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1. Problem and Objectives

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 that confront every state highway department. The public experiences considerable inconvenience and expense as a result of obstruction to traffic caused by reconstruction and making repairs as necessary. Among the major deficiencies of some of the concrete presently used are high permeability, low strength, cracking, low wearing 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 significant 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 ares is required.

The over-all objective of this project is to develop the technology for the economical use of polymers to improve the serviceability of concrete in highways. The immediate goal of this project concerns economically feasible methods for impregnation of both old and new concrete bridge decks in place.

To avoid unnecessary duplication of effort, the work is 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.

More specifically, the work is to include the following:

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1. Selection of a chemical system such as methyl methacrylate or polyester-styrene and appropriate catalysts, accelerators, etc.

2. Development of field techniques and apparatus for surface impregnation of concrete using the selected chemical system. The apparatus will be scaled for field use on bridge decks, although not necessarily developed to the stage of a production item.

3. Evaluation of 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. Demonstration of the techniques in the field on one or more existing bridge decks, and tests thereon as in Task 3(c). At least one of the decks will be chloride-contaminated but otherwise sound except for areas of steel corrosion. Impregnation to the bottom of the top layer of reinforcement, or to a depth of 4 in., will be sought.

5. Preparation of a manual describing procedures that may be used to routinely impregnate concrete bridge decks.

The program is being conducted jointly by Lehigh University and The Pennsylvania State University.

2. Effects of Drying

It is demonstrated that adequate drying rather than penetration per se is a major problem in obtaining deep impregnation in the field. Various methods have been used by groups at BNL, BuRec, and the Kansas Highway Commission, e.g., methods based on gas-fired infrared, RF, microwave, hot air, flame, and electroosmosis devices. However, the best method for the case of deep penetration is demonstrated here. Cost is considered in terms of effectiveness, as has been done for limited-depth-drying at the BuRec facility.

Drying tests were conducted using both small mortar specimens and

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large concrete slabs.

2.1 Mortar Cubes: Effect of Drying on Monomer Loading and Moisture Absorption

A series of tests were conducted to investigate the effect of mortar moisture content on monomer penetration and subsequent water absorption of the polymer loaded mortar. Mortar cubes (ASTM C 109-70T) were cured for $11\frac{1}{2}$ days and then conditioned to various moisture contents (0 to 70% of saturation by drying in an oven for a specified period of time. It is realized that the moisture contents are approximate values. The cubes were then soaked in methyl methacrylate (MMA) for 36 hours, polymerized and soaked in water for 48 hours.

It is found that the water absorbed after polymerization is proportional to the moisture content prior to impregnation, but approaches to within 15% of its limiting value as the moisture content is decreased to 20% of the saturated value. As expected, the monomer loading also approaches closely to the maximum observed for the fully dried specimen. It seems possible therefore that removal of 80% of the water at saturation may be adequate for acceptable performance of an impregnated specimen though acceptability in terms of impermeability remains to be shown.

2.2 Mortar Cubes: Different Modes of Drying

Several means of drying are being evaluated and compared; the methods include ambient air, hot air, infrared, RF, and oven drying. It is found that a smooth inverse relationship exists between the surface temperature reached (regardless of the heat source) and the amount of moisture remaining.

2.3 Mortar Cubes: RF Drying

Since a high surface temperature is needed for deep drying with an external heat source, the possibility of using RF or microwave techniques (each of which generates internal heating of the absorbed water) is of interest. These methods have also been investigated in a preliminary way at

the BNL and BuRec facilities, and are reported to show promise. Though cost will be high, and perhaps too high for drying to obtain shallow penetrations, the great potential efficiency may offset the high cost in the case of deep drying.

Indeed, RF drying of mortar cubes has proved to be the fastest means investigated to date. Three water-saturated mortar cubes were dried in a 500-watt RF oven using different energy absorbing and cooling cycles, but with the same total energy absorbing and cooling times. In this preliminary experiment, the temperature inside the mortar cubes was not recorded. No damage due to excessive boiling of water was observed.

Because of these encouraging results, RF drying of concrete and reinforced concrete will be investigated in more detail. It should be pointed out that considerable engineering research may be required for application in the field. However, as pointed out in the recent BuRec study, the cost of RF should be less than that of microwave equipment.

2.4 Drying by Electro-Osmosis

Investigations are being conducted as to the feasibility of using this technique to impregnate wet concrete with a monomer under the influence of a DC power supply. Saturated concrete blocks (3"x3"x8") were used in the preliminary experiments, and the monomers tried were MMA and tertiary--Butyl styrene, with AZN as initiator. While appreciable impregnation did not occur in either case, the electrical behavior suggested that migration of monomer did occur sufficiently to produce an insulating barrier to electric current. Work is continuing, but it appears that considerable scientific and engineering data need to be acquired before this technique can be applied in the field.

2.5 Concrete Slabs: Drying Techniques

As may be expected, thorough drying of slabs is absolutely necessary if adequate polymer loading is to be achieved. A partially dried slab (24"x 24"x6") exposed to the same conditions of impregnation pressure and time as

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a well dried slab (30 psi for 24 hours) roughly took up only enough monomer to replace the water lost in drying. To determine the kinetics of drying 6" thick slabs in oven, continuous weight measurements were taken during the process of drying at 250°F. Results of numerous tests indicated a time of 45 hours for complete drying. The kinetics of drying exhibit a dependence on $t^{\frac{1}{2}}$, as would be expected for a diffusional process.

Because of the beneficial role of a high air velocity at the heated surface of concrete being dried, two experimental devices have been constructed to permit rapid movement of hot air across the surface of slabs:

1) a kerosene fired heater blower combination, and 2) a propane-fired torch assembly.

2.6 IR Drying

A drying study has been completed on $8"x4\frac{1}{2}"$ concrete blocks. The data obtained include the weight loss and temperature gradient over the $4\frac{1}{2}"$ block. The heating source (IR lamps of various power and heat gun) was applied for extended time intervals.

It appears from this study, that to dry a bridge deck for impregnation to 4" depth in a reasonable length of time, that surface temperatures above 300°F is required.

2.7 Gas Fired Torch Assembly Drying Procedure and Observations

Since the torch assembly is capable of generating very high temperatures and circulation of air, the work was begun using 2 torches to heat up a $24"x24"x6"$ slab from the surface by continuously moving the assembly back and forth over the area. However the consumption of gas by the wide flame torches with standard orifices was excessively high (8 lbs/hour/torch) so that at a surface temperature of approximately 900°F the surface began to spall after 10 minutes. This is consistent with the findings of other researchers, notably the groups at Brookhaven and the Bureau of Reclamation, who observed the spalling problem when a bare concrete surface was heated to as low as 300°F in the

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field. Hence to take care of the problem, heat was immediately reduced and heating was continued with only one torch. In addition, a one-inch sand layer was successfully used as a heat transfer medium on the surface to prevent direct impingement of the flame on the surface and to minimize thermal stresses. In subsequent tests including gas-fired infrared heating tests on the PennDOT bridge deck, the spalling problem was completely avoided with the use of a sand layer on the surface of the concrete, the temperatures reaching as high as 400°F on the surface, and, in the case of slabs, 700°F.

During the course of the experiments, it was interesting to note that for each slab, after an hour of heating, the liquid water started to come out from all sides and bottom of the slab at places where the rebars and inserts were located. This is possibly due to steam formed in the upper region pushing the vapor and liquid water down and out through the path of least resistance, namely around the bars located at 4" below the surface and the inserts, through the water channels created around them during the set-tling down of heavy particles in fresh concrete and the path left by the sub-sequent evaporation of water. Small cracking running over the length of rebars could be seen during the process of further heating, but the cracks closed down completely on cooling the slabs and were not visible to the naked eye.

Results

The experiments were made in such a way that continuous weight measurements could be taken during the process of drying and a continuous curve of drying time versus percent moisture loss could be obtained. It is found that at a surface temperature of 900°F, the slab loses moisture initially at a slower pace, since it is heated from one surface and it takes time to raise the temperature of the slab enough to establish a steady-state of drying. For slab 1 the rate increases until about 30% of moisture is lost, at which point the rate becomes steady at 13.3% moisture loss/hour of heating.

During this phase of drying, the moisture possibly migrates in the liquid phase and escapes from the surfaces in at least a partially liquid form. Such loss proceeds until about 70% of moisture is lost and then there is a sudden drop in rate to another constant rate of 5.3%/hour until almost all the water is lost. The appearance of a second constant rate probably indicates that the 30% of the moisture remaining starts diffusing from the surface in the vapor state. Thus drying at high surface temperatures exhibits kinetics of a nature significantly different from the normal diffusional kinetics exhibited on drying concrete at lower temperatures. For slab 1, drying was stopped when 92% of moisture was removed, the percentage moisture loss calculation based on our experience of the total moisture loss that occurred from slabs of the same mix and batch when dried in the oven until constant weight was achieved.

To take further precautions against spalling and cracking problems, and to avoid using excess heat and large amounts of gas, the size of the orifice of the torch was reduced to such a size that the flame remained blue even at 3 psi pressure of gas as compared to 40-50 psi gas pressure required with the original orifice. The consumption of gas was thus reduced to 3 lbs. of gas/hour/torch. Also a special hood was designed to accommodate and cover 2 torches and spread the flame to further reduce the loss of heat. The rate of drying decreased due to the lower heat output and reduction of surface temperatures from 900°F to 700°F. No spalling was encountered and no cracks were visible whatsoever on cooling the slab and removing the sand layer after the test. Again, two regimes of constant drying rates are exhibited.

It was also observed that on allowing the slab to cool over night the slab lost 3/4 lbs. or about 4% of moisture. Thus, alternate cooling and heating cycle may help in moisture migration to the surface and its efficient removal. To observe this effect further, slab 3 was intermittently heated. In the first heating period of 2.5 hours, the slab lost 6.5 lbs. of water (equivalent to 36% of moisture). The slab was then allowed to cool for 19 hours, during which time lost another 2 lbs. of water (11% moisture). The

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slab was heated again for 5 hours at which time it had lost another 7 lbs. of
water (39% water). The slab was allowed to cool and the reading taken after
16 hours of cooling showed a loss of another 0.5 lb. of water (equivalent to
3% water) to give a total moisture loss of 89% moisture in $7\frac{1}{2}$ hours of heating.
Hence, as was reported earlier for RF drying, the judicious use of heating
and cooling cycles permits higher efficiencies of fuel utilization. Such
cycling could probably be utilized in the field, perhaps by systematically
cycling heating and cooling every hour, or perhaps by specifying the maximum
and minimum safe temperatures for cycling so that the torches could be shut off
when the surface temperature reaches the upper limit and resumed again when
the temperature falls to the lower limit.

Economy of Torch Heating

The average consumption of gas, obtained from the experiments above,
to completely dry 24"x24"x6" slabs, was of the order of 100 lbs. Thus it
would take 5 to 6 lbs. of gas to remove one pound of moisture giving a cost
figure of 50 to 60¢/lb. of moisture to be removed. Although this is high
compared to other estimates, e.g., by the BuRec group, it should be emphasized
that the latter estimate refers to drying of the top layer of concrete, and
not the whole slab, as was the case here. As observed above, the drying rate
falls approximately three times in the 2nd constant rate phase; it takes more
time to remove the last 25% of water than to remove the first 75% of water
from the concrete slab. If this latter portion of heating could be avoided
a considerable savings in cost could be realized. It remains to be seen if a
good loading of monomer could be achieved during impregnation, and comparable
strength and durability could be obtained by removing only ~70% of the moisture.

Field Application of Torch Drying

The cost figures given above are applicable only to the slabs dried
in the laboratory. However, in the field further economy could be achieved
by alternate heating and cooling and by scaling up the apparatus to cover a

much wider area to utilize the heat and time much more efficiently. Thus the
travel of the torch assembly, covering one lane with 6 torches, can be made
as long as 20 feet so that a) no overheating will take place at a section since
the travelling assembly will take longer time to come back to the same section,
b) the possibility of excessive temperatures on the surface will be reduced
c) temperature cycling can be effected on the surface at each section, with
cooling occurring between the two consecutive passes (thus creating a mini-
temperature hysteresis cycle which will help in moisture migration) and d)
reduce the overall time required per square feet of slab surface to be dried
due to the large area covered. All these together could conceivably reduce
the cost to as low as ~30% of the value found in the laboratory.

Summary

        In summary, it may be concluded that drying with torches, with the
proper application of precautions against surface spalling and cracking (by
keeping temperatures preferably below 500°F and using sand layer on the sur-
face) seems to be highly promising for field drying of large areas of bridge
deck. The advantages of using this method are given below.

        1.   It becomes relatively cheaper, the larger the area that could
be dried.

        2.   It could be completely automated like the unit developed in
the laboratory.

        3.   The drying time is less than most of the other methods of
drying developed due to the use of uniform and high temperature heating, as
there is a direct relationship between temperature and moisture removal.
Heating with torches from one side only was approximately 4 to 6 times faster
as compared to oven drying at 250°F, with all concrete surfaces exposed.

        4.   There is no doubt that heating at high temperatures will create
numerous connected microcracks throughout the depth of concrete even if surface
spalling and big cracking could be prevented as explained before. These

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microcracks will inevitably reduce the strength of concrete slightly (probably a primary reason for the lack of work in this area of high temperature drying). However any microcracks will be filled later by monomer during impregnation which will bridge the crack after polymerization. Prior evaluation of strengths of flame dried 3"x6" impregnated concrete cylinders (see ACI-SP40-17) gave approximately the same results as impregnated concretes dried by conventional methods and also an improvement of nearly 250% over the control concrete.

5. One benefit of the connected microcracks formed when concrete is heated at high temperatures is that they act like reservoirs of monomer for the micropores and capillary canals and also facilitate impregnation by forming efficient and continuous paths for deep penetration. This reduces the time of impregnation and also allows much more uniform distribution of monomer throughout the depth of the slab. The need for high pressures during impregnation should also be minimized. Thus work done on the drying of 2 slabs so far show that the time taken is reduced by ~20% as compared to oven dried slabs. Cores taken from these slabs also show the uniform distribution of monomer and fracture of the aggregate when split for visual observation.

6. This method of drying will allow the burning off oil, rubber, dirt and other foreign matter trapped in the pores of the surface layer. These impurities block the channels and thus hinder impregnation besides causing problems during polymerization and they must be removed before impregnation can take place. Using this method, the costly process of preparing and cleaning the surface may be avoided reducing the overall costs for treatment.

2.8 Drying with the Blower Heater

Drying with the kerosene fired blower heater was tried with limited success. Drying the slab continuously at 224-240°F for a total of four days, showed a net moisture loss of only 76%.

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3. Determination of the Rate of Penetration
3.1 Impregnation of Cylinders

A potentially useful method for predicting penetration rate in the field--a critical problem in this program--was developed. Penetration rates for a variety of liquids, from water to methacrylates, were measured using small, dried mortar cylinders (porosity ~14-15%). Interestingly, with the exception of acetone (see next paragraph) liquids penetrated to the same extent at equilibrium, though at different rates. The specific rate itself, which has generally not been measured in most studies, was found to be high initially, but to decrease to a fairly steady value after 10 min. for styrene, a value of 1.6×10^{-3} $gm/min/cm^2$ of surface. This result may be used to predict penetration rates in the field. For example, this rate would correspond to a rate of 3.3×10^{-3} $lb/min/ft^2$ in a slab covered with ponded styrene at atmospheric pressure, and to a penetration time of 10 hrs. to achieve the loading goal (for 4" penetration in a 14.5% porosity substrate) of 2 lb/ft^2. This value is in the same range as that reported at the ACI meeting by Fowler for a 2" penetration by methyl methacrylate (which resembles styrene in its rate) measured during inherently less controlled experiments in the field.

Several other observations were made about porosity: (1) Acetone was found to irreversibly increase the porosity slightly--suggesting that acetone might be a good penetration aid (apart from its flammability). (2) The porosity of 3-year old mortar specimens was found to be only ~9%. Porosity data for both mortar and concrete specimens are being correlated with penetration characteristics. (3) The rates for TMPTMA are much less than for MMA--implying the possibility of a separation of monomers as penetration proceeds. This could be an important point, for TMPTMA is commonly used as a crosslinking agent. (4) The presence of 1% sodium chloride does not affect the penetration of MMA.

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3.2 Impregnation of Slabs

In view of the success achieved on impregnating the first slab, more tests were carried out on 24"x24"x6" concrete slabs to determine the effect of process conditions such as pressure on the rate and depth of impregnation. From the tests it is found that the increase in pressure reduces the time of impregnation remarkably. The depth of penetration, h, in a mortar or concrete of given porosity to the time, t, and the applied pressure, ΔP are related by

$$h = \chi^1 \ t^{1/2} \ \Delta P \ (\gamma/\eta)^{1/2} \tag{1}$$

where χ^1 is a function of pore radius and contact angle, and γ and η are the monomer surface tension and viscosity, respectively.

The rate of penetration is found to be very dependent on applied pressure. Indeed, h is a linear function of ΔP (and not of $(\Delta P)^{1/2}$ as would be predicted by the usual analysis of capillary forces); hence the time to reach a given depth, h, is proportional to $(\Delta P)^2$.

This conclusion is not affected by the fact that a range of times is given. In practice, a range is noted between the time for the observation of first seepage of monomers at the bottom, the impregnation being done from the top surface, and the termination of impregnation. Monomer first seeps through the channels left by evaporating water and through the microcracks but more time is needed to fill up the micropores and big voids in concrete, so that impregnation is continued even after the first observation of monomer at the bottom of the slab.

The advantages of using vacuum and pressure over the whole surface of the slab are obvious when impregnated slabs are broken open for observation. The unpolished surface of the section shows uniform dark coloration throughout the depth of impregnation which was also uniform in the whole impregnated area. In the impregnated area, fracture has taken place in the aggregate rather than around it, as in the unpolymerized section. This indicates the good quality of impregnation achieved.

The vacuum period used, before feeding the monomer and pressurizing, was standardized at 1½ hours. Pressure was varied from 30 to 80 psi and it was observed that a small amount of leakage through the gasket occurred at pressure above 60 psi. Also, at 80 psi tensile cracks developed in the bottom portion of the slab through which the monomer leaked in first 30 minutes. However, although such high pressures may not pose such a problem for 10" or more thick slabs in the field, good impregnation can be achieved within a reasonable time with 60 psi pressure.

All impregnated slabs except No. 2 were polymerized using steam introduced in the chamber and played on the surface of the slab covered with plastic sheet. This minimized the evaporation losses and no losses seemed to occur from the surface of the slab. Slab No. 2 was polymerized by ponding hot water on the surface of the slab for 8 hours. However the water temperature dropped during the course of polymerization from $140^{\circ}F$ to $110^{\circ}F$ so that full polymerization was not achieved resulting in loss of monomer in the bottom portion of the slab.

The effect of salt concentration is of considerable interest. Slabs 4, 5, and 7 were first dried to constant weight and then soaked in salt solution to constant weight. On subsequent drying, it was found that slabs 3 and 5 picked up 0.25 to 0.35% salt by weight and slab 8, soaked in a more concentrated solution, picked up 0.7 to 0.85% salt by weight. Penetration times for slabs 3 and 7 show that the penetration rate fell slightly due to salt throughout the depth of the slab. However this may not be of much practical significance since the maximum salt concentration lies below 0.3% and salt intrusion is effectively limited to the top 2" of the deck for most bridge decks. Estimated monomer loadings were in the range 5.0 to 5.5% for plain concrete and 4.5 and 5.0 for salt-contaminated slabs.

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3.3 Monomer Contact Angle

Previous results reported showed that a methyl methacrylate solution
(MMA + 0.5% AZN) produced no readable contact angle data on concrete and
concrete contaminated with motor oil and linseed oil. Additional contact
angle data were obtained on an especially dense cement paste (1% porosity);
again no measurable contact angle could be observed. These results may be
due to the spontaneous wetting of the MMA on the surface and to the fact that
motor oil and linseed oil readily dissolve in MMA.

Additional results have been obtained using non-contaminated con-
crete and concrete contaminated with salt, motor oil, grease and linseed oil.
Epoxy resin has been used for these contact angle tests because this system
does not tend to dissolve any of the contaminents.

Test results indicate that the contact angle will increase for
monomers that do not dissolve the surface contaminants on concrete. If the
surface contaminants are dissolved by the monomer, as in the case of MMA,
the contact angle does not appear to be influenced, but the dissolved surface
contaminants may be carried into the concrete by the monomer during impregna-
tion. Investigations are presently being carried out to observe if any of the
contaminants affect the polymerization of epoxy and MMA. Preliminary results
indicate that the curing of epoxy, a resin which does not dissolve the con-
taminants, is not affected. However, effects of contaminants on the poly-
merization of MMA, which dissolves the contaminants, remain to be determined.

4. Effects of Salt Contamination

The effect of salt contamination on drying with a propane burner was
investigated.

For the first study, 3x6 in. cylinders were contaminated by sub-
merging in salt solution and subsequently dried to constant weight. Eight
specimens were prepared with 0.77% (CI), and eight specimens with 0.36% salt
(CII).

Impregnation with MMA and 0.5% azobisisobutyronitrile was carried out using $1\frac{1}{2}$ hours of vacuum (28 in. of mercury). After the monomer was added the specimens were kept under pressure (60 psi) for an additional $1\frac{1}{2}$ hours. Finally, the specimens were submerged in warm water (70°-80°C) for 6 hrs. to polymerize. The average polymer loading was 5.1% for specimens CI, and 4.9% for specimens CII. This was about the same or slightly more than for specimens without salt contamination. Since the specimens with the largest salt concentration 0.77% (CI) also gave a slightly higher polymer loading, further experimentation was carried out to see whether more water could be dried out from the salt contaminated specimens, and thereby provide more space for the polymer inside the specimen.

The specimens were cured for 28 days, dried to constant weight and thereafter submerged in salt solution. At the same time control samples were submerged in plain water.

All specimens were weighed wet before drying again at 125°C. No weight loss could be recorded for the controls after 24 hours. This was not the case for the salt contaminated specimen, which required 52 hours to dry completely. Both the controls and the salt contaminated specimens lost on the average the same amount of water (91 grams) but 8 grams (or 0.54%) of salt was left in the second group.

To determine the effect of rapid drying, 30 cylinders were dried with the propane burner used to dry the concrete slabs. The specimens were dried for 8 hours under 2 in. of sand at approximately 750°F. Visual inspection showed no apparent cracks in the cylinders.

Specimens CII were dried at 125°C for 24 hrs., immersed in 3% sodium chloride solution for 24 hrs., and redried for 24 hrs., prior to impregnation. The CI specimens were given an additional salt soaking, before the final drying. Specimens DI and DII were soaked for 48 hrs. in the salt solution (D in plain water) for 48 hrs.; drying to constant wt. was noted to be longer in the presence of salt (nearly 70 hrs., compared to 24 hrs. for D).

Specimens EI were dried using conventional methods, i.e., ovendried at 125°C and the EII specimens were dried at 400°C with a propane burner to simulate high temperature drying such as can be expected to be used for drying of a bridge deck. The effects of the different drying methods were studied by testing both unimpregnated and impregnated (MMA) specimens of both types. All were tested with compression and splitting tensile tests.

The ultimate strengths for all specimens, impregnated as well as unimpregnated, are obtained for both splitting tensile and compressive strengths, and the corresponding modulus of elasticity.

It is found that salt contamination prior to impregnation tends to reduce strength, by 15-20% in compression and by 30-37% in tension, though the reduction is small in comparison with the relative increase due to impregnation. The DI and DII specimens show higher loadings and strength than the CI and CII specimens, presumably due to the longer drying. Interestingly, high-temperature drying (Specimens EI, 400°C at surface) resulted in a 16% decrease in tensile strength compared to the normally dried EII series, but no decrease in compressive strength. Apparently impregnation effectively heals any microcracks produced by the high-temperature drying.

Thus while high levels of salt may increase drying time somewhat (and, as shown earlier, impregnation time), the effect on mechanical properties is minimal. Additional tests on rate of penetration in contaminated cylinders (impregnated under pressure on one face, the sides being sealed) are in progress.

5. Chloride Penetration in PIC Mortar

In view of the generally improved resistance of PIC to corrosion, e.g., by acids and sulfates, it should be expected that penetration by chloride ion may also be reduced, in comparison with the unimpregnated matrix. In fact, others have shown this to be the case for PMMA-impregnated concrete. However, several questions do arise: (1) in practice, polymer impregnation

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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 are being conducted for a period of 18 mo.; similar tests under freeze-thaw cycling conditions are planned. 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 in the cement phase.

Procedures

After impregnation by standard procedures described previously (7→8% loading by wt.) the mortar cylinders were exposed to 8% aqueous $CaCl_2$. $2H_2O$ solutions. Following the convenient procedure for Ost and Montfore, solutions were contained in covered polyethylene sheaths tightly fitted on the cylinders and adjusted to extend above the top surface for about 1 in. The curved surfaces of the cylinders were closely wrapped with water proof tape to insure uniaxial flow; a screen support was used to provide free circulation of air underneath. After different exposure periods, cylinders were broken and the chloride concentration determined at different depths by electron microprobe analysis. At a given depth, small specimens were removed, coated with a thin carbon layer, three areas in the cement phase 8x100 micron-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 relative measure of chloride ions available for corrosive

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reactions. (It is believed that a modified procedure can discriminate between bound and unbound salt.)

Results

Preliminary results show that after only one month of exposure, the plain mortar shows a significant amount of chloride [1.6% $C\ell$ or 6% $CaC\ell_2$. $2H_2O$) at a depth of 0.25 in. (0.6 cm)] at different depths in the mortar. However, for both BA and MMA-impregnated mortars, only traces of chloride [< 0.1% $C\ell$ (= 0.4% $CaC\ell_2$. $2H_2O$) by weight of cement paste] were found at a depth of 0.25 in. At lower depths, the chloride values from microprobe analysis fall into the range of background scatter, so that detection of deeper penetration in the impregnated mortars will require much longer exposure times. At least for a 1-mo. exposure, both BA and MMA impregnated mortars give similar results.

6. Durability of PIC Slabs

For durability tests, cores from the polymer-impregnated and control slabs discussed earlier were compared with those taken from control slabs and impregnated in a closed chamber using our normal laboratory procedure. The tests included freeze-thaw, compressive and split-tensile strength, water absorption, corrosion, and acid-etching tests.

The drilling operation for taking the cores was accomplished with more difficulty for the polymer-impregnated specimens than for the control specimens, the former behaving like granite.

6.1 Freeze-Thaw Tests

Freeze-thaw tests (ASTM Designation C671) were carried out on 3-in diameter cores taken from 6-in slabs of salt-contaminated and uncontaminated polymer-impregnated concrete. Unimpregnated control specimens of both types were also tested. Two methods of impregnation were used: surface impregnation of the slabs, and vacuum-pressure impregnation of the cores in a closed

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chamber. The monomer system used throughout was the 90:10 methyl methacrylate-trimethylolpropane trimethacrylate mixture containing 0.5% azobisiobutyroni-trile initiator. Three specimens were tested for each treatment level. As defined in ASTM C671, the freeze-thaw tests were carried out until the specimen either failed or ten cycles were completed.

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 specimen may be considered to fail when the dilation exceeds 400-500 microinch, the elastic limit for a 6-in. specimen (70-80 microinch/inch). All of the unimpregnated control specimens failed quickly-- the salt-contaminated specimens in the first cycle and the uncontaminated specimens in the third cycle. This poor frost resistance is explained by the fact that only non-air-entrained concrete were used in this study (to sensitize the test). The earlier failure of the salt-contaminated specimens is also in agreement with field observations.

All of the polymer-impregnated specimens (with one exception) displayed exceptional resistance to freezing and thawing, independent of whether the specimen was uncontaminated or salt-contaminated. This exceptional performance in the presence of salt loadings as high as 12 lbs/cu yd shows the potential of polymer-impregnated concrete as a means to alleviate deterioration of highways and bridge decks. The single anomalous specimen was subjected to an additional 25 freeze-thaw cycles (non-instrumented) to expose the freeze-thaw-susceptible part of the specimen. During these cycles, the lower part of the specimen deteriorated badly and separated from the upper part, indicating that the impregnation was incomplete in this lower part. Similar behavior was also observed when the remaining portion was acid-etched and polished.

6.2 Acid-Etching Tests

One core from each concrete slab was sawed lengthwise; one half was etched by soaking in 18.5% aqueous hydrochloric acid for 2 hours, and the other

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was polished to show the morphology and coloration. 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.

6.3 Compressive and Split-Tensile Strength Tests

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 hours at $100°C$ (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 ($> 100°C$) before they were contaminated 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 4-5 and 5-6 in compression and cores 4-8 and 5-6 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 ($220°F$ or $104°C$), 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

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other tests on laboratory specimens. The presence or absence of salt contami-
nation, 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.

6.4   Water Absorption Tests

The cores were saturated by soaking in water for 24 hours at room
temperature and then weighed to the nearest gram; these water-saturated cores
were heated in an oven for 60 hours at 220°F (104°C) to drive off the evap-
orable water and were then reweighed; the difference between the two weights
was taken as the total water absorption of the core.

The following generalizations can be made from these results:

(1) The water absorption of the polymer-impregnated cores was less
than 0.5-1.5% of the total weight of the core and was only 10-20% of that of
the unimpregnated cores, in good agreement with the 83-95% reduction in water
absorption reported for polymer impregnated cylindrical specimens cast and
impregnated in the laboratory under controlled conditions.

(2) There was no significant difference in water absorption between
freeze-thaw-tested polymer-impregnated cores and polymer-impregnated cores and
polymer-impregnated cores not subjected to this test, demonstrating again
that polymer-impregnated concrete is remarkably resistant to freezing and
thawing.

(3) 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, even though the polymer loading was
greater for the former (perhaps the polymer fills the pores of the latter type
in a different manner).

(4) A single polymer-impregnated core taken from a bridge deck
impregnated in the field showed lower water absorption than cores taken from
polymer-impregnated slabs, indicating that equally good or better results may

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be expected from the field trials than from the laboratory impregnations.

6.5 Corrosion Tests

Some slabs were cored in such a way that a section of the steel reinforcing rods placed at the 4-inch (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, 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. 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.

The development of polymer-impregnated concrete technology may influence the present policy of replacing bridge decks when the salt content at the level of the top reinforcing rods reaches 2 lb/yd^3, since the polymer-impregnated cores tested here contained 12 lbs/yd^3 of salt, yet showed no evidence of corrosion.

7. Deep Impregnation of Slabs (March 1973)

        The feasibility of obtaining impregnations to a depth of 6 inches
was demonstrated on a 24x24x6 inch concrete slab using a prototype pressurized
impregnation device. Four such slabs were prepared using a 1:1.92:6.10:6.75
water-portland cement (Type 1)--sand-coarse limestone aggregate (maximum size
3/4 inches), with nominal steel reinforcement at a depth of four inches from
one face. Four holes were provided for bolting down the impregnation device.
The slab was cured for 6 hours in the form, then removed and steam-cured for
24 hours.

        Since drying has been shown to be a critical requirement for im-
pregnation, the slab was dried to constant weight (7 days) in an oven at 150°C.
The water removed by this drying treatment amounted to 5.2% of the total
weight, a value smaller than expected but consistent with the steam curing.

        The slab was placed on supports with its lower surface exposed.
The impregnation device consisted of a 6x10 inch chamber welded to a 20x20x1
inch steel plate, equipped with suitable gauges and valves to permit convenient
filling with monomer and pressurization during impregnation. The device was
bolted to the slab, separated by using a 16-inch circular neoprene gasket.
This method of attachment was used to equalize the pressure so as not to
exceed the maximum allowable load for bridge decks of 150 lbs/sq ft. A
90:10 methyl methacrylate (MMA)--trimethylolpropane trimethacrylate (TMPTMA)
mixture containing 0.5% azobisisobutyronitrile was applied at a pressure of
30 psi. After 17 hours, a dark spreading patch of monomer appeared on the
underside of the slab and grew to a diameter of 18 inches in 24 hours.

        After the impregnation device was removed, a $\frac{1}{2}$-inch layer of sand
was spread on the area enclosed by the gasket, and enough monomer was poured
on the sand to wet it. This technique was used by Fowler et al. to minimize
evaporation losses during polymerization. The slab was then wrapped in poly-
ethylene film, and live steam was played on its surface for 5 hours (2 hours
to reach 75°C plus 3 hours for polymerization to high conversion). The polymer
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loading was calculated to be about 6%.

The slab was then broken to show that the polymerization had proceeded to high conversion (only a slight monomer odor was detectable) and that the appearance of the fracture cross-section was similar to that of other PIC specimens.

Closer examination with a magnifying glass showed that in the impregnated area fracture occurred through the aggregate particles, but in the unimpregnated region, around the aggregate particles. Also, many voids were observed underneath the aggregate particles, especially near the lower face of the slab. These are attributed speculatively to the water drops which move upward during setting and curing and become entrapped underneath the aggregate particles. The voids in the upper $3\frac{1}{2}$-inch thickness were either filled or completely lined, while those at greater depths were filled only partially or not at all.

8. Bridge-Deck Impregnation

Earlier work by BNL and University of Texas showed that the impregnation of new or badly-deteriorated decks could be achieved by surface-drying and monomer-ponding techniques. The goal of Lehigh-Penn State team, however, was to achieve a 4-in. penetration in sound salt-contaminated decks. Thus an interpenetrating network of polymer would envelop the top layer of reinforcing steel and seal off the capillary channels of the concrete, and thus prevent the permeation of salt solutions and subsequent corrosion of the steel. Such penetration requires enchanced drying and impregnation.

8.1 Deep Drying

Using a series of 4-in. and 8-in. slabs, it was found in Sec. 2 that concrete can be impregnated with polymer to any depth provided it is thoroughly dried to that depth. Such drying requires that the temperature at the depth desired be at least $110^{\circ}C$. While drying of a slab in an oven at $110^{\circ}C$ presents no problems, drying from one side, as is necessary in the

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field, requires a surface temperature high enough to permit equilibration at
the depth desired, but low enough to prevent excessive degradation. Fortunately,
the desired temperature at a 4-in. depth could be obtained by use of either a
gas-fired infrared heater or a propane-torch assembly. Some cracks were,
however, observed on heating, especially with reinforced slabs, or at uncon-
strained edges of reinforced slabs; on cooling, the cracks closed up. Other
tests on torch-dried cylinders showed that impregnation appeared to heal any
cracks which developed, and to yield values of compressive strength equal to
those typical of specimens dried less rigorously prior to impregnation. It
was concluded that such cracking should probably not be deleterious per se,
though thermal expansion might limit the area that can be heated at once.

8.2   Impregnation

In order to predict with reasonable accuracy the times required for
impregnation, it was necessary to establish the rate for impregnation. Using
mortar cylinders, the impregnation of styrene, methyl methacrylate, and water
was found in Sec. 3 to depend on $(time)^{\frac{1}{2}}$; a similar dependence was later found
for bridge deck cores, concrete cylinders, and slabs and confirmed elsewhere.
Such a dependence is consistent with a capillary-rise mechanism. As might
be expected, the rate is slowed by the presence of salt in the pores, and
increased by pressure. In fact, at salt levels typical of real decks, the   .
rate of penetration was reduced only slightly. Two impregnation units were
constructed and used, one a simple box (2.5'x1.5'x1.0') and the other a
pressure chamber (14 in. in diameter). The former was used for ponding
experiments, and the latter, when bolted to a slab, for pressure impregnation.

8.3   Polymerization

As shown by BNL, it was possible to use a conventional thermocatalytic
polymerization: a 90:10 or 100L10 methyl methacrylate (MMA)--trimethylolpropane
trimethacrylate (TMPTMA) mixture with 0.5 parts azobisisobutyronitrile as
initiator. A polymerization temperature of at least 50°C was found to be
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satisfactory, with a reaction time of ~12 hrs.

8.4 Preliminary Field Trials March 1974

The principles developed above were demonstrated in small-scale field trials using the bridge deck at the PennDOT test track, State College, Pa. 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. (Thermocouples were used to follow the heating to the temperature required.) Both techniques yielded relatively dense impregnation to a depth of 4 to 5 in., with no cracking. Thus either ponding or pressurization techniques appear to be suitable for deep impregnations. The former is simpler, and should be easily adaptable to the large-scale impregnation of decks which can be closed to traffic for the several days required. The latter is more complex, but should yield higher loadings of polymer, and be adaptable to large-scale impregnations in which time is all-important.

8.5 Larger-Scale Field Trials August 1974

Following the successful small-scale trials, the impregnation of larger adjacent 4'x12' sections was attempted. The gas-fired infrared drying, pressure impregnation, and steam polymerization techniques were selected, and a closed box designed and constructed to serve as a pressure chamber. With minor problems and modifications, the trial was conducted successfully over a period of 3 days. As before, satisfactory impregnation up to a 4-in. depth was observed, with a less dense band extending 1 in. or more further downwards. Thus the deep impregnation of lane-width sections has been demonstrated for the first time. Further work is required to optimize the process and reduce costs, to determine the maximum area that can be heated without causing buckling, and to ensure that significant damage is not caused remotely. However, one can readily envisage improvements in the efficience of heating, the further scale-up of the equipment, and alternate means of effecting

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the impregnation. A field trial on a deck in service (Pa. Rt. 378) is planned.

8.6 Other Impregnants and Processes

Current research is directed towards the use of other impregnants, by either soaking or pressure impregnation. It has recently been found that sulfur, .tar, and oils can be impregnated in several ways. All these reduce water absorption (and presumably salt penetration) by up to 99%; in addition, sulfur may not need rigorous drying of the substrate, and confers an extra-ordinary degree of mechanical reinforcement, increasing strength by a factor of nearly 3. A novel technique for impregnation is also under development-- the use of a mechanically pressurized rubber mat. In this way, penetrations of up to 4.5 in. have been achieved in concrete slabs with tar and linseed oil, using a variety of load cycles; in contrast, only surface penetrations are observed in conventional treatments. Thus, it is in principle feasible to simplify the deep impregnation process or to use conventional sealants in a new way.

8.7 Corrosion and Mechanical Behavior of PIC

It is important to know how well impregnation in the field restricts the permeation of water and salt, immobilizes salt already present in the con-crete, and improves the resistance to freeze-thaw cycling. While cores from the field trials have not yet been tested, tests on cores taken from reinforced slabs impregnated from one side indicate significant improvement in strength, resistance to abrasion and acid, and freeze-thaw durability. Moreover, exam-ination by scanning electron microscopy of a core from a slab laden with 0.3 wt.-percent sodium chloride prior to impregnation and freeze-thaw cycling, re-vealed no detectable corrosion of the steel, in contrast to a core from an un-impregnated control slab, which showed deep pitting in the steel. Similar re-sults should be obtainable with careful field impregnation.

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9. Papers and Reports

1. Blankenhorn, P. R., et al., "Enclosed System for Deep Polymer Impregnation of Concrete Bridge Decks," Transportation Engineering Journal, ASCE, Vol. 101, No. TE1, Proc. Paper 11102, Feb. 1975, pp. 65-75.

2. Chen, W. F. and Dahl-Jorgensen, E., "Stress-Strain Properties of Polymer Modified Concrete," Polymers in Concrete, American Concrete Institute Publication SP40-17, 1973, pp. 347-358.

3. Chen, W. F. and Dahl-Jorgensen, E., "Polymer-Impregnated Concrete as a Structural Material," Magazine of Concrete Research, Vol. 26, No. 86, Mar. 1974, pp. 16-20.

4. Chen, W. F. and Mehta, H. C., "Structural Use of Sulfur for Impregnation of Building Materials," Proceedings, Pan-Pacific Tall Building Conference, Hawaii, Jan. 26-29, 1975.

5. Chen, W. F., Mehta, H. C., et al., "Use of Polymers in Highway Bridge Slabs," Proceedings, Inter-Associations Colloquium on Behavior of Concrete Structures, Liege, June 4-6, 1975.

6. Dahl-Jorgensen, E., et al., "Polymer-Impregnated Concrete: Laboratory Studies," Transportation Engineering Journal, ASCE, Vol. 101, No. TE1, Proc. Paper 11101, Feb. 1975, pp. 29-45.

7. Manson, J. A., et al., "Stress-Strain Behavior of Polymer-Impregnated Concrete," Polymer Preprints, Vol. 14, No. 2, Aug. 1973, pp. 1203-1208.

8. Manson, J. A., et al., "Use of Polymers in Highway Concrete," Quarterly Progress Reports, NCHRP Project 18-2, Oct. 1972-Mar. 1974.

9. Manson, J. A., Chen, W. F., et al., "Polymer-Impregnated Concrete for Highway and Structural Applications," International Congress on Polymer Concretes, Proceedings, London, U.K., May 5-7, 1975.

10. Manson, J. A., Chen, W. F., et al., "Polymer-Impregnated Concrete for Highway and Structural Applications," Interamerican Congress of Chemical Engineering, Caracas, Venezuela, July 13-16, 1975.

11. Mehta, H. C., et al., "Polymer-Impregnated Concrete: Field Studies," Transportation Engineering Journal, ASCE, Vol. 101, No. TE1, Proc. Paper 11103, Feb. 1975, pp. 1-27.

12. Mehta, H. C., Chen, W. F., et al., "Innovations in Impregnation Techniques for Highway Concrete," Transportation Research Board, Washington, D.C., Jan. 1975.

13. Vanderhoff, J. W., Hoffman, J. D. and Manson, J. A., "Polymer-Impregnated Concrete: Rate of Penetration of Monomer," Polymer Preprints, Vol. 14, No. 2, Aug. 1973, pp. 1136-1142.

14. Whiting, D. A., Blankenhorn, P. R. and Kline, R. E., "Epoxy Impregnation of Portland Cement Concrete," Polymer Preprints, Vol. 14, No. 2, Aug. 1973, pp. 1154-1156.

10. <u>Acknowledgments</u>