

SCHOOL OF  
CIVIL ENGINEERING

INDIANA

DEPARTMENT OF HIGHWAYS

JOINT HIGHWAY RESEARCH PROJECT

FHWA/IN/JHRP-82/15

POLYMER TREATMENT OF NON-DURABLE  
AGGREGATES

D. N. Winslow

W. L. Dolch



PURDUE UNIVERSITY



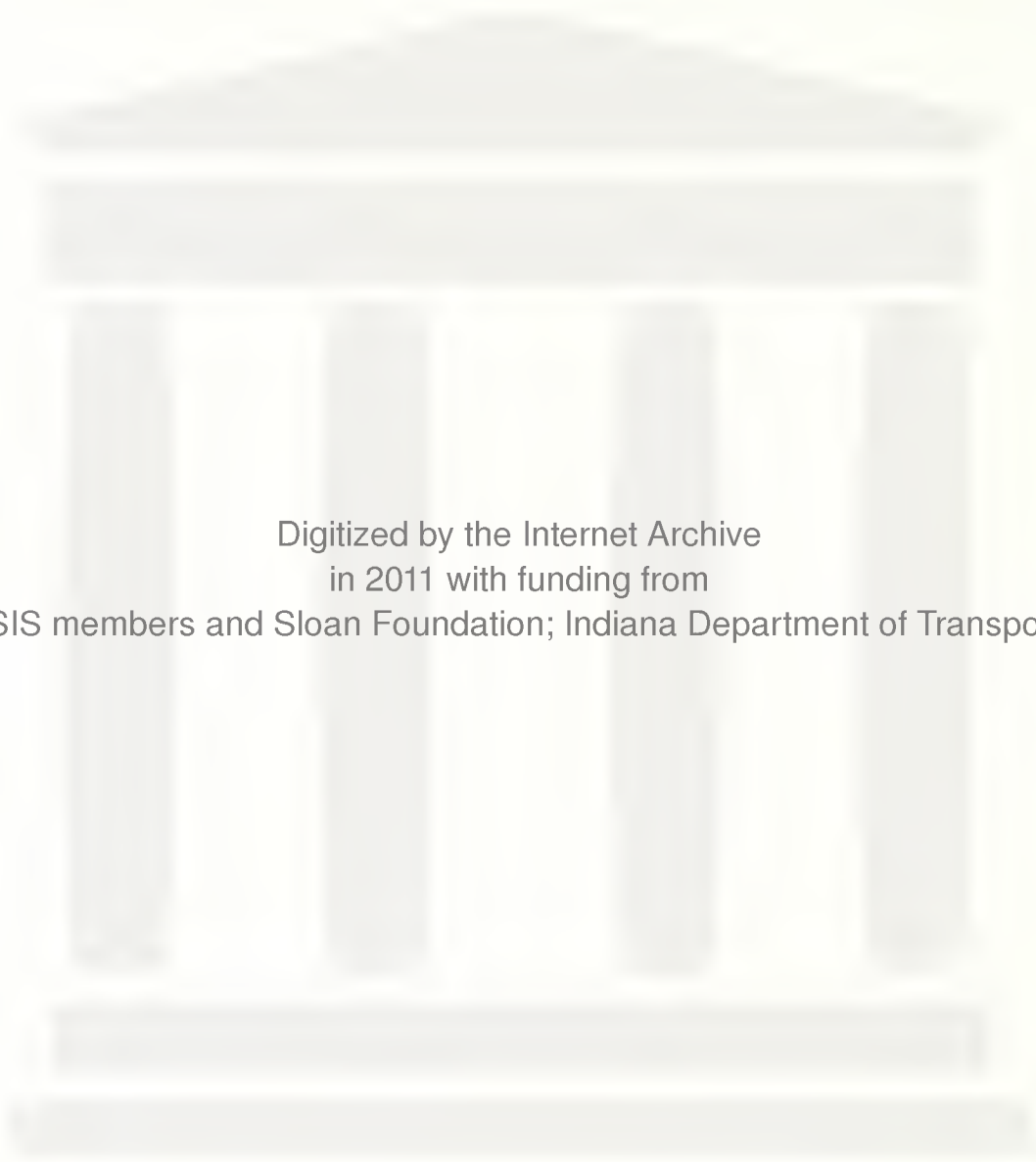
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Final Report

POLYMER TREATMENT OF NON-DURABLE AGGREGATES

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

September 9, 1982

FROM: D. N. Winslow, Research Associate  
Joint Highway Research Project

Project: C-36-47N

File: 4-6-14

Attached is the Final Report on the HPR Part II Study titled "Improvement of Non-Durable Aggregates in Portland Cement Concrete". The title of the Report is "Polymer Treatment of Non-Durable Aggregates".

The Report indicates the use of urea formaldehyde as the best of four tried. It significantly reduced the water absorption of aggregates. Analysis of the cost of such treatment indicated it would be competitive where transportation of better aggregates would involve over 50 miles.

The Report is submitted as completion of the objectives of the Study and after reviews have been completed is planned for publication.

Sincerely,



D. N. Winslow  
Research Associate

DNW:ms

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Final Report

POLYMER TREATMENT OF NON-DURABLE AGGREGATES

by

Douglas N. Winslow  
and  
William L. Dolch  
Research Associates

Joint Highway Research Project

Project No: C-36-47N  
File No: 4-6-14

Prepared as a part of an investigation

Conducted by

Joint Highway Research Project  
Engineering Experiment Station  
Purdue University

in cooperation with the

Indiana Department of Highways

and the

U.S. Department of Transportation  
Federal Highway Administration

The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data represented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration. This report does not constitute a standard, specification or regulation.

Purdue University  
West LaFayette, Indiana  
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16. Abstract  An attempt to improve the freeze/thaw durability of several non-durable aggregates was made. The approach was to impregnate the aggregates' pores with a polymer. The polymers were selected on the basis of their low cost. The aggregates were treated by briefly dipping them in polymer-containing liquids.  Four (polymers, polystyrene, polymethyl methacrylate, phenol formaldehyde and urea formaldehyde) were tried and urea formaldehyde was found to be the best. It significantly reduced the water absorption of aggregates. Freeze/thaw test results were inconclusive. Its cost is competitive with shipping better aggregates from as far away as fifty miles.					
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#### HIGHLIGHT SUMMARY

An attempt to improve the freeze/thaw durability of several non-durable aggregates was made. The approach was to impregnate the aggregates' pores with a polymer. The polymers were selected on the basis of their low cost. The aggregates were treated by briefly dipping them in polymer-containing liquids.

Four (polymers, polystyrene, polymethyl methacrylate, phenol formaldehyde and urea formaldehyde) were tried and urea formaldehyde was found to be the best. It significantly reduced the water absorption of aggregates. Freeze/thaw test results were inconclusive. Its cost is competitive with shipping better aggregates from as far away as fifty miles.

## INTRODUCTION

This is the last in a series of reports dealing with the freeze/thaw durability of the coarse aggregate in portland cement concrete. The original concept of this research project was to investigate the possibilities of improving non-durable aggregates by altering their pore structure. However, so little was known about the relationship between an aggregate's pore structure and its durability that the project was divided into two phases. Phase I was to be a detailed study of the pore structure-durability correlation. Phase II was initially planned to be a study of improvement possibilities. However, the findings of Phase I resulted in an altered proposal being submitted and approved for Phase II. This altered research plan somewhat shifted the emphasis of Phase II.

### Phase I

In Phase I, many aggregates, both durable and non-durable, were obtained from quarries. Their pore structures were determined by mercury intrusion porosimetry. Crushed and graded samples of each aggregate were used to make concrete freeze/thaw specimens that were then tested in accordance with ASTM C-666

(A). A correlation between two parameters of the pore structure (the total pore volume and the median pore diameter) and the measured durability was then established. The results of this work have been reported (1) and published (2).

The importance of the findings of Phase I lies in the determination that an aggregate's durability is not merely a function of its pore volume but, also, of the size of its pores. If the pores have a small diameter, then only a small volume of them can be tolerated if the aggregate is to be durable. Conversely, if the pores have a sufficiently large diameter then a much larger pore volume can also be tolerated. This represents a different acceptance criterion than others currently in vogue.

Often, non-durable aggregates that have passed current acceptance tests have been used in concrete pavements. The result has been premature failures and extraordinary maintenance costs. The findings of Phase I showed that an aggregate's durability could be predicted from a knowledge of its pore structure and that this might be a superior acceptance test for screening out non-durable aggregates. Thus, it seemed appropriate to redirect the emphasis of Phase II to look into the validity of this presumption. As a result, an amended proposal was submitted and approved that aimed to develop a potential acceptance criterion based on pore structure along with work on the possibilities of aggregate improvement.

## Phase II

The acceptance-test possibility was studied by examining the aggregate in existing highways with observable durability histories. Core samples were removed from pavements ranging in condition from excellent to highly deteriorated. The porosimetry technique was then used to determine the pore structure of the aggregate in the cores and to find the expected durability of each core. These laboratory results were then compared with field observations to determine what the pore structure of an aggregate must be to give good pavement performance. It was also possible to set a limit on the amount of poor aggregate that is acceptable in a pavement section, and the technique was found to be equally applicable to gravels and crushed stone. These findings have also been reported (3) and published (4).

The importance of this work is that it established an acceptance test that is clearly more discriminatory than methods now in use. All the pavements that were examined contained aggregates that had been accepted as durable. Yet, many were showing freeze/thaw distress originating in the aggregates, some in as short a time as five years. The work showed that, had the pore structure of the aggregates been determined and the proposed acceptance criteria invoked, the non-durable aggregates would have been excluded from use. The extraordinary maintenance costs occasioned by the presence of these non-durable materials have, so far, totaled many millions of dollars.

This research report concerns the final aspect of Phase II. It details efforts to alter the pore structure sufficiently to make a non-durable aggregate acceptable for use in concrete pavements.

## GENERAL CONSIDERATIONS FOR POTENTIAL AGGREGATE IMPROVEMENT

Other workers (5) have also attempted to improve non-durable aggregates by treating them with some sort of pore altering material. It was the purpose of this work to try other, and more economical, processes. The question of economy is important since, usually, a source of good aggregate can be found at some distance and can be shipped to the job site. Thus, a potential treatment must be cost competitive with shipping. As a basis for considering treatments, it was decided to assume that a good aggregate could be found within 50 miles. Currently, it costs about \$0.11/ton mile to truck aggregate in Indiana. Hence, potential treatments were restricted to those likely to cost less than about \$5.50/ton.

The general notion of the potential treatments that were considered was to infuse the aggregate's pore structure with some sort of polymeric material that would lessen the pore volume available to water. This reduction might be effected in one or more of several ways.

1. The pores might be completely filled.
2. The entrances to the pores might be blocked.

3. The surface of the pore walls might be coated with a hydrophobic film.

Several constraints were placed on potential treatments to keep down their cost. To reduce machinery expenses, it was decided that the process must work at atmospheric pressure and at nearly ambient temperature. It was also decided that it must be rapid. Thus, high pressures and temperatures were excluded as were long exposure times.



## SELECTION OF MATERIALS

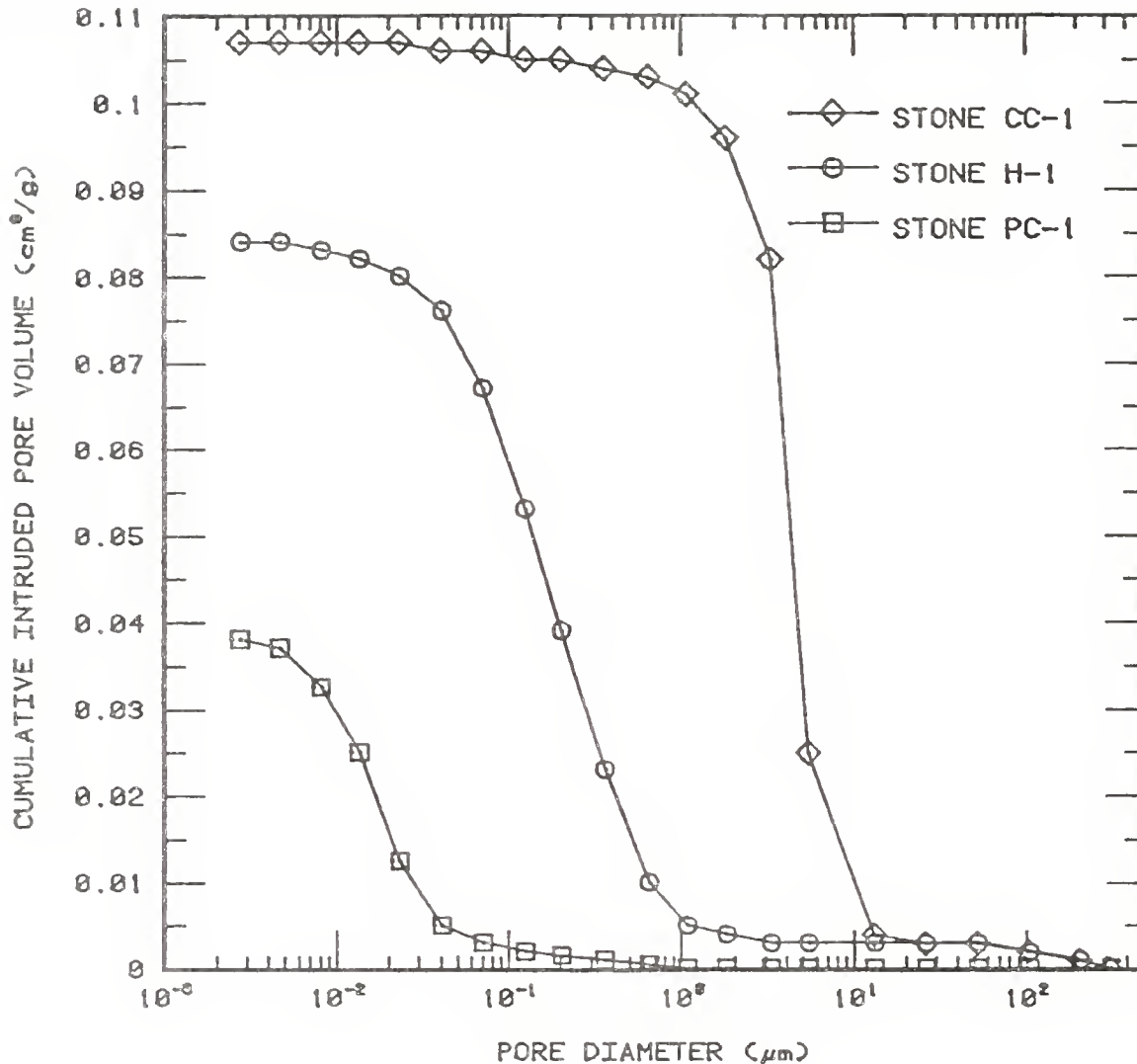
Many polymers are expensive. A potential polymer for this application must be cheap as well as meeting the above infusion constraints. Discussions were held with polymer chemists about likely candidates and four polymers seemed to be suitable. They were:

1. polystyrene
2. polymethyl methacrylate
3. phenol formaldehyde
4. urea formaldehyde

It was decided to attempt to improve three, different, non-durable aggregates with each of these polymers. The aggregates were selected because of their widely different median pore sizes that seemed representative of the spectrum of non-durable aggregates found in Indiana. They were three of the aggregates already studied in Phase I, namely: PC-1, CC-1 and H-1. Their pore size distributions are given in Figure 1.

Figure 1

Pore Size Distributions of Test Aggregates



#### INITIAL TESTS of POTENTIAL TREATMENTS

The general scheme for infusing the aggregates with any of the polymers was to dip the stone in a liquid containing a monomer. This would be allowed to enter the pores and would subsequently be polymerized. Small-scale trials were carried out at first to investigate this process.

The monomer liquids were in two different forms. In the cases of polymethyl methacrylate and polystyrene, the liquids were composed solely of the monomer, and polymerization was brought about by exposing them to light and air. For the other two, the liquids were water solutions containing formaldehyde and either phenol or urea, as appropriate. In either case, the polymerization was effected by a brief follow-up dip in a dilute (pH = 6) hydrochloric acid solution. With the water based treatments, air drying for about 24 hours allowed the polymerization to proceed while the extra water left the rocks.

Small cylinders (1/2" dia. by 1" long) were cut from each of the three stones in the trial suite. These were then dipped in the monomer bearing liquids for varying times up to 10 minutes.

Ten minutes was selected as, probably, the longest treatment time that would be economically practical. After polymerization had occurred, the polymer uptake and the change in the 24-hour absorption were measured for each sample.

It soon became apparent that it was not possible to infuse stone PC-1 with a significant amount of any of the four polymers. Nor was it possible to reduce its adsorption. Under the constraints set for treatments (atmospheric pressure and short exposure time) the liquids would not enter the exceedingly small pores in PC-1. Hence, PC-1 was excluded from further testing and the suite of trial stones was reduced to CC-1 and H-1.

During these initial experiments it also became apparent that the water-based liquids were doing a much better job of infusing the rocks. Both the urea formaldehyde and the phenol formaldehyde entered the rocks to a greater extent and gave a greater reduction in absorption than did the other two. This may have been because the water-based liquids were less viscous and may have had a greater rate of permeation. Whatever the reason, the chances of significant improvement seemed to lie only with the water-based materials. No further tests were run with either the polymethyl methacrylate or the polystyrene, and the suite of potential polymers was reduced to urea formaldehyde and phenol formaldehyde.

Both phenol formaldehyde and urea formaldehyde produced generally good results. However, urea formaldehyde gave somewhat greater reductions in absorption. Also, its formulation did not involve the handling of phenol, a dangerous chemical. Therefore, the polymer chosen for further experiments on the stones was urea formaldehyde. Its effect on the stones' absorption as a function of treatment time is shown in Figure 2. The maximum polymer loading, after ten minutes of treatment is given in Table 1. The details of the preparation of the urea formaldehyde solution and the treatment of the aggregate with it are given in the appendix.

Table 1

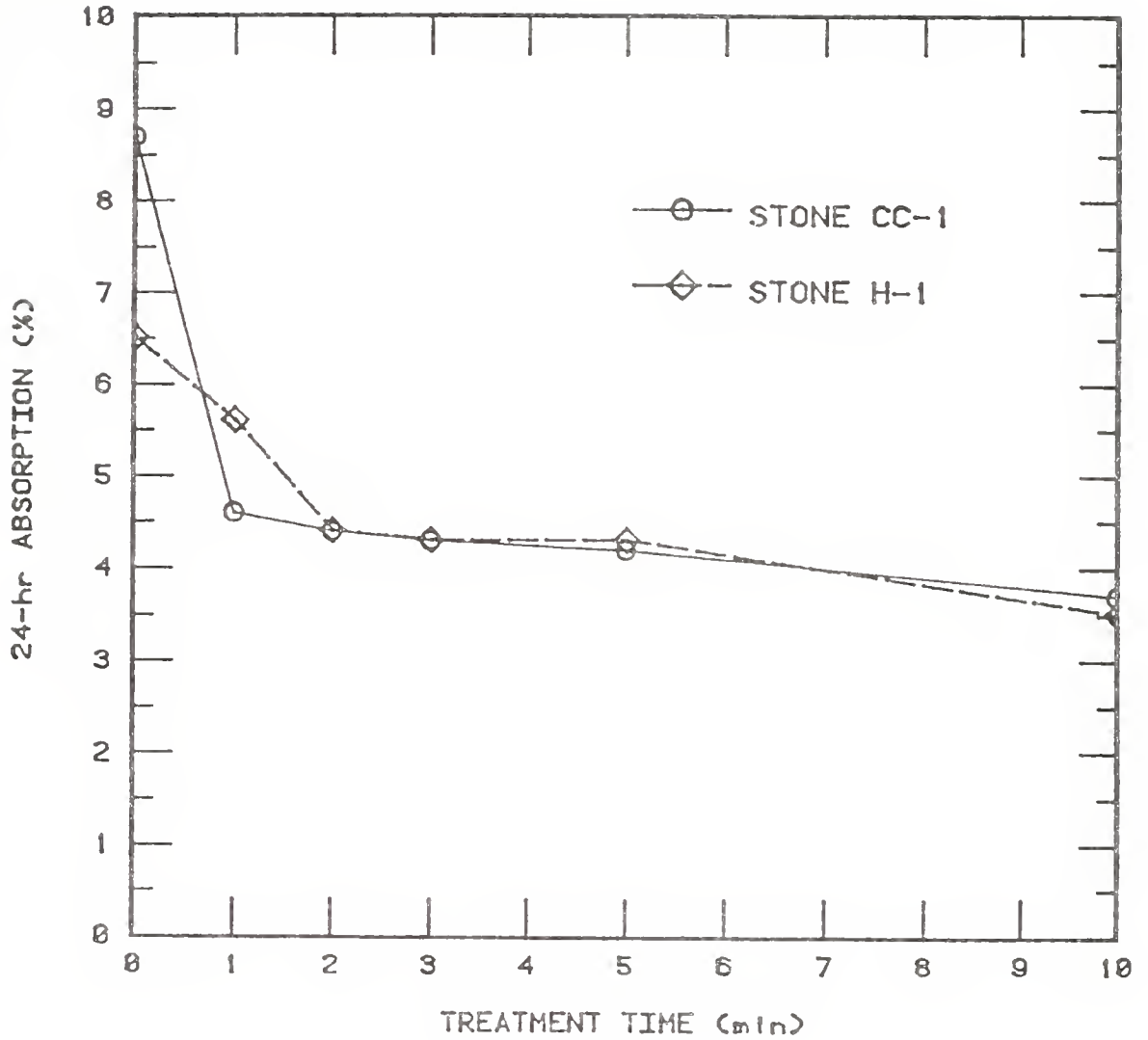
Urea Formaldehyde Loading (10 minute treatment)

Stone	CC-1	H-1
Loading, by weight (g urea formaldehyde/g stone)	0.0462	0.0247
Loading, by volume (*) (cc urea formaldehyde/g stone)	0.0308	0.0165

(\*) Assumes a urea formaldehyde density of 1.5 g/cc.

Figure 2

Reduction in Absorption with Treatment Time



#### OTHER ASPECTS OF POTENTIAL TREATMENTS

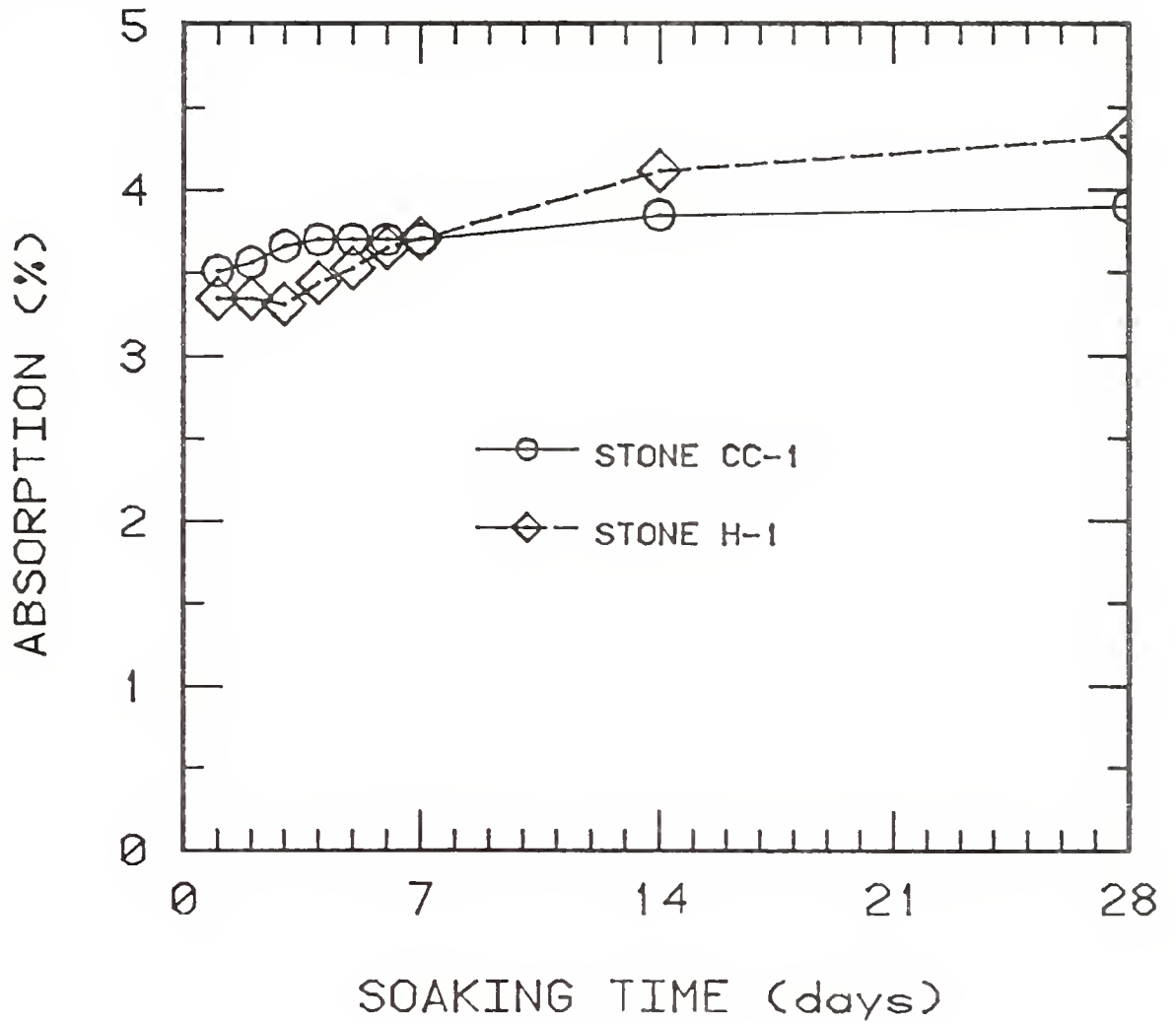
Two additional aspects of the urea formaldehyde treatment were considered before freeze/thaw testing was carried out. One was the permanence of the absorption reduction that the treatment brought about. The other was the effect, if any, on the strength of concrete made with the urea formaldehyde-treated aggregate.

To investigate the permanence of the treatment, stones were allowed to continue to soak in water for a period of about one month after initially being treated with urea formaldehyde. Their saturated surface dry weights were determined periodically during this period and their absorptions calculated. If the polymer improvement degraded with with time, the absorption should increase with continued soaking. Figure 3 has the results of this test and shows that, even in the face of continuous soaking, the treatment is reasonably permanent.

The effect on strength was examined by making concrete with treated and untreated aggregates and then measuring the compressive strength of cylinders made from that concrete. Table 2 shows the results of these tests for aggregate that was treated

Figure 3

Change in Absorption with Continued Soaking



with urea formaldehyde for ten minutes. It shows that the compressive strength is not affected.



Table 2

Compressive Strengths of Concrete  
made with  
Treated and Untreated Aggregate

Treatment	CC-1	H-1
Untreated	3060 psi	2980 psi
10 Minute Treatment	3150 psi	2950 psi

### FREEZE/THAW TESTING

Following the preceding experiments, concrete was made with urea formaldehyde-treated aggregates to determine the effect on freeze/thaw durability. Both CC-1 and H-1 were crushed and graded in the same proportions used earlier (1). Air entrained concrete beams were made as described previously and were allowed to cure for about two months before testing.

It was originally intended to batch the aggregates in the air-dry state as this approximates the way in which they would normally be batched. However, this proved to be unworkable. The two stones, even when treated, have appreciable pore volumes and, they were found to absorb mix water rapidly. Thus, each aggregate abstracted some of the mix water while the concrete was plastic and, produced concretes with varying water/cement ratios. This could be partially corrected for by the addition of extra mix water, but this procedure was not found to be sufficiently accurate with aggregates of varying pore volumes and rates of absorption.

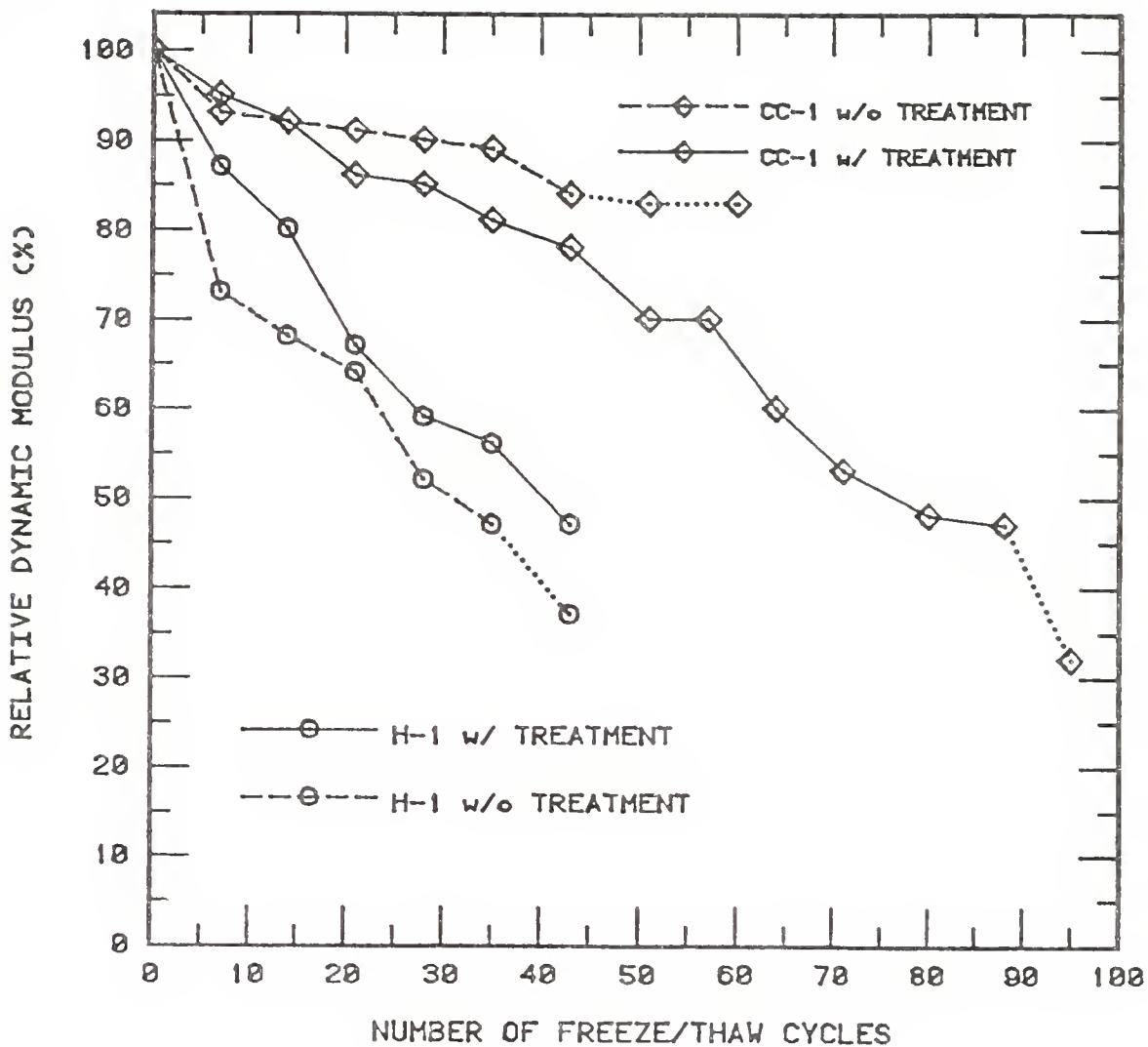
It is crucial to maintain a constant water/cement ratio in the various concrete mixes. Any aggregate can be made to appear more durable by simply surrounding it with a cement paste of a lower water/cement ratio that is denser and less permeable. For highly absorptive aggregates, this abstraction of mix water may even have the bazaar effect of making the poorer aggregate appear to have the better freeze/thaw durability.

Because of the above difficulties, it was decided to vacuum saturate all of the aggregates. They were then surface dried just before to being placed in the concrete mixer. This procedure produces a severe freeze/thaw condition and early failures. But, it does, at least, yield concrete mixtures with nearly constant water/cement ratios that can be compared to one another.

Figure 4 has the results of the freeze/thaw testing. Three companion beams of each mix were tested. As long as all three from a mix were still whole, a point in Figure 4 represents the average relative dynamic modulus of all three. When one or more beams broke, then the points on the plot are the average of the remaining beams. The point at which the first beam of any one mix broke is the point at which the line on the plot, either solid or dashed, turns into a dotted line.

Figure 4

Relative Dynamic Modulus vs. Number of Freeze/Thaw Cycles



## DISCUSSION

The effects on freeze/thaw durability that resulted from the urea formaldehyde treatment were found to be mixed. H-1 was clearly improved. However, the treated CC-1 had a lower relative dynamic modulus than the untreated material. It did though, withstand many more cycles before it completely disintegrated.

### The Case of H-1

Concrete made with urea formaldehyde-treated H-1 aggregate had a greater relative dynamic modulus at all stages than did concrete made with untreated stone. The treatment reduced H-1's absorption by about 3% or, by about 0.03 cc of absorbed water per gram of stone. The volumetric loading with urea formaldehyde was estimated at about 0.016 cc/g. The reduction in pore volume as measured by mercury intrusion was found to be about 0.02 cc/g; the average pore size of the treated stone was unchanged. Thus, it appears that slightly over half of the absorption reduction that was achieved probably came from filling pore space and the remainder from the creation of hydrophobic pore walls.

### The Case of CC-1

Urea formaldehyde-treated CC-1 showed a generally poorer freeze/thaw performance than did untreated CC-1. However, its absorption was reduced by about 5% or, 0.05 cc/g and, one would expect it to have been improved. Its volumetric loading with urea formaldehyde was estimated at about 0.03 cc/g and its mercury intrusion pore volume was reduced by about 0.025 cc/g. From this it would seem that, for this stone also, some of the absorption reduction stems from pore filling and some from the creation of hydrophobic surfaces.

The presence of these surfaces, coupled with the vacuum saturation, may have inadvertently caused a peculiar problem in this large pored aggregate. Water does not wet a hydrophobic surface and will not voluntarily enter a pore with such a surface. However, CC-1 was vacuum saturated. Thus, the pressure inside its pores was essentially zero while, after release of the vacuum, the pressure outside was one atmosphere.

These circumstances duplicate the situation that obtains during mercury intrusion porosimetry with water substituted here as the intruding liquid. All pores that can be intruded by a pressure of one atmosphere will be filled with water. The pores in CC-1 are sufficiently large for this to happen while those in H-1 are not.

The above offers a possible explanation for the failure of CC-1 to appear to be improved. The water in the treated pores is being held in place by the atmospheric pressure. The water in the untreated pores is held by only a capillary pressure of about one half that magnitude.

Thus, the water in the pores of the treated material may be more tightly held against either accidental removal during surface drying or, against subsequent competition with the cement paste. These two water removal mechanisms would yield a less saturated stone surrounded by a denser paste. The result of this would be a better freeze/thaw performance for the UNTREATED material.

Thus, vacuum saturation may have inadvertently caused an unusually severe condition for this large-pored, treated stone. If it were possible to mix air-dried aggregate, treated and untreated, with a constant water/cement ratio paste then, the treatment might show an improved performance. This artifact of the experimental procedure may be masking a true improvement that one would expect from the reduction in absorption. This problem does not arise in the case of H-1 as its pores are too small.

#### The Cost of the Urea Formaldehyde Treatment

The authors are not qualified to make an estimate of the cost of the machinery that would be required at a quarry to treat poor aggregate with urea formaldehyde. However, it seems

reasonable that this capital expense, when averaged over all of the aggregate that would be processed during the machinery's lifetime, would be small compared to the cost of the urea formaldehyde itself.

Currently, the price of the formaldehyde solution that is used is about \$0.05 per pound and the urea is about \$0.08 per pound. If the weight loadings shown in Table 1 were to be achieved then, the cost of urea formaldehyde per ton of rock would be:

CC-1	\$5.87/ton
H-1	\$3.14/ton

The price to treat H-1 is clearly competitive with the cost of \$5.50/ton to ship aggregate 50 miles. However, the improvement in H-1's performance was only about a one-third increase in the time required for the relative dynamic modulus to fall to 50%, assuming the freeze/thaw results to be "real" and not to have been adversely affected by the experimental artifact discussed above. Thus, although the urea formaldehyde treatment is effective for H-1 and, although it is cost competitive with hauling, the improvement may not be sufficient to justify the cost of the treatment. The authors do not know how to translate this improvement into additional years of pavement life but, such a translation would be required to accurately judge the cost effec-



tiveness of the treatment.

The price to treat CC-1 is slightly over the \$5.50 limit but, it is close. With this aggregate, the question of cost effectiveness is confused by the mixed data on the improvement of CC-1. The absorption reduction certainly indicates that the aggregate should be improved but the freeze/thaw results indicate that it is not. These results may, however, be an artifact of the test procedure.

## CONCLUSIONS

Simple and rapid treatment of non-durable stone coarse aggregate with urea formaldehyde polymer results in a significant reduction in the aggregate's water absorption and is probably competitive with the cost of shipment of a better material from as far away as fifty miles.

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## DETAILS OF UREA FORMALDEHYDE TREATMENT

(based on using 100 g of formaldehyde solution)

1. Warm 100 g of 37% formaldehyde solution to 30-35<sup>o</sup>C (86-95<sup>o</sup>F).
2. Add 82 g of urea and stir until completely dissolved.
3. Dip aggregate in solution for desired period of time.
4. Remove aggregate and allow to drain briefly (15-30 sec.).
5. Dip aggregate in hydrochloric acid solution (pH = 6) for about 30 sec.
6. Remove aggregate and allow to air-dry for about 24 hours.



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