceeding one drum (55 gal [0.2 m^3]), and the batched material must be kept away from ambient temperatures above 70°F (21°C) to minimize the chances of the material "going exothermic." "Going exothermic" means starting to polymerize before impregnation such that the temperature of the mixture rises very rapidly, resulting in severe explosion potential.

After completion of the impregnation step, all unused monomer mixture must be safely disposed of immediately.

DRYING

Requirements

Before concrete can be impregnated with a monomer, it is necessary

to remove water from the pores of the concrete. All concrete retains moisture very tenaciously. Tests have shown (1) that even after a long dry spell, the concrete deeper than 1 in. (2.5 cm) from the surface of a bridge deck will remain 60 to 70 percent saturated, and most of the time it is 90 to 100 percent saturated. In order to permit the ingress of the monomer, this water must be removed to the required depth of impregnation. This should be done by means of high-temperature radiant drying, taking care that the area heated at any one time is not so large as to produce excessive thermal stresses and buckling of the slab due to high thermal gradients.

Criteria

The basic criterion for obtaining sufficient dryness to assure impregnation to the required depth is the attainment of a temperature of 230°F (110°C) at the required impregnation depth. This can be determined in one of the following ways:

1. Drill a thermowell to the required impregnation depth and monitor the temperature with a thermocouple.

2. Measure the surface temperature with a thermocouple and stop heating when a rate of increase of the surface temperature drops below a predetermined value. (see below).

The second procedure is easier from the standpoint of not having to drill thermowells. However, the rate of change of the surface temperature for a given temperature profile may vary somewhat with the composition of the concrete (principally, the aggregate type). Typically, for example, it has been found that for a limestone aggregate concrete, the temperature at 4 in. (10 cm) deep reaches 230°F (110°C) when the rate of temperature change at the surface decreases to 10°F (5.5°C)/hr. The surface temperature at this point is 620°F (327°C) (2).

I-4

In order to prevent disruption of the concrete due to excessive steam pressure or too-steep thermal gradients, the surface temperature should not exceed 500°F (260°C) one hour after starting and should never be allowed to go above 675°F (357.2°C). A layer of sand up to 1 in.(2.5 cm) in thickness will be useful in minimizing surface cracking (3, 4).

The time required to carry out the drying at each set-up will vary with: (1) the required depth of drying (depth of impregnation); (2) heat input at the surface; (3) the chill factor (air temperature and wind velocity); and (4) the moisture content of the concrete. For a 4-in. (10-cm) drying depth using a heat input that results in a 500°F (260°C) surface temperature after 1 hr, the drying time varied from 3.75 hr at 70°F (21°C) air temperature and zero wind velocity to 9.75 hr at 30°F (-1°C) air temperature and brisk winds. In both cases, the slabs were in nominally saturated condition (80-90 percent saturation). The same decks at the same conditions reached the dry state at 2.5 in. (6   cm) in approximately 2 and 6.5 hr, respectively (2).

Equipment

To carry out the drying operation, a gas-fired infrared heater with a rated output of approximately 9,000 BTU/hr/sq ft (100 MJ/hr/m²) should be used. A unit consisting of supercharged, propane-fired Inconel elements was found to satisfactory for this purpose. The heater must be capable of vertical adjustment to permit varying of the distance between the heater elements and the concrete surface. This feature is necessary to maintain temperature control in accordance with the criteria previously cited.

It is recommended that a reradiating shield constructed of galvanized steel sheet metal be used around the perimeter of the drying area to maximize drying efficiency by reducing radiant heat loss as well as conductive and convective losses.

Procedure

The initial set-up of the heater must include provisions for monitoring the surface temperature and the temperature at the required impregnation depth. This can be done by means of any suitable temperature-sensing device (thermocouples, thermistors, etc.) having the appropriate temperature range and capable of withstanding the high temperatures. The sensing element on the surface must be covered with about 0.5 in. (1 cm) of sand to prevent it from being exposed to the direct radiation from the elements. The thermowell for the temperature sensor at the required level of impregnation should be drilled from the bottom side of the deck, if possible. This will reduce the possibility of erroneous readings due to conduction of heat from the surface to the sensor through the leads or sensor jacket. A 1/4-in. (6 mm) diameter hole will suffice for the thermowell if thermocouples are used as sensors.

After the temperature-sensing devices are installed, the heater can be fired up. Utilizing temperature readings at frequent intervals, appropriate changes should be made in the vertical position of the heater above the deck to reach a surface temperature of 500°F (260°C) or slightly less at 1 hr. An accurate log of times and temperatures should be kept. From this point on, the temperature should be allowed to rise at a continually

decreasing rate, but should not be permitted to go above 675°F (357°C). When

the temperature of the deck at the level of the required impregnation depth

reaches 230°F (110°C), the time and surface temperature should be recorded

and the heater shut down. From the time-temperature data, the rate of change

of the surface temperature during the last hour of drying should be determined.

For the remaining heater set-ups on the deck, it will be necessary only to

monitor the surface temperature, terminating the run when the temperature

change during a 1-hr period is equal to or less than the final rate

of change determined previously.

Cool-Down Period

    After the concrete has been dried, it must be allowed to cool down

to 100°F (38 °C) or below before the impregnation with monomer can

be commenced. During the cool-down period the concrete must be protected

from rain or snow. A convenient means of doing this is to use large

pieces of sheet metal supported on a frame made of two by four lumber

lumber. A continuous dike constructed of two by four lumber

calked around the outer edge must be used around the perimeter of the

dried area. It is not necessary, nor even desirable, to cover the dried

area until near-ambient temperatures are reached. Plastic sheeting

may be used if surface temperatures are not so high as to melt the plastic.

Tenting the area with plastic or canvas sheeting can also be done during

inclement weather if the tent can be constructed to prevent ingress

of blowing rain and surface flow.

IMPREGNATION

Requirements

    The impregnation should begin as soon as possible after the concrete

has reached ambient temperature or 100°F (38 °C). Otherwise, the dried

concrete will begin to resaturate by conductive movement of water from

undried areas within the concrete and by the process of capillary

condensation of moisture vapor from the atmosphere. Acceptance require-

ments for depth of impregnation are presented later in this manual.

Equipment

Equipment should include an impregnation chamber, monomer pumps, a

vacuum pump, and compressed gas suitable for pressurization. The

chamber must be capable of being bolted to the deck, and of withstanding

pressures up to 15 psi (103 kPa). The chamber must also permit

recovery of any monomer which leaks through the inner gasket. The

dual gaskets for the chamber should be fabricated from a monomer-

resistant grade of Neoprene or silicone rubber; a fresh gasket should be

used for each impregnation.

Preparation for Impregnation

The deck should be carefully inspected for cracks, surface roughness

and irregularities, and wear pattern. Visible large cracks should be

filled with an epoxy patching compound.

The area where the gaskets will be located should be as level as

possible to facilitate proper sealing by the gaskets. All rough or

worn areas which will lie under the gasket should be made level using

a nonporous, quick-setting mortar, e.g., a 50/50 mixture of high-strength

plaster (such as Hydrostone) and cement or a cement grout which will bond

well to the surface and not crack during shrinkage.

The cores taken as above should be tested for average porosity

after drying and evacuation, and also for the penetration rate of monomer. Use of the pressure-type apparatus is recommended for this purpose, so that a rate can be established at zero pressure and at 15 psig (0.10 MPa). The depth of penetration may be estimated from the porosity and the weight of monomer taken up. From the rate determined as a function of pressure, the desired operating pressure can be selected within the pressure rating of the field impregnation chamber.

Mounting of the Chamber

First the top layer of rebars must be located using a pachometer and must be marked. It is important that the rebars be located accurately in order to avoid contact during drilling. Should a rebar be hit accidently, the drill should be capable of cutting through the rebar to avoid enlarging the hole (which can cause leakage). However, as far as possible, hitting rebars should be prevented so as not to damage the slab structurally.

Next, positions of the insert holes should be marked on the surface of the slab. This may be done conveniently using a template with holes corresponding to the holes in the chamber. The mounting holes in the chamber should be slotted so that a given bolt can be inserted anywhere within a 2-in. (5-cm) distance along the mounting flange, in order to avoid rebars.

Self-drilling, expansion-type inserts should then be drilled in to a depth of at least 4 in. (10 cm). Driving the inserts as deep as possible increases their carrying capacity. The size and length of the inserts should be suitable for carrying the design load for the inserts created by application of the specified pressure.

Following the drilling of the inserts, the dual gasket should be placed around the insert holes and the chamber aligned into position. The mounting bolts should then be screwed into the inserts, and the bolts tightened at a uniform torque up to a point at which a vacuum of 28 in. (95 kPa) of mercury can be held inside the chamber prior to feeding in the monomer.

Monomer can now be fed into the chamber under vacuum until the monomer chamber (within the inner gasket) is filled with the monomer mixture. The mixing and storing of monomer mixture prior to impregnation at site is described in the previous section. Extreme care must be taken to see that the chamber vessel and monomer inside it are protected from solar radiation when the impregnation is carried out during the day. Thick insulation should cover the entire chamber (to keep temperature $\leq 80°F$ [27.7°C]) as the monomer can polymerize, prior to impregnation, by an autoaccleration mechanism.

Pressure should now be gradually raised to the pressure selected and the impregnation process continued for the required time to reach the required depth of penetration at that pressure. However, the pressure may have to be reduced if excessive leakage occurs on the underside or surface. If so, the impregnation time will have to be increased.

On completion of impregnation, the pressure is released and any unused monomer is pumped out to a storage container and the amount measured. However, if on estimation of the monomer materials balance (allowing for losses due to leakage and evaporation) it is found that the amount of monomer taken up does not correspond to full impregnation to the required impregnation depth, the monomer should be pumped back into

the chamber and pressure reapplied for the required time.

POLYMERIZATION

Once the excess monomer is removed, the chamber is filled with
hot water (200° - 210°F [93.-99°C]) to a depth of at least 5
in. (13 cm). As the heat is transferred to the slab, chamber walls,
and surrounding atmosphere during the process of feeding in the hot water,
the temperature will drop quickly to 160° - 170°F (71°-77°C).
To keep the water temperature in the range of 175° to 185°F (80°C to
85°C) during the whole process, electric heaters, steam, or a circulating
water heating system may be used. In any case, the chamber should be
insulated during the whole process of polymerization by covering it
with 3-in. (8-cm) fiber-glass insulation and exterior-grade plywood
sheets. If the temperature of 175° - 185°F (80° - 85°C) is maintained
on the surface for at least 12 hr, the rise in temperature should be
sufficient to polymerize the monomer to at least 4 in. (10 cm) deep.

In a continuous process, once the polymerization is completed, the
water can be stored to be reused later. The chamber is unbolted after
removal of the water and polymer froth and nuggets on the surface
are removed. The whole process is now repeated on the adjacent section
using one line of inserts already drilled.

ACCEPTANCE CRITERIA

General

In order to assure that the specified depth of impregnation has
been achieved and that polymerization has been completed, an acceptance

sampling program should be carried out. This program may vary in accordance with the practices of the individual highway agency.

Sampling

Depth of impregnation and degree of polymerization should be verified by obtaining core specimens of the completed job. Two core samples will be obtained from the area covered by each set-up of the heater or the impregnator, whichever covers the smaller area. However, in no case shall there be less than one core per 20 lane-ft (6.1 m) of bridge deck surface. The locations for coring should be designated by the owner's representative or engineer. All coring should be done at the expense of the contractor. The core diameter should be at least two times the maximum size aggregate particles in the concrete. The cores should be drilled to a depth of 1 in. (2.5 cm) greater than the specified impregnation depth and broken off by driving wedges into the annular-core-bit cut. The cores should be located so as to avoid cutting through the steel reinforcing bars in the deck. These can be located by means of a Pachometer or similar device. Each core must be identified as to location. The contractor will be required to patch the core holes with a polymer-aggregate mixture.

Testing

The owner's representative or engineer should perform the necessary inspection and measurements on the cores to assure compliance with specifications. All cores that exhibit the odor of methyl methacrylate should be placed in an evacuation chamber at 70°F (21 °C) and 2 cm Hg (3 kPa) for 24 hr before measurement of impregnation depth to remove nonpolymerized monomer. The cores should be etched with technical grade

concentrated hydrochloric acid until the depth of impregnation becomes
clearly evident. The minimum depth of impregnation observed around the
perimeter of each core should be measured and recorded.

Acceptance Criteria

The criteria for acceptance of the job without penalty are as follows:

1. The average depth of impregnation for all of the cores from
   one bridge deck shall equal or exceed the specified value.

2. The average depth of impregnation for the two cores from each
   equipment set-up shall equal or exceed the specified depth less
   0.5 in. (1.3 cm). Two additional cores shall be taken
   from each area that fails to meet this criterion, and the
   average of the four cores from the area must equal or exceed
   the criterion.

Penalties

In the event that the acceptance criteria are not met, penalties
shall be applied as follows:

1. Acceptance Criterion No. 1: The contract price shall be
   reduced by the amount:

$$\left[\frac{\text{Specified depth-average depth}}{\text{Specified depth}} \right] \text{ X Contract Price}$$

2. Acceptance Criterion No. 2: The contract price shall be
   reduced for each instance by the amount:

$$\left[\frac{\text{Area of setup}}{\text{Total deck area}} \right] \text{X} \left[\frac{\text{(Specified depth-0.5 in. [1.3 cm])-avg. depth}}{\text{(Specified depth-0.5 in. [1.3 cm])}} \right] \text{X Contract Price}$$

Notice that the penalties are additive. That is, if the average depth
for all cores is less than the specified depth and the average depth
of four cores from each of several of the individual equipment set-up

areas is less than the specified depth minus 0.5 in. (1.3 cm), the total penalty will be 1 plus the penalties for each of the deficient areas calculated in accordance with procedure 2.

SAFETY CONSIDERATIONS

General

All applicable national (OSHA), state, and local safety codes shall apply to protect the persons and properties of the owner and his representatives, the contractor and his employees, and the general public. Special conditions worthy of note here are high temperatures, volatile and highly flammable substances, noxious fumes, and vehicular traffic. The owner shall be responsible for traffic control.

Monomer

The highly volatile and flammable nature of the monomer (flash point = 55°F [13°C]) will require special precautions to assure that the liquid and its vapors are contained at all times. Extreme care must be exercised regarding the use of open flames, non-explosion-proof electrical gear, and smoking in the vicinity of all operations involving the monomer. Fire extinguishers suitable for Class B fires must be readily available whenever the monomer is stored or being handled or mixed and at the impregnation site. All workmen at the impregnation site should be thoroughly instructed in the use of the extinguishers. Water must not be used to extinguish fires associated with monomer.

Provision must be made by the contractor to safely dispose of all unused, catalyzed monomer.

Drying

The major hazards associated with the drying equipment are the high temperatures generated which could result in burns through carelessness and the propane gas used for firing the heaters. Provision must be made for securely anchoring the gas containers, both while they are being used and during storage.

When drying and impregnation are going on simultaneously at different locations on a bridge deck, special precautions must be observed to assure that monomer vapor or liquid does not come within near proximity of the heating device.

Impregnation

The major hazards associated with the impregnation process are associated with the handling of large volumes of the monomer. Every effort must be made to keep the monomer liquid and its vapors contained. Therefore, even if the impregnation is being conducted at atmospheric pressure (ponding), containment is required. Constant vigilance must be maintained for detection of monomer leakage. This includes the underside of the deck because the presence of cracks or other discontinuities that extend through the deck will permit rapid passage of the monomer to the underside, often long before the required depth of impregnation is achieved over the entire surface. If leakage occurs at gaskets, pressure must be reduced, and impregnation time adjusted accordingly. Workmen should wear chemical eye protection (goggles) when working in the vicinity of the impregnator and when the impregnation is to be carried out at pressures above atmospheric. Prolonged breathing of monomer fumes must be avoided.

For the safety of the public, the impregnator should be attended at all times. No unauthorized personnel should be permitted in the vicinity. Smoking, use of open flames, welding, and non-explosion-proof electrical gear are strictly forbidden in the vicinity of the impregnator.

Polymerization

The major potential hazard involved in the polymerization process is the possible escape of monomer vapors, especially during the initial stages. If hot water is used for the polymerization process, small, though potentially dangerous, quantities of monomer remaining on the surface may be volatilized creating a potential explosion hazard. Therefore, smoking, use of open flames, welding, and non-explosion-proof electrical gear should not be permitted in the proximity of the polymerization operation. Another potential hazard associated with the polymerization step is the hot water employed to initiate and maintain the polymerization reaction. Workmen should guard against careless acts that might result in burns.

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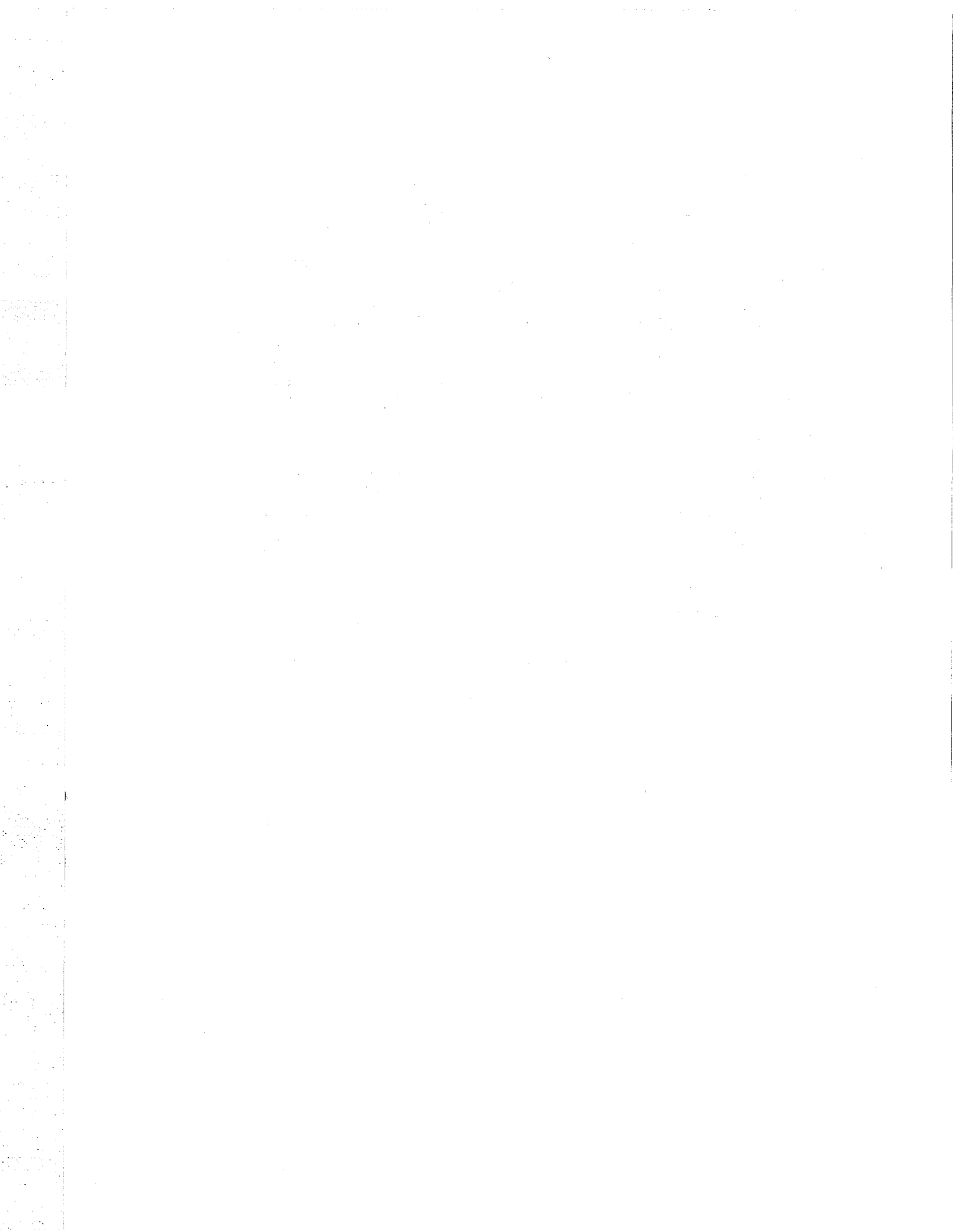
APPENDIX J

PROJECT STATEMENT AND AMPLIFIED RESEARCH PLAN

RESEARCH PROBLEM STATEMENT

Introduction

Deterioration of concrete bridge decks, reduction of skid resistance
on concrete surfaces, unacceptable concrete wear rates, and a need for
thinner and stronger concrete slabs are problems confronting every state
highway department. Considerable inconvenience and expense to the public
are caused by obstruction to traffic caused by reconstruction and making
repairs as necessary. Some of the major deficiencies of some of the con-
crete presently used are high permeability, low strength, cracking, low wear-
ing ability, and spalling. The mechanisms causing deterioration include
frost action, differential expansion and contraction, reinforcement corrosion,
chemical attack, traffic loads, and wear.

Polymer-impregnated concrete has been reported to provide signifi-
cant increases in strength and durability. However, present developments
and techniques have not progressed to the extent that they are adequate
for field use; therefore, more work in this area is required.

Objectives

The overall objective of this project is to develop the technology
for the economical use of polymers to improve the serviceability of con-
crete in highways. The immediate goal of this project concerns economi-
cally feasible methods for impregnation of both old and new concrete bridge
decks in place.

More specifically, the work shall include the following and shall be
structured to consider all known related work completed or in progress at

such institutions as the U.S. Bureau of Reclamation, Brookhaven National Laboratory, and the University of Texas so as to avoid unnecessary duplication of effort:

1. Select a chemical system such as methyl methacrylate or polyester styrene and appropriate catalysts, accelerators, etc.

2. Develop field techniques and apparatus for surface impregnation of concrete using the selected chemical system. The apparatus shall be scaled for field use on bridge decks, although not necessarily developed to the stage of a production item.

3. Evaluate the effectiveness of the technique as related to (a) properties and condition of the concrete to be impregnated, (b) preparation of concrete for impregnation, and (c) properties of impregnated concrete (especially durability, skid resistance, abrasion resistance, strength, impermeability, etc.).

4. Demonstrate the techniques in the field on one or more existing bridge decks, and conduct tests thereon as in item 3 above. At least one of the decks shall be chloride contaminated but otherwise sound except for areas of steel corrosion. If possible, tests will also be run on the bridge at the Pennsylvania Transportation Research Facility in order to provide information on the effects of controlled loading. Impregnation to the bottom of the top layer of reinforcement, or to a depth of 4 in. (10 cm), shall be sought.

5. Prepare a manual describing procedures that may be used to routinely impregnate concrete bridge decks.

AMPLIFIED RESEARCH PLAN

Introduction

The specific research approach, including the literature survey and technical plans designed to meet the objectives outlined in the RFP, will now be presented.

Literature Survey and Liaison

The investigators will update their existing surveys of the technical and patent literature, and will consult with individuals, institutions, and organizations in this country and abroad who have had experience with the polymer impregnation of concrete, especially as related to highway applications.

Organizations will include: the Federal Highway Administration, PennDOT, the Brookhaven National Laboratory, the Bureau of Reclamation, the Waterways Experiment Station, the Concrete Research Laboratory of the Danish Atomic Energy Commission, the Concrete Research Institute of Norway, the Portland Cement Association, the American Concrete Institute, the American Cement Corporation, and the RILEM.

Liaison will be maintained with individuals and organizations throughout the contract period; a running file will also be maintained on technical developments reported in the literature. Visits will be made to facilities doing similar work; in particular, at least one visit will be made to the facilities of the University of Texas, the Bureau of Reclamation, and the Brookhaven National Laboratory by the principal investigator or his delegate.

There will be participation in symposia if appropriate. Several such

symposia are anticipated, including one sponsored by the American Concrete Institute in March 1973; one sponsored by the Highway Research Board during its annual meeting, 1974; and one planned by the Polymer Division, American Chemical Society, for its annual meeting, September 1973 (Chairman, J. A. Manson).

The state-of-the-art survey will be made available to committee members.

Selection of Monomer System

Selection will be based on the best and most recent information available from the sources mentioned above, and on an analysis of other ideas generated. Both fluid monomer and prepolymer systems will be considered thoroughly, including MMA, styrene, mixtures of monomers, crosslinking monomers, and epoxy and polyester-styrene resins. The best of the monomer and prepolymer systems will be selected, based on the likelihood of meeting the best combination of the following materials and application requirements:

1. Ability of monomer or prepolymer to physically wet and penetrate into the pore (and, preferably, capillary) system of the concrete to the depth agreed on above (if possible, to 4 in. [10   cm]) with a minimum of evaporation and drainage. To achieve this, attention will be given to selecting both viscosity and surface tension characteristics, or modifying them by the use of thickeners or surface-active agents.

2. Ability to be polymerized in situ (in a typically alkaline matrix) at ambient temperatures if possible, without excessive shrinkage.

3. Ability of the resulting polymer to resist excessive swelling by water, which will tend to develop undesirable internal stresses and permeation of water and salts, specifically sodium and calcium chloride.

4. Ability of the polymer to retain its mechanical integrity and, if possible, to contribute to the strength and toughness of the impregnated layer on exposure to water, temperature cycling, freezing and thawing, and the basic (alkaline) environment characteristic of at least new and relatively new concrete.

5. Ability to meet acceptable standards for abrasion or polishing, and skid resistance.

6. An acceptable overall cost, evaluated in terms of original materials and labor costs, as well as expected durability.

7. Adaptability to scale-up application in the field, using labor of variable skill, with concern not only for the application itself, but also for such factors as toxicity and environmental acceptability.

Screening tests will be conducted using small specimens of mortar and then concrete (3-in. x 6-in. [7.6 -cm x 15.2 -cm] cylinders) to determine the inherent feasibility of impregnation and polymerization or curing in situ. The concrete mix will be standardized to permit comparison of results from different groups. Evaluation of impregnation will include, as appropriate: penetration rates of either monomers or polymers; drying procedures such as thermal heating or solvent exchange; other surface treatments such as washing or etching; vacuum, pressure, or thermal gradient techniques to promote penetration; use of carrier liquids, surface active

agents, and aqueous dispersions. The latter would be inherently desirable for several reasons, but the possibility requires verification, especially with respect to whether or not complete fillage of the pores is required. Catalyst systems to be considered, depending on the monomer, include peroxides, azo compounds, amine or ferrous ion activated peroxides, amines, and dianhydrides, and the use of aqueous dispersion techniques to control catalyst release. Particular attention will be given the new activated two-component catalyst systems recently described by the groups at the University of Texas and the Brookhaven National Laboratory. Preliminary evaluations of corrosion resistance will be conducted using accelerated tests such as immersion in diluted hydrochloric acid. Typical mechanical properties will also be determined on specimens which show uniform penetration and satisfactory performance otherwise. The best systems will be applied to slabs simulating deck sections.

To expedite progress with field evaluation, the monomer selection work will be in two parts. First, the Brookhaven and Texas catalyst systems (monomer type) and several existing epoxy and polyester-styrene systems will be tried, and the best applied in scale-up tests as soon as possible. Development of improved or replacement systems will run concurrently.

In any case, candidates will be tried on large slabs as soon as practicable.

Development of Techniques and Apparatus for Field Impregnation

Virtually the entire existing body of knowledge in the area of polymer-impregnated concrete deals with evaluation of various chemical systems in the laboratory. While screening as described previously is certainly needed, a major aspect in applying the demonstrated benefits of polymer

impregnation (already demonstrated in the laboratory) to bridge decks is the development of techniques and apparatus to implement field application. A major problem is that in addition to the obvious problem of how to get the monomer into the bridge deck, one must recognize that, especially with old decks, some surface preparation is going to be needed to "open the pores" of the concrete. Older deck surfaces such as those of prime interest in this project will be contaminated to varying degrees with grease, oil, rubber, dirt, etc., which will inhibit any impregnation process. Salt may well also inhibit impregnation, though its precise role will have to be established. Approaches will include two general ones: cleaning, drying, and penetration from above; and pumping through to drilled holes.

Preparation of Deck. Cleaning processes which appear to offer most promise at this time include: use of solvent, lye wash (NaOH), sand or grit blasting, scarifying, and combinations of the above.

It is anticipated that these methods, and possibly others, would be first evaluated in the laboratory on cores or sections removed from existing bridge decks. Then, the most promising technique or techniques would be tried in the field. Evaluations would be based on microscopic investigations. It will probably be necessary to dry the concrete before impregnation. It is proposed to investigate several possible alternative techniques for drying the deck surfaces, including the following: infrared or microwave radiation, blowtorch devices, salamanders or similar devices, and electrical resistance curing blankets.

The most promising techniques will be tried out on a bridge deck in the field using Monfore relative humidity gages or the stacked disc technique, both of which have been used successfully by researchers at Penn State in the past.

Impregnation. In view of the stated goal of deep penetration, this stage of the project is viewed as the most difficult stage of the proposed research program. While it is a simple matter to apply vacuum or pressure or both in the laboratory to cause impregnation, the added difficulties presented by field conditions are obvious. One approach to this problem, which will be carefully examined, is to maximize the wetting ability of the monomer either by choice of monomer or by addition of surfactants or a combination of these. In this way, the monomer need only be pooled over the surface and impregnation will occur by capillary attraction. Experience by others, however, has shown limited success in terms of depth of penetration, so that vacuum or pressure techniques must be considered.

Although vacuum techniques appear at first sight to be unsuitable, pressure methods should be investigated. The method of drilling holes at appropriate distances and pumping the fluid has been tried by several investigators with limited success due to uneven distribution of fluid. To overcome this difficulty, a pressure mat ($\sim$ 150 to 200 sq ft [13.9 to 18.6 m^2]) could be used which would be held in place by a weighted trailer or similar device.

The pressure mat consists of a steel head plate with a flexible flange of vulcanized rubber which is forced against the concrete surface by the weighted trailer. Monomer is then fed through a series of small holes in the back of the head plate and forced into the concrete by air (or nitrogen) pressure. In order to maintain a seal between the head and the concrete surface, the applied pressure times the area must be less than the weight of the trailer. The time required for impregnation will

depend on surface preparation, concrete permeability, depth of penetration required, and applied pressure. The pressure can be varied according to the condition and strength of the bridge deck. The novel idea of providing vent holes in the concrete deck will also be tried. The holes being open to atmospheric pressure will provide a quick circulation and thus cut down on the time of impregnation. Also, this arrangement will economize the loss of monomer since the extra monomer can be recovered through the vent holes after required depth of penetration has been achieved.

The impregnation area, being completely covered during impregnation, will also tremendously reduce the loss of monomer due to evaporation. The impregnation can be continued until sufficient monomer is collected through the vent holes. This will ensure uniform depth of penetration.

Impregnation by thermal diffusion has been suggested, and will be tried also; this process would entail heating the surface of the concrete to be impregnated and allowing the monomer to progress by thermal diffusion toward the cold face (bottom) of a slab. Penetration may also be aided by use of a readily absorbed carrier material (which may or may not be incorporated later in the polymer) as a vehicle in impregnating the concrete with a monomer; an aqueous dispersion of monomer or polymer might be especially attractive.

Polymerization. Once the concrete has been impregnated with monomer, it will have to be polymerized. Thermal methods employing IR or microwave heating devices appear to offer considerable promise, providing that the volatility of the monomer system will permit the use of elevated temperatures. Alternately, an activated catalyst system, which can be

self-heating, should be feasible. Indeed, in principle, it should be possible to scale-up and apply any of the systems discussed above. Precautions will probably have to be taken to minimize evaporation, e.g., by use of a membrane or water.

In any case, it is assumed that existing bridge decks will be used for study; at least one will be contaminated with salt but structurally sound. Techniques which work on old decks should work on new ones probably with the elimination or simplification, rather than addition, of steps. Equipment used will be of a scale suitable for the impregnation of full-scale decks.

Evaluation of Field Techniques

The effectiveness of the technique selected as related to the properties and condition of the concrete to be impregnated and the preparation of the concrete for impregnation will be evaluated in both laboratory and field studies. In particular, evaluation of the effectiveness of the impregnation techniques as related to the properties of the concrete is required. In this case, it will be necessary to test selected impregnation techniques on concretes of varying porosities (varying water/ cement ratios). Air content will be maintained in the range of 6 ± 1 percent, which is typical of good paving concrete. It will be necessary to determine whether or not air content must be considered as a test variable. In general, the air voids are frequently considered to be isolated and discrete in contrast to the more or less continuous capillary system that results from the hydration process and varies in extent with the water/cement ratio of the concrete mixture. However, there may be connections between the voids and the capillary system.

The method for evaluating the effectiveness of the selected techniques as related to preparation of the concrete would consist of microscopic examination of etched cross sections of specimen removed from test areas of field concrete that had been prepared, impregnated, and cured in the manner or manners selected.

The effectiveness of the technique as indicated by the resulting properties of the impregnated concrete will be evaluated in terms of properties selected from the following with whatever adaptation may be required:

1. Freeze-thaw durability (ASTM C-671)

2. Resistance to deicer scaling (ASTM C-672)

3. Skid resistance: standard broom finish and British portable skid tester (ASTM E-303)

4. Permeability: use air permeability extrapolated to infinite mean pressure (see NCHRP Report 15)

5. Tensile and compressive strength through indirect tensile tests, simple compressive tests, and flexural tests

6. Static and dynamic modulus of elasticity

7. Abrasion resistance: shot blast test or a modified test (ASTM C-418)

8. Fatigue strength

9. Creep behavior.

The above tests will be carried out only to the extent necessary to supplement the existing body of experimental work already developed elsewhere, e.g., in the Bureau of Reclamation, Brookhaven National Laboratory, or University of Texas studies. Tests shall be selected to reflect the emphasis

on permeation characteristics, both as observed after impregnation and after a suitable period of service; tests shall be conducted on only the most promising candidate systems. Mechanical tests may be used when appropriate for characterization of uniformity and soundness of the concrete, though they are not of interest per se in this application. ASTM standard test speciment and procedures will be used when applicable, as indicated above, with sufficient replication to provide results significant at the 95 percent confidence level. Preliminary evaluations will be made using appropriate slabs or other specimens.

The next stage will be selection of suitable bridge decks, with the cooperation of PennDOT, for trial of the best techniques. At least one deck will be selected to meet the following criteria (based on core sampling):

1. Mechanically sound

2. Contaminated with chloride

3. Exhibiting an active corrosion potential

4. Reasonable proximity to test facilities.

The third criterion may be assessed in terms of a standard technique such as the Stratful method.

Subject to the obtaining of permission, tests will be run with controlled traffic loadings using the Pennsylvania Transportation Research Facility In this phase, at various locations in the bridge deck, the top reinforcement is placed at depths varying from 1/2 in. to 2 in. (1 cm to 5 cm) and deicers (NaCl and $CaCl_2$) will be applied during the winter months to develop a contaminated deck. Before impregnation, the structure will be loaded with greater than one million cycles of variable axle loads

which will be equivalent to at least one million cycles of an 18 kip axle.

Data Analysis and Measurements

The following measurements and observations will be made at various stages of the test program:

1. Survey of bridge deck (non-test-track)

    a. Complete survey of bridge deck, recording all visible cracks resulting from static loading.

2. During repeated load tests

    a. Detailed load history (test track)

    b. Weekly survey of crack patterns

    c. Weather conditions.

3. Corrosion tests (concurrent with repeated load or during inclement weather by Stratful [California] method)

    a. Map of concrete deck deterioration

    b. Crack pattern over reinforcing bars.

The test data will be analyzed as they become available. Data from the several different deck areas will be compared.

Preparation of Field Manual

Throughout the program, technical procedures will be continuously revised and updated, with attention to both desirable and undesirable procedures, and with an eye to the drafting of a manual suitable for use in the field. Thus, when the contract is completed, the writing of a suitable manual will have been simplified.