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Control of Concrete Deterioration Due to Trace Compounds in Deicers

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ABSTRACT

This report presents results of research on ways to reduce the detrimental effects of sulfate-tainted rock salt deicers on portland cement concrete used for highway pavements.

Repetitious experiments on the influence of fly ash on the mortar phase of concrete showed significant improvement in resistance to deicing brines is possible. Fifteen to twenty percent by weight of fly ash replacement for portland cement was found to provide optimum improvement. Fly ashes from five sources were evaluated and all were found to be equally beneficial.

Preliminary results indicate the type of coarse aggregate also plays an important role in terms of concrete resistance to freeze-thaw in deicing brines. This was particularly true for a porous ferroan dolomite thought to be capable of reaction with the brine. In this case fly ash improved the concrete, but not enough for satisfactory performance. An intermediate response was with a porous limestone where undesirable results were observed without fly ash and adequate performance was realized when 15% fly ash was added. The best combination for making deicer-resistant concrete was found to be with a non-porous limestone. Performance in brines was found to be adequate without fly ash, but better when fly ash was included.

Consideration was given to treating existing hardened concrete made with poor aggregate and no fly ash to extend pavement life in the presence of deicers, particularly at joints. Sodium silicate was found to improve freeze-thaw resistance of mortar and is a good candidate for field usage because of its low cost and ease of handling.

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INTRODUCTION

In Iowa DOT Project HR-271, it was demonstrated that natural rock salt can contain enough sulfate as an impurity to reduce the strength of portland cement mortar by much as sixty percent in comparison to specimens subjected to freezing and thawing in water. A worst-case sulfate concentration of two percent produced the most alteration to pores, and also made mortar most vulnerable to frost action. The mechanism for accelerated deterioration was determined to be pore structure alteration by formation and deposition of compounds enhanced by the presence of sulfate.

The damage mechanism of classic sulfate attack consists of internal stresses caused by expansive products of chemical reactions. The mechanism for deterioration investigated in this research differs from that of classic sulfate attack in that pore alteration is coincident with freezing, and results from a combination of chemical products and precipitation of salts.

Internal stresses culminating in rapid deterioration result from freezing of liquid in a network of pores incapable of accommodating expansion. Mortar exposed to brines containing sulfates has been reduced to rubble in 120 freeze-thaw cycles, about one-third the expected life, whereas specimens in water and pure sodium chloride brines have survived 300 freeze-thaw cycles. Companion specimens in sulfate-tainted brines not subjected to frost action showed no sign of deterioration after four years.

In the first phase of this project, sulfate concentrations in rock salt stockpiles throughout the state were evaluated. It was found that ninty-five percent of these stockpiles had enough sulfate to support the deterioration mechanism. As it was concluded that restrictive specifications could make the cost of deicing prohibitive, alternative solutions were considered desirable.

A second Phase I objective was to evaluate the effect of other trace compounds known to occur with rock salt. It was found that sulfate was the causative factor. Regardless of source compounds, non-sulfate compounds of magnesium, previously suspected as deleterious, were found innocuous. It was also found that 15% replacement of portland cement with Ames fly ash arrested deleterious sulfate action.

RESEARCH OBJECTIVES

One objective of this research is to find solutions other than rock salt prohibition which will increase the life of new portland cement concrete pavements and prolong the life of those now in service. More specific to this objective are the following goals:

1. Verify previous preliminary experiments which indicate fly ash as a replacement to portland cement can arrest the deleterious action of sulfate containing deicing brines.

2. Evaluate the influence of sulfate containing deicers on concrete made with coarse aggregate exhibiting different degrees of resistance to freezing and thawing in water.

3. Determine whether fly ash composition has an influence in reducing deleterious action of deicers.

4. Establish requirements and limits for fly ash usage.

5. Initiate experiments to monitor disposition of deicers applied to pavements.

6. Initiate experiments to compare temperature fluctuation in pavements with that of laboratory tests.

EVALUATION OF FLY ASH

The mortar phase of concrete is compared in water and a sulfate-tainted rock salt brine to evaluate the influence of fly ash concentration and type on the resistance of concrete to deterioration.

Fly Ash Type

One hundred twenty repetitive mortar specimens were cast in twelve sets of ten. Type I portland cement, Ottawa sand, and water were used to represent an IOWA DOT C-3 paving concrete. In ten of these specimen sets, fifteen percent of the five fly ashes listed in Table 1 were substituted for portland cement. The remaining two sets were control groups and used portland cement alone. The fly ashes were selected to include both Type C and F materials typical of those available for use in Iowa. Type I portland cement of the composition noted in Table 2 was used throughout the experiment.

Two-inch diameter by four-inch long cylindrical specimens were cast in accordance with ASTM C-192 and then cured in a lime bath for 28 days. These specimens were subjected to 300 freeze-thaw cycles per ASTM C-666, Method B. Exceptions to ASTM C-666 procedures were as follows: (1) half the specimens were in a saturated brine of sodium chloride with two percent calcium sulfate; and (2) the other half underwent freezing and thawing in water. Also, the freeze-thaw test was modified such that the fluid level was maintained at the mid-height of the specimens, as described in previous reports.

Indicators of specimen performance include description of visible damage, ultrasonic pulse velocity measured at 25 cycle intervals, and

Table 1. Elemental composition and classification of fly ashes.

Element (or oxide)		N4	N3	WST	LAN	OTT
		(Percent by weight)				
SiO_2		32.7	39.0	34.8	31.3	34.3
Al_2O_3		19.9	19.6	18.0	16.6	19.3
Fe_2O_3		5.51	10.1	5.34	5.75	5.24
	TOTAL:	58.1	68.7	58.1	53.7	58.8
CaO		26.7	19.8	26.6	30.1	25.1
SO_3		2.58	2.45	2.59	3.72	3.30
MgO		4.70	5.41	5.53	5.94	5.03
K_2O		0.40	1.30	0.35	0.26	0.41
TiO_2		1.55	0.83	1.41	1.42	1.50
Na_2O		2.98	0.18	1.41	1.95	3.78
P_2O_5		1.22	1.96	1.23	1.25	1.08
BaO		0.78	0.31	0.81	0.79	0.72
SrO		0.42	0.14	0.34	0.45	0.39
LOI		0.37	0.17	1.15	0.92	0.39
Class		C	C/F	C	C	C

Table 2. Elemental and compound composition of portland cement.

Element (or oxide)	PCC	PCC (Compounds)	
	Percent by weight		
SiO_2	20.6	C_3S	55.3
Al_2O_3	4.34	C_2S	17.3
Fe_2O_3	3.24	C_3A	6.0
CaO	62.3	C_4AF	9.9
SO_3	2.78		
MgO	2.19		
K_2O	0.71		
TiO_2	0.24		
Na_2O	****		
P_2O_5	****		
BaO	****		
SrO	0.18		
LOI	3.08		

tensile strength at the conclusion of freeze-thaw testing.

The first part of Table 3 compares the behavior of samples made with different fly ashes after freezing and thawing in water and brine. Damage characterization ranges from cases where no change is visible to the naked eye to what is assessed as total failure because the part of the sample beneath the fluid level falls away under its own weight. Intermediate degrees of damage are light cracking and heavy cracking. In light cracking, one or two discontinuous cracks are visible. In heavy cracking several continuous cracks lace the sample, yet it remains intact. Surface scaling was also observed in some cases; although undesirable, scaling is not considered nearly as serious as cracking.

Samples in water survived freezing and thawing regardless of whether fly ash was used. All specimens in the brine suffered total disintegration unless fly ash was used. When fly ash was used, some crack-free specimens survived, regardless of the fly ash source; however, all suffered some surface scaling.

Ultrasonic pulse velocity measurement is an objective, nondestructive method of monitoring damage caused by crack formation. As microcrack formation causes the material to become less continuous, pulse travel time increases and pulse velocity decreases. The measurement technique used in this research is known as direct transmission; it measures the travel time required for a compression wave to travel the length of a specimen.

Ultrasonic pulse velocity measurements shown in Figure 1 depict the behavior of the brine-treated specimens throughout the test. These test results are the average for each set of ten specimens, after having been normalized by pretest velocities.

Table 3. Visual description after 300 cycles of freezing and thawing.

Batch Mix	Treatment	Description[a]
Fly ash source and type		
No fly ash	Water	No visible cracking
	Brine	Ten samples disintegrated
15% Neal #4	Water	No visible cracking
	Brine	No visible cracking, slight scaling
15% Neal #3	Water	No visible cracking
	Brine	No visible cracking, slight scaling
15% Weston	Water	No visible cracking
	Brine	No visible cracking, slight scaling
15% Lansing	Water	No visible cracking
	Brine	No visible cracking, slight scaling
15% Ottumwa	Water	No visible cracking
	Brine	No visible cracking, slight scaling
Fly ash content		
No fly ash	Water	No visible cracking
	Brine	Five samples disintegrated; one sample lightly cracked; scaling
5% Neal #4	Water	No visible cracking
	Brine	Two samples cracked; two lightly cracked; two no visible cracking; slight to heavy scaling
10% Neal #4	Water	No visible cracking
	Brine	One sample lightly cracked; remainder no visible damage; slight scaling
25% Neal #4	Water	No visible cracking
	Brine	No visible cracking, slight scaling
35% Neal #4	Water	No visible cracking
	Brine	All samples show light cracking at top; moderate scaling
50% Neal #4	Water	No visible cracking
	Brine	All samples show heavy cracking at top; moderate to heavy scaling

[a]Damage ratings are: No visible cracking; light cracking; heavy cracking; and disintegration; scaling implies near surface damage.

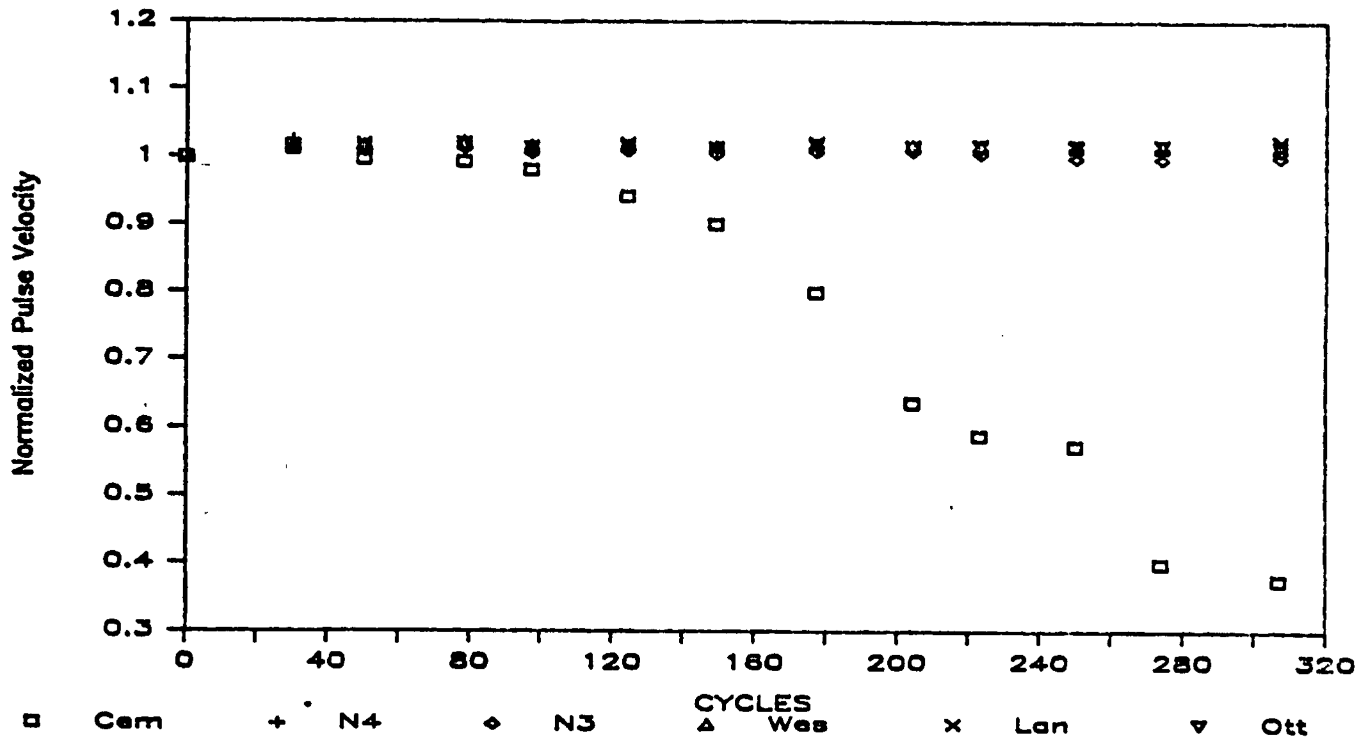

Figure 1. Normalized pulse velocity data for different fly ash sources.

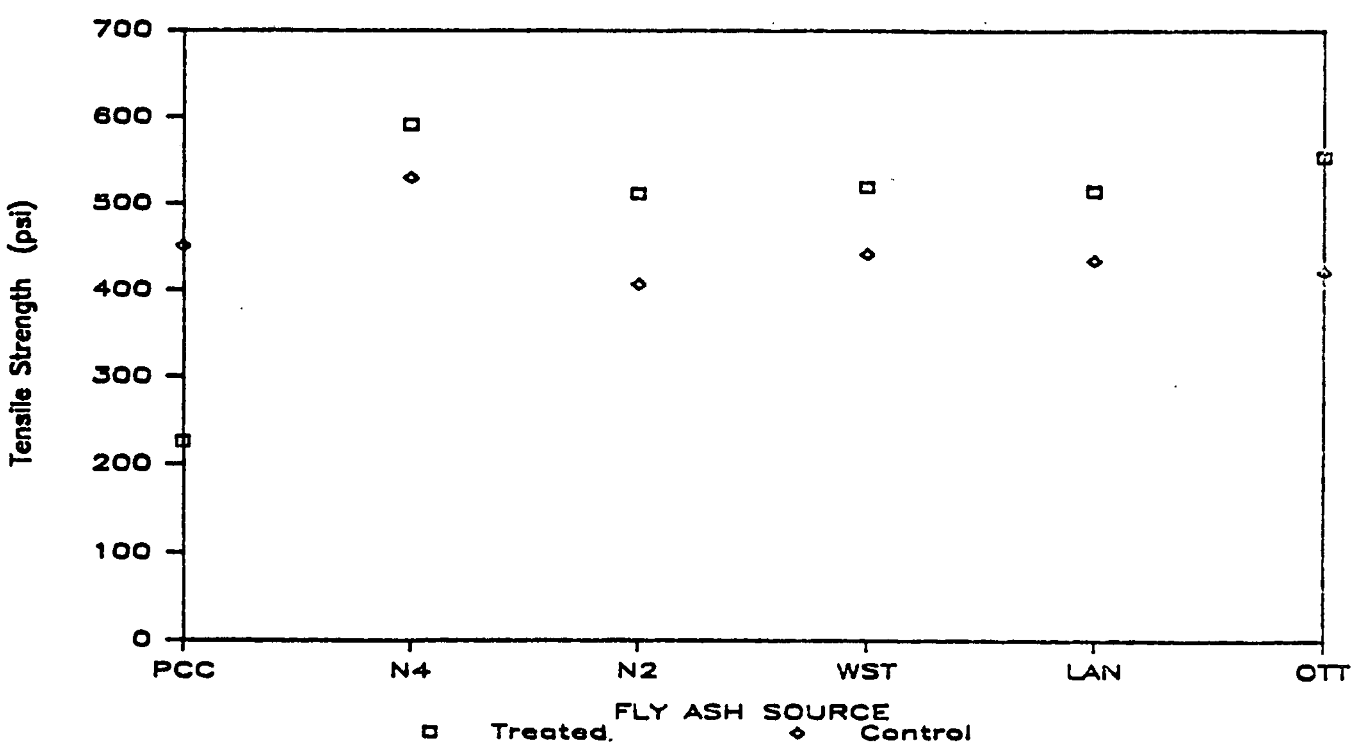

Figure 2. Tensile strength vs. fly ash source.

The ultrasonic pulse velocity measurements are consistent with visual observations: samples with fly ash had no loss in pulse velocity; samples without fly ash started a decline in pulse velocity at forty cycles, on average. After three hundred cycles, the pulse velocity was reduced to roughly one-third the initial value.

Pulse velocities for all specimens in water remained constant and therefore were not plotted.

Strength at conclusion of freeze-thaw testing is plotted in Figure 2. Without fly ash, the average strength of ten specimens tested in brine was less than one half that of specimens tested in water. Where the five fly ashes were used, specimens in brine survived with slightly higher strengths than those tested in water.

Fly Ash Proportions

In an effort to establish limits on the effectiveness of fly as in reducing sulfate damage, fly ash concentration was varied from zero to fifty percent using the test conditions described in the previous section. The second part of Table 1 describes the amount of fly ash used and gives a visual description of the results.

Specimens tested in water appeared to survive the adversity of freezing and thawing at all fly ash concentrations. The percent of fly ash replacement for tests in brine led to observable differences in behavior, however. Specimens containing 5, 35, and 50 percent fly ash showed some cracking. Specimens containing 10, 15 (in previous section), and 25 percent fly ash replacement showed no cracking, except for a single specimen that showed light cracking. Severity of surface scaling was observed to increase with increasing fly ash concentration.

Specimens without fly ash replicated performance of their equivalents discussed in the preceding section.

Ultrasonic pulse velocity measurements shown in Figure 3 correlate to the visual observations. Significant losses in pulse velocity were observed for 0 and 50 percent fly ash replacement. Lesser, but still distinguishable, losses in pulse velocity observed for 5 and 35 fly ash percent replacement. These measurements suggest the optimal range for fly ash replacement is, therefore, more than 5 percent and less than 35 percent.

Tensile strength results shown in Figure 4 suggest an optimum for fly ash concentration on the order of fifteen percent. Specimen behavior was not overly sensitive to this optimum. All fly ash substitution rates resulted in more strength when compared to a standard of portland cement mortar in water.

Analysis of Experimental Results

Fly ash has been observed to reduce the undesirable effects of sulfate in brine. One explanation for this is reduced permeability from pozzolanic reaction products. Mercury intrusion porosimetry research from this work and from that of other investigators indicates that fly ash in a hardened mortar causes reduction in pore size and volume. Post-hardening reaction products from fly ash evidently do not cause a detrimental form of pore alteration. This is in contrast to the pore alteration observed when portland cement mortar without fly ash is subjected to sulfate in sodium chloride brine. Both mechanisms fill the pores in the hardened mortar: sulfate allows rapid deterioration; fly ash appears to prolong life.

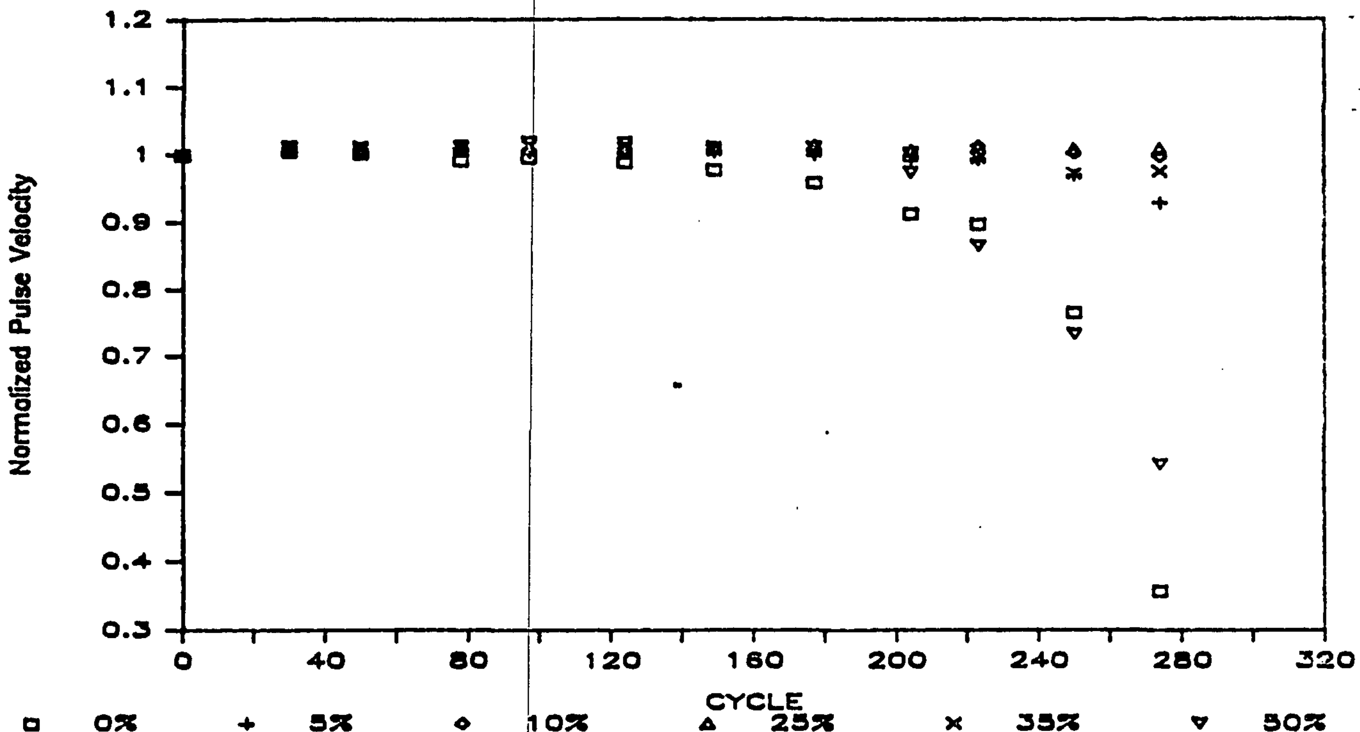

Figure 3. Normalized pulse velocity data for different fly ash concentrations.

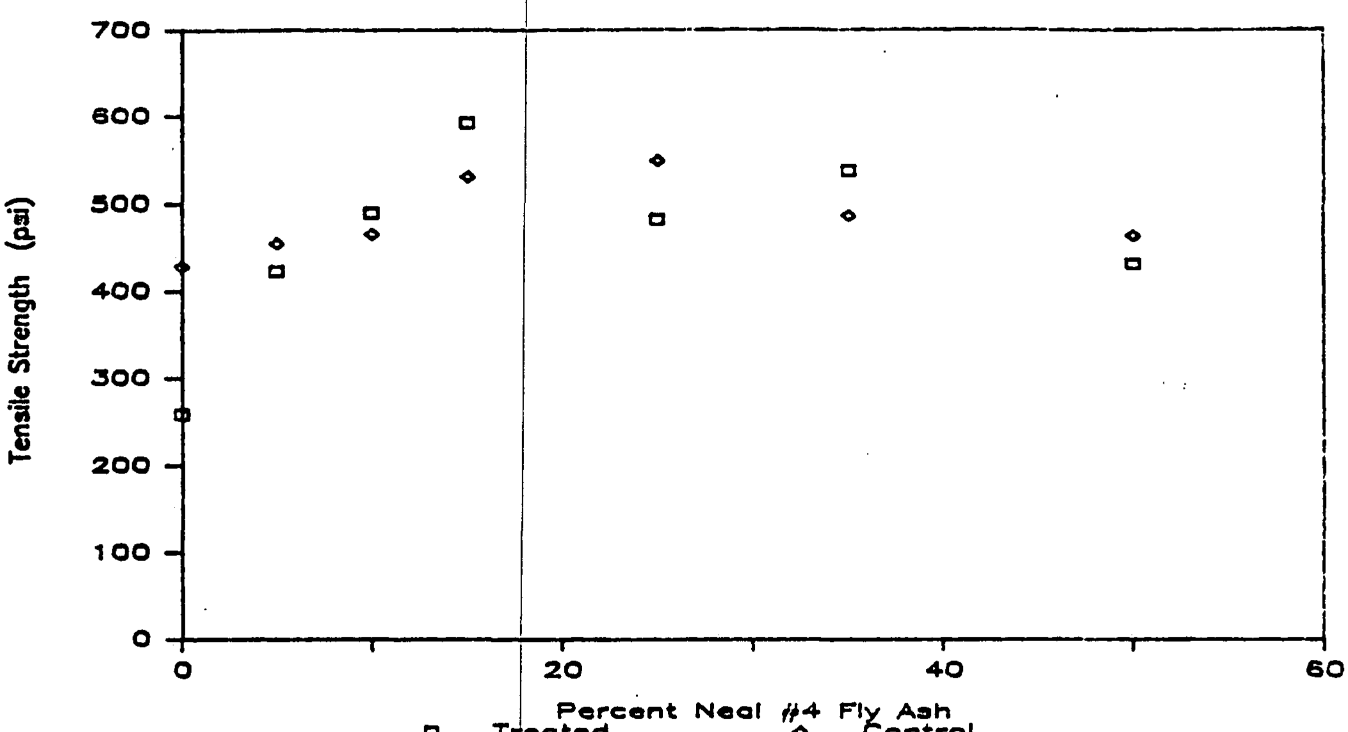

Figure 4. Tensile strength vs. fly ash content.

A glimpse at the aftermath of the process can be had from the two scanning electron micrographs in Appendix A, showing fragments of mortar taken above the visibly damaged area of specimens having undergone 250 cycles of freeze-thaw in a sulfate-tainted brine. The specimen with 10 percent fly ash has less than one-half the length of fractures observed for portland cement alone. Both of these specimens represent an early stage of deterioration and explain why continued decay would occur most quickly in the one without fly ash: The extended and continuous fracture system allows entrance of more solution, thus promoting mechanical destruction and increasing chemical reaction. Deterioration might be arrested by filling these pores when the mortar is dry.

The effect of pore size with respect to fly ash content was investigated by use of mercury intrusion porosimetry. This method allows quantative evaluation of pore sizes with respect to fly ash content. Fragments of intact specimens like those photographed in the scanning electron microscope were tested in a scanning porosimeter. The results, summarized in Table 4, are cumulative percentages of total pore volume for the nominal radius, measured in angstroms, of cylindrical pores modeled by the analysis.

The number of pores in the 500 to 5000 angstrom range correlates to three hundred cycle performance. Specimens exhibiting the best performance tend to have the fewest pores in this size range. For the data used in this research, the most distinct differentiation in performance occurred at 1000 angstroms. The best specimens had 26 percent of their pores greater than 1000 angstroms; the poorest had cumulative percentages of pores greater than 1000 angstroms on the order of 37 to 40 percent. Little

Table 4. Mercury Porosimetry.

Pore Radius (Angstroms)	Fly Ash Content						
	0%	5%	10%	15%	25%	35%	50%
	Cumulative Percentage of Pore Volume						
10,000	5%	6%	2%	3%	3%	2%	2%
5,000	15%	10%	4%	8%	7%	4%	4%
2,000	32%	24%	14%	17%	18%	10%	12%
1,000	40%	34%	26%	26%	30%	20%	37%
500	52%	52%	45%	48%	45%	49%	52%
200	75%	75%	73%	80%	74%	72%	70%
100	88%	88%	86%	92%	86%	85%	85%
50	95%	94%	93%	97%	94%	92%	93%
20	99%	99%	99%	100%	99%	99%	99%

difference was observed in the number of pores greater than 1000 angstroms and those smaller than 200 angstroms.

Pore size is relevant because it affects the transfer of deicing brines into the mortar. The method by which deicing brine is transferred into the interior of concrete can be modeled by a simple test originally developed to measure the ability of soil to take on water. The matric potential or suction of concrete is relevant because a saturation gradient often occurs in pavement sections. A wicking action where fluid moves from saturated regions to dry regions because of capillary rise in unsaturated material also moves salt-laden brines. In portions of a concrete structure where drying leaves a material unsaturated, water evaporates and salts are concentrated. This explains the high chloride and sulfate concentrations in specimens that were subjected to cyclic wetting and drying and to continuous drying at the tops, as reported in a previous report [1].

In real pavements, zones near the bottom of joints are most likely meet the conditions of: (1) wetting and drying or localized continuous saturation, and (2) prolonged contact with concentrated deicing brines. This is because the joint will eventually leak, regardless of the method of joint treatment used. If deicers are used, salt-laden brines will fill the joints. Repetitions of filling and drying produce a reservoir of concentrated, and possibly saturated, brine in a position to enter the concrete at the joints. Field evidence shows significantly higher chloride and sulfate concentrations at joints than in the interior of pavement slabs [1].

The amount of head (driving force) tending to move the fluid and the rate at which the fluid moves is controlled by a complex interrelationship among such factors as capillary geometry and size, capillary continuity, vicosity, fluid surface tension, and wetting angle between the fluid and solid.

Since it is impractical to sort out all of these parameters a composite measurement, utilizing an inexpensive tensiometer, was sought. The tensiometer was built from a glass U-tube and valve, a rubber stopper, and some mercury. Following construction of the tensiometer, a masonry bit was used to drill a 3/8-inch diameter hole into the top of mortar specimens made with different fly ash concentrations; the holes were drilled to a depth of 1.25 inches. The samples were then oven dried for 24 hours, the tensiometer stopper was placed in the hole and sealed, and water was introduced through the valve. With the valve closed to the atmosphere, suction was determined from mercury depression. Results shown in Figure 5 are expressed as head (in feet) per unit of fluid contact area. Except for ten percent fly ash, which may be unreasonably high, the data generally show a trend of minimum suction occurring at the better performing fly ash concentrations. The poorer performers had a greater tendency to draw water.

Measurement of matric potential is an attractive method for predicting freeze-thaw performance of mortar and possibly concrete because the test relates directly to the mechanism by which water and deicing brines are imbibed. The test is quick and easy to perform, and the apparatus is inexpensive. One caution to using matric potential is dependence on moisture content. Suction decreases as moisture content increases; when specimens become saturated, the suction is zero. Thus standard unsaturated moisture conditions must be established by drying to a constant state.

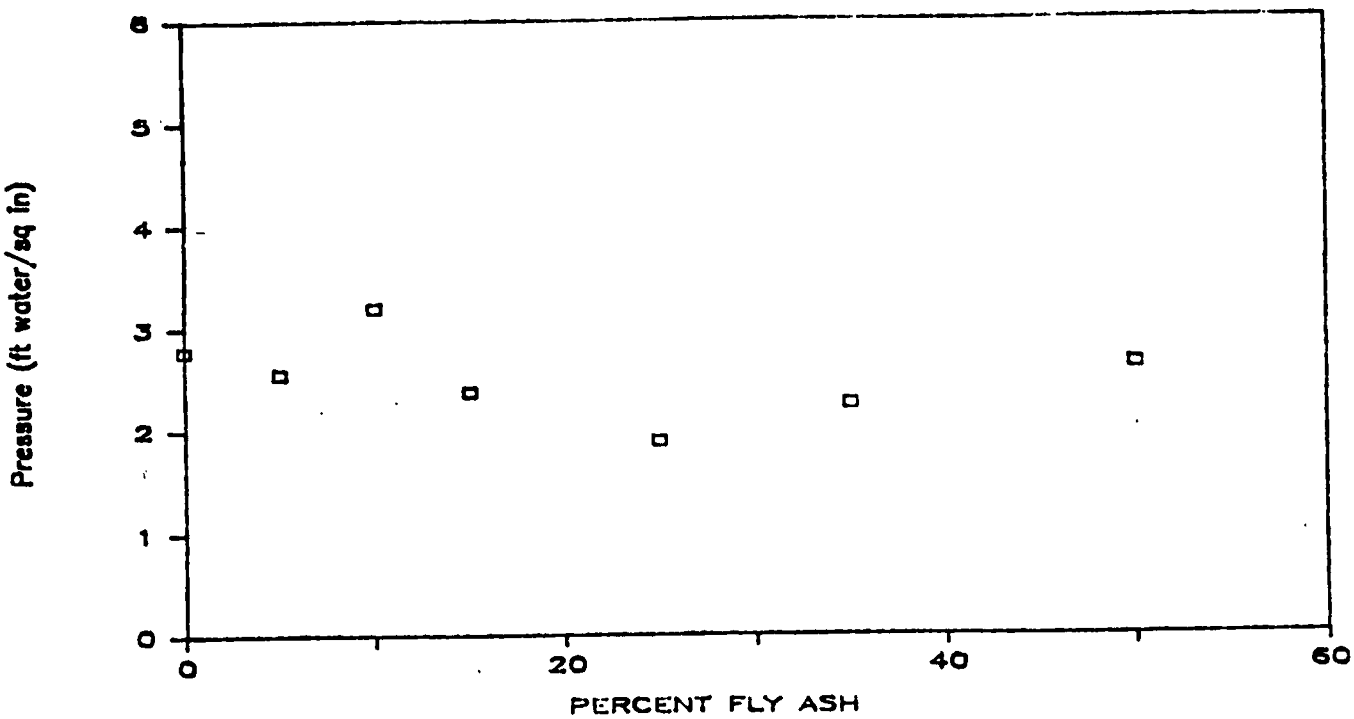

Figure 5. Matric potential of mortar.

EVALUATION OF AGGREGATES

Background

The work reported previously herein was done with mortar because more extensive experimentation is possible with small specimens. Use of mortar also eliminated variables introduced by natural aggregates and facilitated establishment of direct cause-effect relationships among fly ash source, fly ash concentration, and deicer brine treatment. However, systematic progression to prototype conditions requires that coarse aggregates be tested.

The coarse aggregate fraction of concrete plays an important role in freeze-thaw durability with "D-cracking" being the most notable form of deterioration in pavements. D-cracking is generally used to describe deterioration by progressive disintegration from the bottom to the top of pavements near their joints. In one study, D-cracking was observed to occur in pavements placed on clay subgrades, vapor barriers, stabilized subbases, and granular subbases with and without deliberate drainage systems [2].

Coarse aggregate pore structure has been identified as the factor controlling D-cracking. This is because the pores become saturated to the extent that expansion of water upon freezing causes sufficient pressure to break the material apart. The degree of saturation allowing destructive internal pressures upon freezing is called "critical" saturation, and is achieved when about 90 percent of the voids are filled with water. Non-porous aggregates are considered immune to freeze-thaw because they cannot become saturated. At the other extreme are highly porous aggregates which do not reach critical saturation, either because their voids accommodate all water available from the exterior or because the tendency to fill the voids is low. It has been speculated that porous aggregates can offer pressure relief to water freezing in mortar in the same way as does air entrainment. Absorption-adsorption studies by the Portland Cement Association indicate an intermediate range of pore sizes and volumes which are prone to D-cracking.

While recognizing that some factors may have been omitted from this explanation of aggregate participation in freeze-thaw of concrete, one might observe that the explanation offers a framework that aids in the interpretation of the preliminary experimental work involving deicers. It is known that deicer brines, and in particular sulfate-tainted brines, fill pores in mortar and make the material less resistant to freeze-thaw. Extrapolation of this information to aggregate in concrete leads to the possibility that aggregate pores may be modified for good or bad durability. Some other possibilities include: porous aggregates acting as conduits for brines, thus increasing brine contact with mortar, and the reaction of brines with compounds in the aggregates.

Experimental Design

An experimental program was devised to determine whether deicers interact with aggregate in concrete. These experiments utilized four types of aggregate and six freeze-thaw fluids. A comparison of concretes with and without fly ash also was performed.

General characteristics of the aggregates used are as follows:

1. <u>Alden</u>: This is a Class 2 or 3 aggregate, depending on bed. It has a good field service record and a corresponding response to accelerated freeze-thaw testing. The Alden aggregate is nearly pure calcium carbonate with a porous structure.

2. <u>Garrison</u>: This is a Class 2 aggregate with an intermediate field service record. It has shown good response to accelerated laboratory testing. Its dolomitic composition with traces of pyrite and its open pore structure make this stone suspect for chemical interaction with deicers.

3. <u>Waucoma</u>: This is a Class 3 aggregate of nearly pure calcium carbonate with a closed pore structure and a good service record. This aggregate was selected because its composition is similar to the Alden stone but with a different pore structure.

4. <u>Ames Mine</u>: This is a Class 2 aggregate of nearly pure calcium carbonate that performs moderately well in accelerated freeze-thaw tests. This aggregate has a pore structure of intermediate size (between Waucoma and Alden). Its chemical composition is similar to that of the Alden and Waucoma aggregates.

Mercury intrusion porosimetry tests were conducted to verify the pore structure characteristics of the aggregate samples used. The results of these tests are summarized in Table 5. While the cumulative pore size distributions were found to hold with the general character of each stone, a better quantative comparison of pore sizes can be made from the median pore sizes listed at the bottom of the table. To summarize: median size, or one-half of the pores in the Alden and Ames Mine aggregates, were either larger or smaller than 3,000 and 5,500 angstroms. The median for the Garrison sample exceeded 10,000 angstroms. In contrast, the Waucoma stone's median was only 120 angstroms.

Composition of freeze-thaw solutions used in tests are identified and listed in Table 6. Solutions 1 and 6 are controls. Solution 2, of the impurity of magnesium chloride, was formulated because of preliminary

Table 5. Pore Size Distribution of Aggregates.

Pore Radius (Angstroms)	Alden	Garrison	Waucoma	Ames Mine
	(Cumulative Percentage of Pore Volume)			
10,000	16	57	0	1
5,000	53	72	8	5
2,000	68	83	12	71
1,000	72	88	13	83
500	75	90	18	89
200	80	93	31	92
100	84	96	60	95
50	90	98	80	97
20	98	99	98	99
	(Median Pore Size, Angstroms)			
	5,500	10,000	120	3,000

Table 6. Brine Compositions Used in Concrete Freeze-Thaw Testing.

(Weight Percent by Solute)

Solution	NaCl	$MgCl_2$	$CaCl_2$	$CaSO_4$	$MgSO_4$	Comments
1	100.0	0	0	0	0	Control
2	98.0	2.0	0	0	0	Synthetic
3	98.0	0	0	2.0	0	Synthetic
4	96.1	0.2	0	3.61	0.09	Kansas salt
5	94.6	0.2	1.57	3.55	0.09	Kansas salt + $CaCl_2$ sand
6	0	0	0	0	0	Control

results from tests on mortar where it was once thought to be a worst-case condition. This was later found to not be the case. Solution 3 was fabricated as representing a worst-case sulfate concentration. Solution 4 is a sample typical of Kansas salt sources. Solution 5 is the Kansas salt modified with calcium chloride to represent sand-salt deicing mixtures commonly used.

Experimental Procedure

The Type I portland cement described in Table 2 was used to cast freeze-thaw test beams of an Iowa DOT C-3 paving mixture with 6% air entrainment. One-half of the specimens contained Neal #4 fly ash as replacment for 15% portland cement.

Specimens were moist cured for 28 days and then subjected to freezing and thawing per a modification of ASTM C-666, Procedure A.

To evaluate the influence of brines and remain consistent with the evaporative transpiration model used for mortars, the fluid media used in these tests were saturated brines maintained at the mid-height of the beams.

Dynamic modulus of elasticity was measured every 25 cycles with an apparatus defined in ASTM C-215. Durability factor was computed according to procedures in ASTM C-666. Flexural strength was measured per ASTM C-78.

Durability Factor

Table 7 summarizes the average durability factor for three repetitions of each test variable. Interpretation of these data are as follows:

Table 7. Durability Factor.

Aggregate	Sol. 1	Sol. 2	Sol. 3	Sol. 4	Sol. 5	Sol. 6
	Brine Solution Used					
Alden w/o FA*	61	52	52	51	53	80
Alden w/FA**	84	99	98	95	98	93
Garrison w/o FA	58	81	79	51	52	67
Garrison w/FA	68	72	75	60	81	76
Waucoma w/o FA	90	86	94	91	96	89
Waucoma w/FA	102	98	101	99	99	103
Ames Mine W/FA	96	96	95	90	92	99

- <u>Alden</u>: Concrete made with this stone just met the lower expectation for Class 2 aggregate tested in water, DF = 80 %.

  Comparison of water and brine tests showed that pure sodium chloride (solution 1) was more damaging than water, but less damaging than any of the adulterated brines (solutions 2,3,4,& 5). The adulterated brines all produced about the the same amount of deterioration.

  When fly ash was included in the Alden mix, a significant and consistent improvement was observed for all of the solutions. The fact that fly ash produced a significant improvement for all of the brines suggests that mortar is an important factor. The porous aggregate offering a conduit to the mortar could also contribute to deterioration.

  The same amount of deterioration resulting from the magnesium chloride adulterated brines and those brines containing sulfate is an enigma. Previous work showed magnesium chloride to be inert.

- <u>Garrison</u>: Tests in water with this sample of Grarrison aggregate produced a lower durability factor than indicated by experience, DF = 67%. As these experimental results are inconsistent with baseline experience, conclusions should be regarded as tenative. This particular sample of Garrison aggregate could be an outlier, i.e., not representative of the deposit; also, some inadvertent error could have been made in the batching and testing process.

  A 9 point loss in durability factor resulted from sodium chloride (solution 1); the two brines from natural rock salt (solutions 4 & 5) depressed the durability factor by 15 points.

  However, the durability factor was enhanced by the two synthetic brines with magnesium chloride or calcium sulfate (solutions 2 & 3).

  An increased durability factor occurred with fly ash concrete in the natural brines, but slight reductions were observed with the sythentics.

  While there may be some sensitivity to types of brines, adding fly ash was found to have a mixed influence on frost resistance. This suggests an aggregate-brine interaction rather than an attack on the mortar.

  A perplexing feature of these results is the conflicting consequences of the natural and synthetic brines. Either the factors controlling the process are more complex than previously envisioned, or the observed ten point differences in durability factor may be a measure of test variability and not a reflection of concrete or aggregate behavior.

- Waucoma: Concrete with this aggregate is consistent with previous experience when tested in water, DF = 89%.

  Sensitivity to brine composition is not apparent and use of fly ash corresponds to a consistent increase in durability factor, also without regard to type of brine.

  The importance of a non-porous aggregate pore structure on freezing and thawing in a deicing environment is indicated by these data. The difference between this and the two stones previously discussed is closed versus open pore structures. Open pores in the aggregate may be the conduit by which deleterious brines are allowed to make contact with the mortar.

- Ames Mine: Concrete for test slabs using this aggregete was purchased from a local ready-mix producer. All slabs contained fly ash (i.e., concrete without fly ash was not tested). The concrete performed better in water than experience suggests. Limited sensitivity to brines was observed, with the the most severe degradation occurring for solutions 4 and 5, those with natural salt. These results support the observation that a closed pore system in aggregate can be beneficial to resisting deterioration. A median pore size of 3,000 Angstroms performed well.

Tensile Strength

An alternative appraisal of freeze-thaw performance with deicers is flexural strength after three hundred cycles. Figures 6 through 9 are plots of strength versus solution for the aggregates included in this study. These results correspond to those for durability factor, in that fly ash most increased strength when used with the Garrison aggregate; fly ash was observed to have a lesser impact with Alden stone and caused minimum response with Waucoma.

An important result of this test was the finding that fly ash reduces variability in strength when used with the Garrison aggregate. Some Garrison aggregate samples mixed without fly ash were found to have no flexural strength, an extreme condition; however, the average was close to

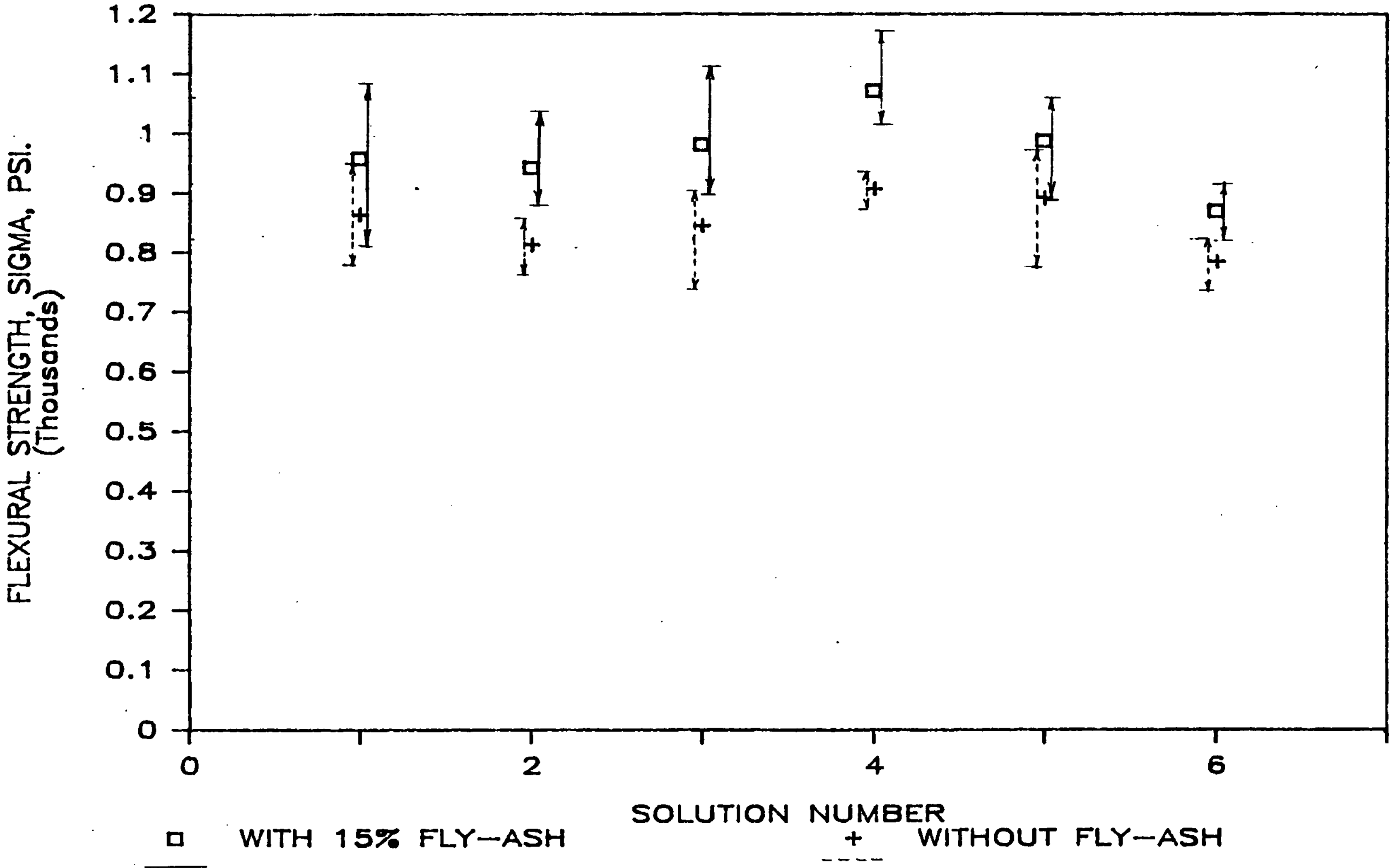

Figure 6. Flexural strength with Alden aggregate.

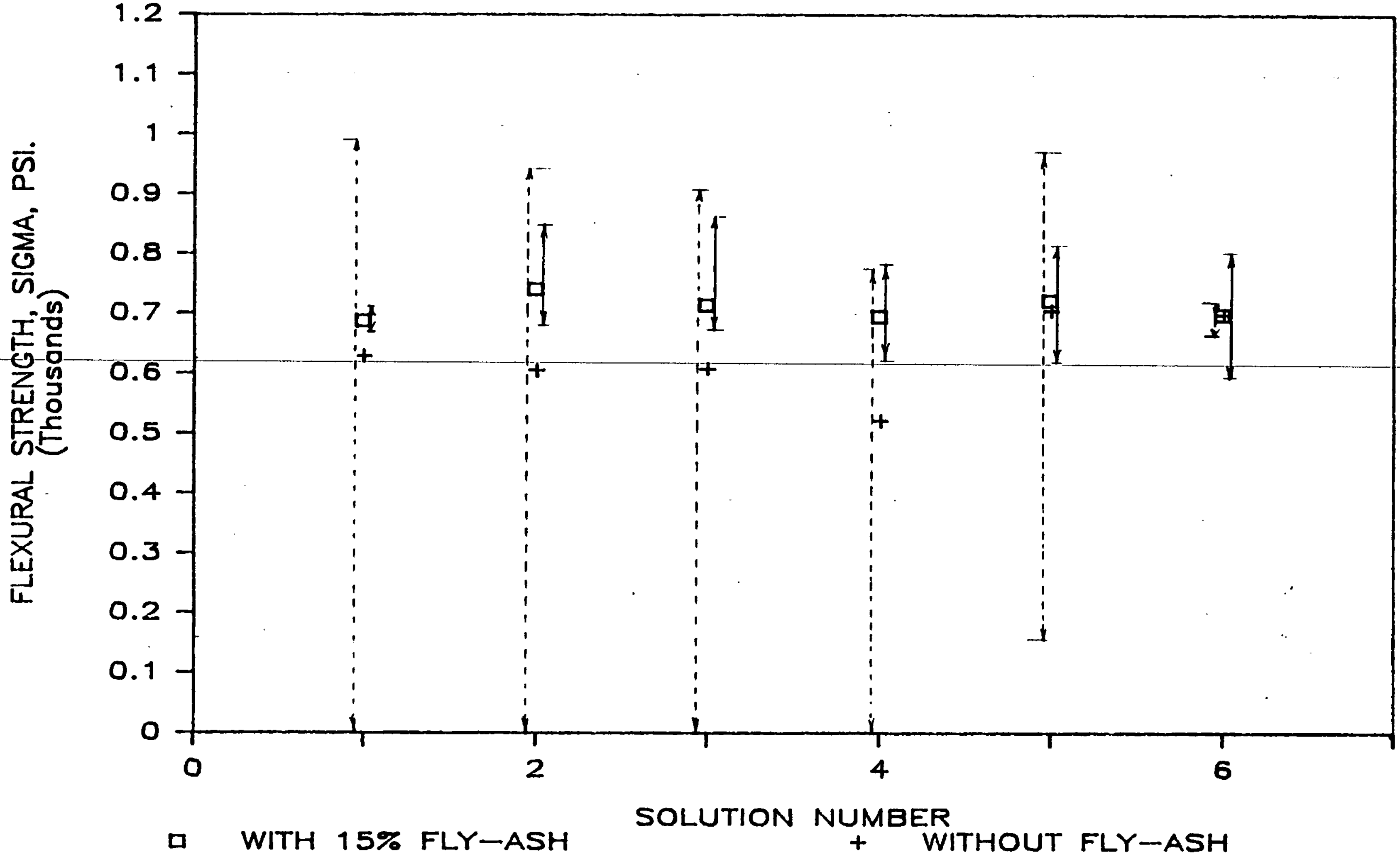

Figure 7. Flexural strength with Garrison aggregate.

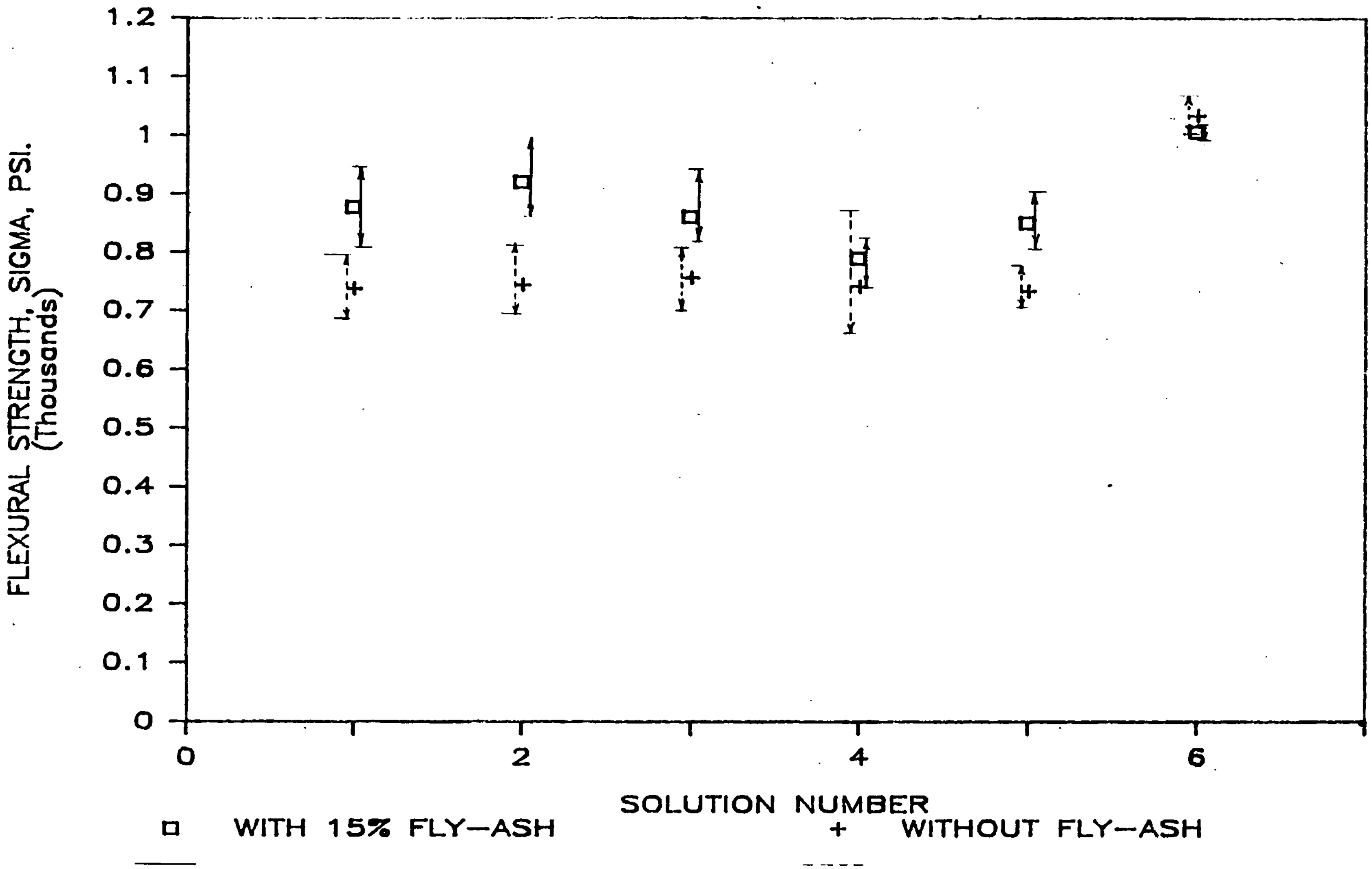

Figure 8. Flexural strength with Waucoma aggregate.

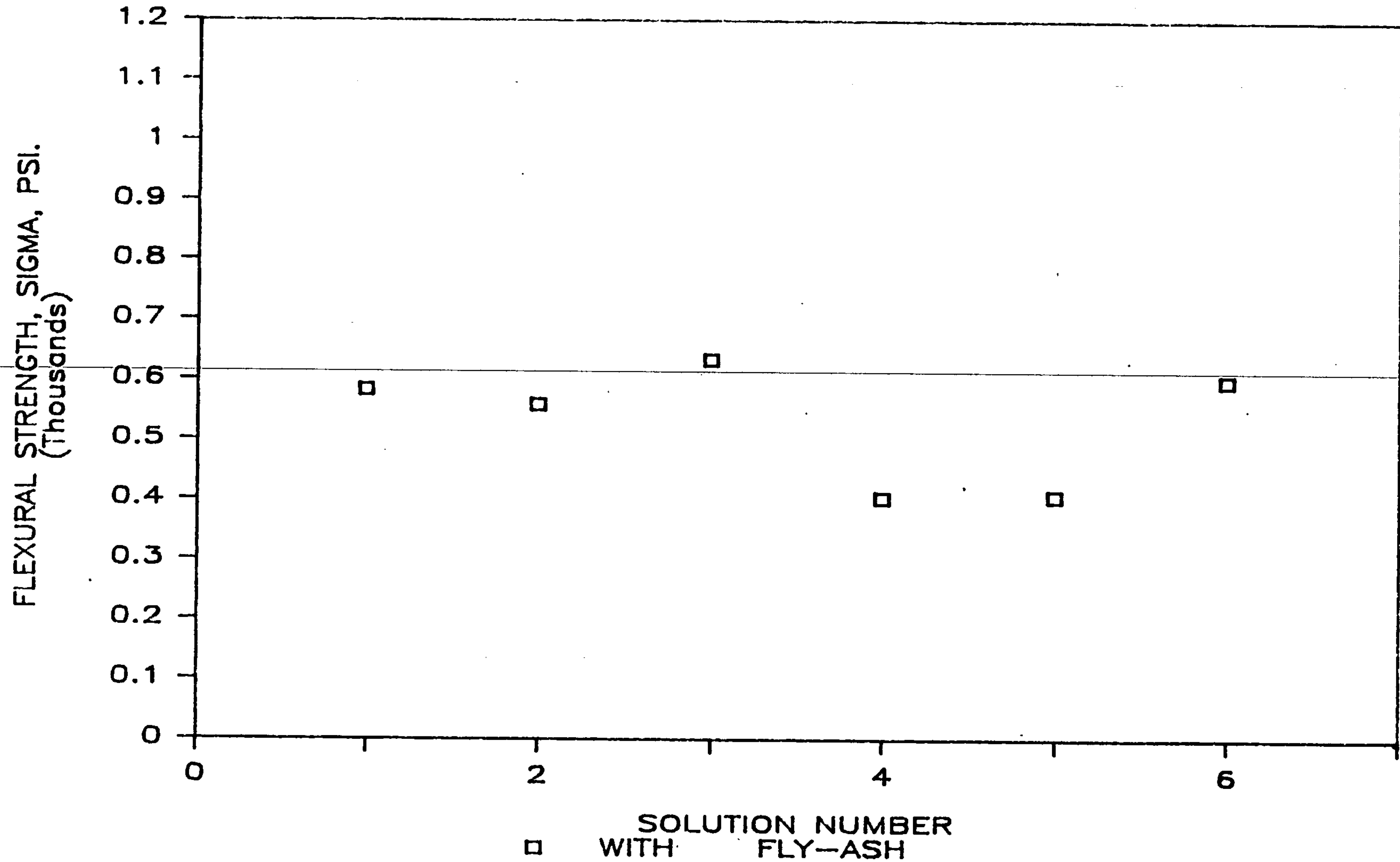

Figure 9. Flexural strength with Ames Mine aggregate.

the average for fly ash concrete. If pavement deterioration is controlled by a "weak link" mechanism, these findings suggest that concrete mixed with the Garrison aggregate and having no fly ash content is least desirable of the materials tested.

When concretes made with the Waucoma and Ames Mine aggregates were treated with the natural brines, flexural strength was found to be minimum. Flexural strength tests were found to be ineffective at differentiating the effects of brine treatments for the other aggregates and brines.

Analysis of Experimental Results

Conclusions drawn from these accelerated freeze-thaw tests are prefaced with the understanding that there were only three repetitions of specimens for each set of variables, and thus far no duplication of batches. This is in contrast to the experimental work done on mortars, where tests were duplicated on at least three occasions in several repetitions of specimens. Thus there is a danger of assessment being based on of a statistical fluke, possibly due to materials sampling, specimen preparation, or test procedure.

These sources of uncertainty being stated, the available evidence suggests that deterioration of concrete in the presence of deicers depends on the resistance of the mortar, as is suggested by improvement in durability factor with addition of fly ash. The better aggregates, Waucoma and Ames, are influenced less by the mortar than the poorer stones.

Coarse aggregate also appears to have a significant influence on resistance to deterioration; that is, a porous stone capable of adequate performance in water (Alden) was observed as being affected more by deicers than a chemically equivalent non-porous stone (Waucoma). Durability factors for the porous stone thought to be chemically active (Garrison) paralleled performance at a somewhat lower level than aggregates of similar porosity with inert chemistry (Alden). Thus porosity, not chemical composition, may also be a significant factor.

TREATMENT OF EXISTING CONCRETE

Present and previous research undertaken in this project suggests that concrete can made to resist sulfate contaminated deicers through prudent selection of aggregate and use of fly ash. However, this solution does not apply to existing concrete pavements.

The ability of fluids to saturate pores in mortar and aggregate phases of concrete is a significant component of the deterioration mechanism. Any method of reducing the rate of fluid intrusion should also reduce the problem. This assertion has been demonstrated by research with polymer-impregnated and latex modified concretes, and also with epoxy and silane treatments as reported in earlier phases of this research. These approaches are technically sound, but all are impeded by high cost of the materials needed to perform them. Some are simply impractical. Therefore, the need exists for an inexpensive, practical method of treating existing pavements.

A possible method involves using a sodium silicate treatment. Sodium silicate is an inexpensive colloidal suspension derived from the reaction between silica and sodium carbonate. It has potential for desirable modification of pore structure in existing concretes.

As part of a preliminary evaluation of sodium silicate as a concrete treatment technique, cylindrical cement mortar specimens brushed with sodium silicate were subjected to 250 freeze-thaw cycles in a natural rock salt brine modified by calcium chloride, as defined by Solution 5. The average of three ultrasonic pulse velocity measurements at the conclusion of freeze-thaw resulted in 98 percent of initial velocity being retained for sodium silicate treated specimens and only 30 percent for untreated specimens. The average tensile strength of the treated specimens after freeze-thaw was 506 psi, while strength for the untreated companions was reduced to 320 psi.

Sodium silicate is used extensively as an injected grout to reduce permeability and compressibility, and increasing strength of soil. This application involves a setting agent, normally calcium chloride, which offers free calcium cations to form silicate hydrate, a product similar to that resulting from pozzolanic reactions in concrete. Similar reactions are thought to occur when sodium silicate is brought into contact with hydrated portland cement. The sodium silicate makes a hard cement because it reacts with free calcium coming from portland cement hydration or with calcium from chloride deicer treatments. Capillarity should assist pore filling by drawing the sodium silicate into the mortar.

The ability to glue a sawed beam back together provides a second means of preliminary evaluation of sodium silicate/concrete reactions. This is the same procedure used to test epoxies as described in the Iowa DOT Supplemental Specification for Epoxy Deck Injection Repair. Three beams were sawed in half, soaked for two hours in water, painted with sodium silicate on the sawed surfaces, and placed together with one section on top for 24 hours. The beams were wet cured for 13 additional days, then tested in flexure. The average flexural strength at the bond was 338 psi. Such strength indicates a significant reaction with the concrete because the sodium silicate alone would simply go into solution. Although the strength is somewhat less than the 400 psi required for epoxy, 338 psi is significant and suggests a potential as a binder for severely deteriorated concrete.

To perform as a deicer inhibitor, bond strength may not be as significant as propensity for absorption. Based on high surface tension and low contact angle, the capillary potential or the tendency for absorption into concrete should be greater than water. However, a factor working counter to capillary potential is greater viscosity than water. This means it will take longer to saturate a porous material than water, but total saturation may not be essential and a protective shell of filled voids may arrest deterioration. Viscosity of sodium silicate is variable, it depends on the silica to sodium ratio, concentration of solids, and temperature. All variables can be controlled, but the ones needing control are yet to be determined.

As the intent of this research is to find ways of extending the life of existing concrete, sodium silicate applications might be most effective at existing joints that have undergone some deterioration but are still salvageable, and at or on old concrete exposed when joints are sawed and removed. In the latter case, sodium silicate could be introduced by painting or spraying of exposed surfaces before the patch. For undisturbed joints, simple painting or pressure injection is possible.

Potential advantages of sodium silicate over alternative pore filling compounds are chemical compatibility with concrete, insensitivity to moisture, and single component application. More important is cost: the W. J. Jaques Company routinely uses sodium silicate to grout in soil; they indicate the materials can be delivered to Des Moines for slightly less than $1.00 per gallon. This is in contrast to $60.00 per gallon for epoxy. Although using sodium silicate to improve resistance to freeze-thaw in deicers may be new, the material is an ingredient in curing and surface hardening compounds that have been available for several years.

PAVEMENT SECTIONS

Twelve concrete 4 x 4 foot slabs twelve inches thick were constructed on exposed terrain near the Spangler Geotechnical Laboratory to measure the number of natural freeze-thaw cycles and the rate of deicer contamination for typical application rates used in this state. An Iowa DOT Type C paving mixture of Ames Mine crushed stone and a local gravel was provided by a local vendor. Plastic guttering was attached and sealed to the sides of the slabs to collect runoff.

Deicers representing Solutions 1 through 5 were applied 11 times at a rate of 800 pounds of salt per lane mile during the winter of 1988-1989. This was done to simulate deicing for heavily trafficked roadways for this particular winter in the Ames area. Runoff collected from the slabs was neglible, indicating thus far that everything that went onto the concrete went into the concrete. The intent is to continue the process for several years and monitor chloride and sulfate concentrations annually.

Temperatures were automatically measured and recorded every 30 minutes by a dedicated portable computer and thermisters cast into the slabs. Air temperature, temperature on the surface of the slab, and temperature at the depths indicated in Table 8 were monitored.

A long-term goal of this work is to relate meteorologic data to temperatures and number of freezing cycles within pavements such that freeze-thaw behavior in pavements can be estimated for locations throughout the state. An immediate objective is to compare the laboratory tests with field behavior. Table 8 summarizes measurements taken from January 21, 1989, to March 21, 1989, or the last thaw of the season. Annual freeze-thaw cycles were estimated by factoring the two-month record to include

Table 8. Pavement temperatures.

Depth, Inches	Freeze-Thaw Cycles	Estimated Annual Freeze-Thaw Cycles	300 Cycle Life, Years	Minimum Temperature, °F
0	37	55	5.5	0
2	27	40	7.5	8
4	22	33	9.1	11
6	18	27	11.1	12
8	13	20	15	18
12	9	13	23	22

another month. This was done because shipment delays caused the computer to arrrive late. The number of annual cycles were divided into 300 cycles to arrive at an equivalent life represented by the standard test.

The number of cycles decrease with depth and the corresponding increase in life represented by the standard lead to the estimate that the standard test corresponds to 20 years of freeze-thaw cycles, although the temperatures in nature are not as low as those in the laboratory test.

These data also show a significant influence of pavement thickness on potential pavement life. The observed bottom to top progression of D-cracking suggests that critically saturated freeze-thaw cycles begin at the base of the pavement. If number of critically saturated cycles controls pavement life, the data available thus far suggest that apvement depth is a dominant factor. A 6-inch pavement has about one-half the life of a 12-inch pavment. These data also imply that pavement depth should be an important consideration in evaluating field performance of materials. Materials that do well in a thick pavement may not meet expectations in a thin pavement.

The significance of minimum field temperatures being higher than the $0^{o}F$ in the standard laboratory test is not totally understood. As the freezing point of fluids is depressed in capillaries, a first inclination is to speculate that the field temperatures may not be cold enough to freeze the fluid, thus doing no damage. A quick computation using the median capillary radius for aggregate and mortar indicates from $0.1^{o}F$ to $0.4^{o}F$ degrees depression below freezing for all of the materials used in this research. If true, this suggests all of the field temperatures encountered are sufficiently low to freeze most of the water in the capillaries. The fact that the deicers further depress the freezing point some unknown amount may also be important, but there is insufficient information about this phenomenon to support a rational speculation.

CONCLUSIONS AND RECOMMENDATIONS

Within the context of the experimental work in this phase of the research, the following conclusions concerning concrete mortar can be made:

Fly ash from five sources available in Iowa was found to significantly improve freeze-thaw resistance of mortar in sulfate-tainted brines.

An optimum amount of fly ash to resist sulfate-tainted rock salt brines was found to be 15 percent weight replacement of fly ash for portland cement. This amount of fly ash produced 130 percent improvement in tensile strength over specimens without fly ash after freezing and thawing.

Improvement of mortar by fly ash is associated with decrease in pore size, with the best performance occurring when pores larger than 1000 angstroms was a minimum of 26 percent.

A simple test measuring the capillary potential of mortar was devised. This test showed optimum freeze-thaw performance corresponded to minimum capillary potential.

Based on the limited data available for freeze-thaw deterioration of concrete with different types of coarse aggregate and use of sodium silicate as a restorative treatment, tentative conclusions are as follows:

In addition to the mortar phase, the pore structure of coarse aggregate has a significant influence on the ability of concrete to resist freeze-thaw deterioration in the presence of sulfate-tainted rock salt brines.

Porous aggregates used in this study were the most vulnerable, in that the deicer brines produced sizable reductions in durability factor. Although altering the mortar phase with fly ash was beneficial, the amount of improvement depended on the chemical composition of the rock. Improvement was adequate with a limestone, but only marginal with a dolomite.

A non-porous stone was least affected by the brines. Also, fly ash improved durability of a good quality concrete.

Sodium silicate treatment improves the freeze-thaw durability of hardened mortar which has not had fly ash incorporated at mixing. Thus, sodium silicate may be a viable treatment for concrete placed before fly ash use was common.

Suggestions for implementation resulting from this research are based on the presumption that rock salt deicers will be used, regardless of source and amount of contamination. Fifteen to twenty percent replacement of portland cement with the types of fly ash used in this study should make a significant improvement in resistance to freeze-thaw in deicers. This is on track with what is understood to be existing DOT policy, which allows up to 15 percent fly ash. A somewhat stronger statement requiring fly ash where deicers are to be used seems appropriate.

Although fly ash will improve a concrete, its use may not insure desirable performance with all aggregates, in particular those which are porous and of dolomitic composition. Non-porous stone with fly ash appears to be the best combination for durable, deicer-resistant concrete. Although stipulation of rehabilitative techniques such as sodium silicate treatment is premature, it might be speculated that pavements without fly ash but with open-pored aggregates are likely candidates for rehabilitation. Such work should probably be done before the pavement looks as though repair is needed, or when the cracks are small, like the one shown in Appendix A.

CONTINUED RESEARCH

Although details for Phase III of this project should be developed after consultation with the Highway Research Board and Iowa DOT staff, some suggestions based on the author's perception of the problem are offered. First, it seems that information on the role of coarse aggregate needs to be expanded to support a greater assurance in assessment, and more refinement in categorizing good, intermediate, and bad aggregates. This can be accomplished by continuation of the work done on coarse aggregates, with emphasis being placed on reproducibility and extension to include a bigger sampling of the large number of aggregates available.

A second goal is to explore techniques by which the lives of vulnerable pavements now in place can be extended. The work done with aggregates should help identify problem pavements. Although a brief excursion was made with sodium silicate during this research, other materials are possible and should be evaluated if for no other reason than comparison. Some possibilities are polymers and hydrophobic compounds used in soil stabilization; others, of course, are epoxies, latex, and silanes.

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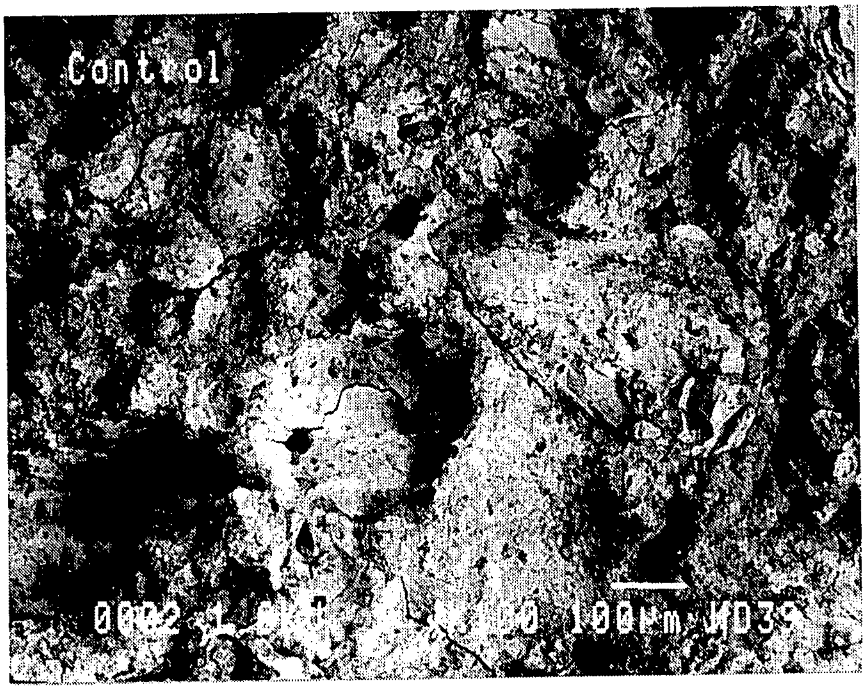
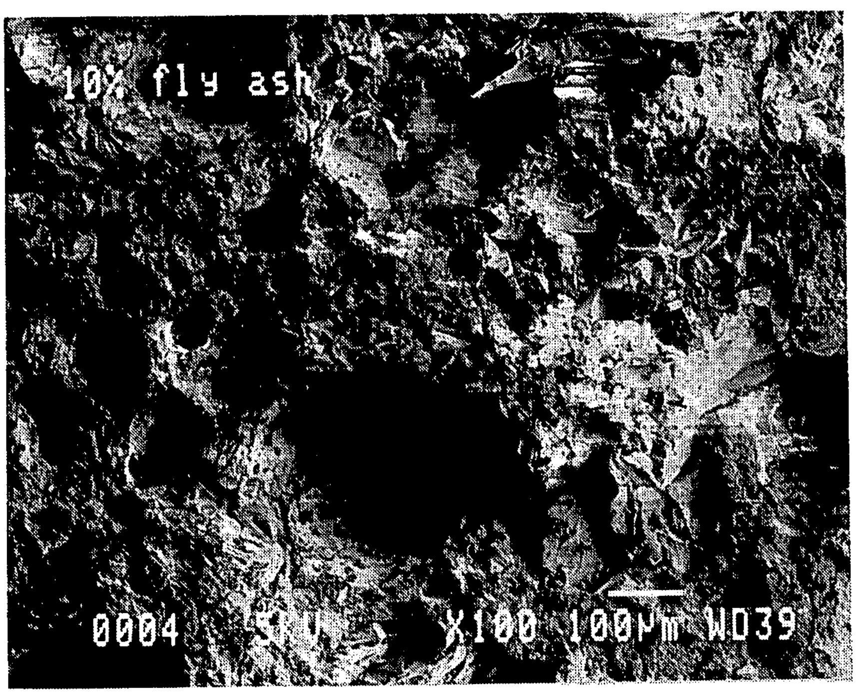
APPENDIX A



(a) No fly ash--- 4050 linear µm of fracture



(b) 10% fly ash--- 1725 linear µm of fracture

Figure 1. Benefit of fly ash in mortar samples subjected to freeze-thaw action. Comparison of fracture length shows that the control (no fly ash) specimen displayed more than twice the linear fracture present in the fly ash treated specimen.