J.M. Pitt M.C. Schluter D.Y. Lee W. Dubberke
January 1987

Effects of Deicing Salt Trace Compounds on Deterioration of Portland Cement Concrete

Sponsored by the Iowa Department of Transportation, Highway Division,
and the Iowa Highway Research Board

Iowa Department of Transportation

final report

Iowa DOT Project HR-271
ERI Project 1771
ISU-ERI-Ames-87107

College of Engineering
Iowa State University

ERRATA: on page 9, paragraph 2, line 6, the word "Type III" should read "Type II"

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Highway Division of the Iowa Department of Transportation.

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department of civil engineering
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iowa state university

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INTRODUCTION

Naturally occurring rock salt is vital to ice removal procedures in the northern states. In 1980, 6.4 million tons of rock salt were used by federal, state, and local agencies for ice and snow control. This is approximately 40 percent of the rock salt mined [1].

There are many sources for deicing salts. Rock salt purchased by the Iowa Department of Transportation comes from mines in Michigan, Louisiana, and Kansas. Figure 1 is a compilation of Iowa DOT contract data for deicing salt origins. Contours represent percentages of Kansas deicing salt delivered to storage sites during the period 1961 to 1984. Halites having origins other than Kansas were from Louisiana and Michigan. Salt purchases are made using a low-bid process explaining the high percentage of Kansan halite in the western half of the state.

The current specification for deicing salts (ASTM D632) addresses only particle size gradation and sodium chloride content, which is limited to a minimum of 95 percent by weight. This allows up to 5 percent impurities, the most significant of which is calcium sulfate; see Table 1.

This document reports research on the effects of calcium sulfate in halite on portland cement durability. Much has been published about sulfate ions causing expansive reactions in portland cement concrete [2,3], on scaling caused by sodium chloride [4,5], and the participation of magnesium sulfate in seawater attack [2]. However, little work has been done on the influence of sodium chloride and

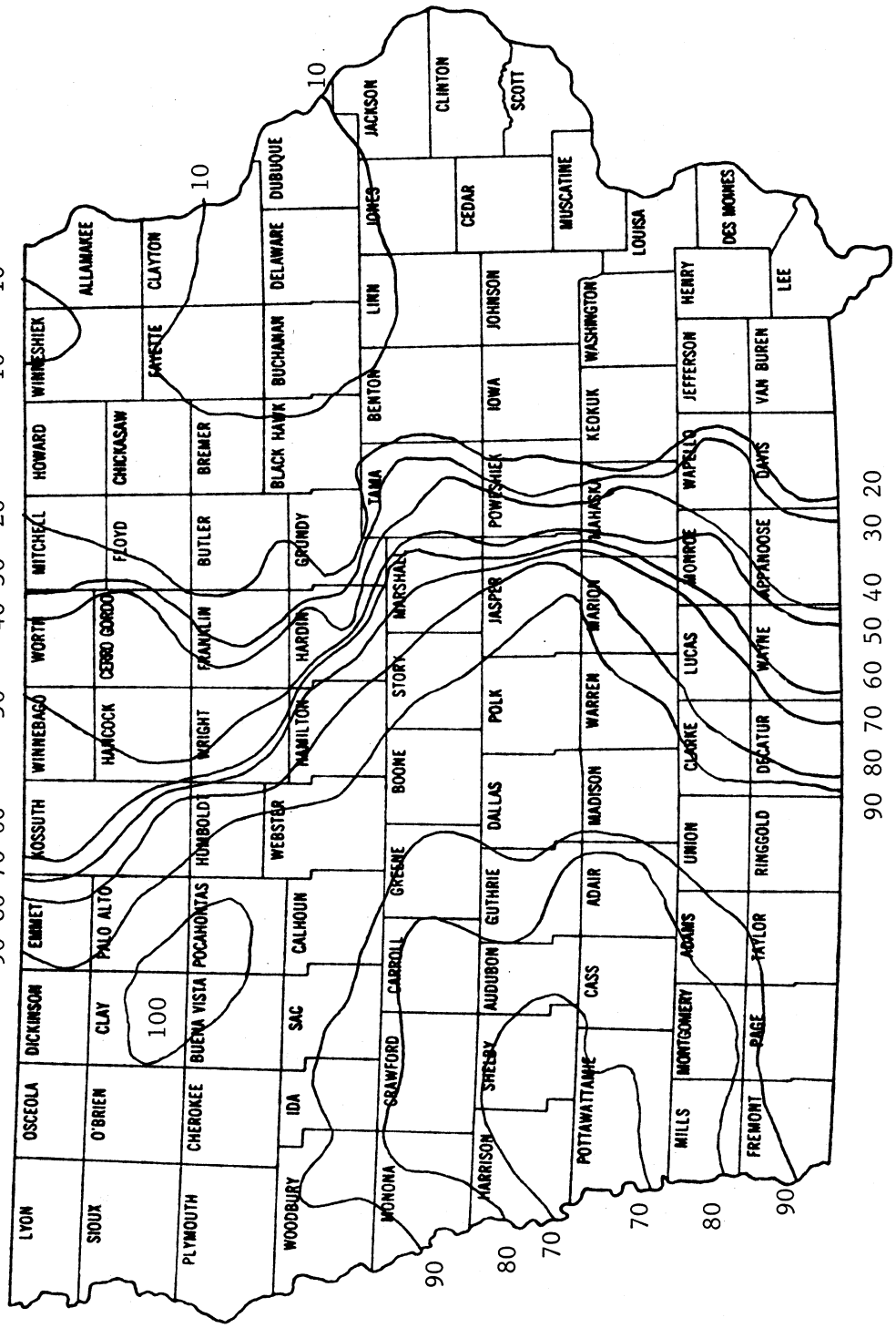

Figure 1. Distribution of Kansas salt application, contours equal percent of Kansas salt

calcium sulfate solutions as they are found combined in natural rock salt. Durability studies were conducted using brines containing different amounts of gypsum as an impurity. Damage mechanisms, reaction products and pore structure changes were evaluated.

Table 1. Chemical analysis of rock salt from various sources [from Kaufmann (6)]

Chemical	Source		
	Michigan	Louisiana	Kansas
Moisture	0.141[a]	0.023	0.095
Water Insolubles	2.484	0.765	-----[b]
Calcium Sulfate, $CaSO_4$	0.881	0.215	3.596
Calcium Chloride, $CaCl_2$	0.049	0.006	-----
Magnesium Chloride, $MgCl_2$	0.047	0.004	0.199
Sodium Chloride, NaCl	96.398	98.987	95.715
Acid Insolubles	-----	-----	0.295
Iron Oxide, Fe_2O_3	-----	-----	0.012
Magnesium Sulfate, $MgSO_4$	-----	-----	0.088

[a] Percent by weight.

[b] No appreciable amount.

BACKGROUND

Typical of a sulphate bearing halite deposit is the Hutchinson member of the Wellington formation of the Kansas salt beds. Such deposits are thought to have originated in shallow, shelf seas that were connected to the oceans by deep feeder channels. These channels supplied the necessary minerals to facilitate sodium chloride and gypsum precipitation. As mineral concentrations increase, gypsum is first to precipitate, followed by concurrent precipitation of gypsum and halite, and at high brine concentrations, pure halite will precipitate. Brine concentrations vary depending on seasonal variations in weather and amount of influx or recharge by the feeder channels.

The resulting deposits are predominately halite with alternating layers of gypsum. The amount of gypsum varies but averages from 2.0 to 4.0 percent by weight [6,7]. Gypsum converts to anhydrite as overburden pressure builds from overlying evaporites or other sediments. Hence, halite deposits can contain both gypsum and anhydrite.

Calcium sulfate can reach significant concentrations in a brine containing sodium chloride. According to Madgin and Swales [8], the solubility of calcium sulfate combined with sodium chloride increases to 3.5 times the ordinary solubility. A saturated brine from this salt could contain as much as 4000 ppm sulfate, more than enough to cause sulfate attack in concrete [9].

Mechanisms for sulfate attack have conventionally been considered

a three step process. The first involves sulfate ion diffusion where diffusion rate is dependent on permeability and ion concentration. A second step, which is dependent on the cation present, involves reactions between calcium hydroxide and sulfate ions to form gypsum, known as gypsum corrosion. The third and most damaging step is sulfoaluminate corrosion, where sulfate ions from gypsum react with sulfate-starved calcium-aluminum hydrates to form ettringite [9]. Ettringite is a stable product occupying greater volume than its constituents.

The presence of sodium chloride may alter conventional sulfate attack mechanisms. For example, calcium hydroxide from the cement mortar has been found to be more soluble in chloride solutions thus enhancing gypsum corrosion and increasing porosity [10]. Also, sulfoaluminate corrosion may be more complex in the presence of chlorides. Ettringite is known to have a chloride-bearing analogue [11]. In addition, sulfate damage has been reported to be worse at lower temperatures which coincides with deicing salt application [12].

It is reasoned that sulfate contamination of pavements can occur from deicing salts melting ice and snow and collecting in joints and cracks. These joints and cracks may act as reservoirs that can, with time and replenishment, build significant sulfate concentrations. Sulfate deposition from these brines may resemble the depositional sequence that occurred during the creation of the halite beds. Gypsum is precipitated first, followed by precipitation of gypsum and halite concurrently and finally by pure halite. This sequence could provide

all of the necessary components for severe chemical attack on portland cement pavements.

Deicing salt impurities may explain some early pavement failure previously attributed to aggregate related D-cracking. Concrete from aggregates capable of withstanding laboratory durability tests has displayed premature joint failure in the field. It seems possible that sulfate attack resulting from sulfate contaminated joints could appear similar to classic D-cracking.

RESEARCH OBJECTIVES

The principal objectives of this research were:

1) To test the proposed hypothesis that sulfate contamination from deicing salts can significantly reduce life of pavement joints.

2) To develop an appropriate laboratory procedure for applying the salt and sulfate impurities to accurately represent actual field conditions.

3) To define chemical and physical mechanisms responsible for the breakdown and deterioration of the cement matrix.

4) To relate laboratory testing to existing pavements suspected of having joint failure caused by this phenomenon. Conclusions from laboratory tests might also be able to predict future failure of pavements.

5) To consider remedies that will reduce the impact of deicers on portland cement durability. These remedies could be applied to mining or processing to reduce sulfates in rock salt, treatment of existing pavements, and modifying new pavement construction.

EXPERIMENTAL DESIGN I

Objective

To test the hypothesis that sulfates from deicers can be significant to concrete deterioration, experiments were designed to observe physical properties and mortar chemical composition of portland cement mortar subjected to various deicing brines, brine application techniques, and freeze-thaw action.

Several factors were considered in establishing the appropriate laboratory model. One of the most important is the saturation level that exists in conjunction with pavement contamination from the sodium chloride-sulfate solutions. Pavement moisture levels will vary from extremely low levels in summer to complete saturation during extended periods of precipitation and exposure to deicing salt melt water.

The brine concentrations that joints are exposed to should also be considered. The brine solutions collect in the joints where the level of concentration will be dependent on evaporation rates, amount of flushing, and the particular rock salt being used. Investigation of various concentrations of sulfate will establish rates of deterioration. By using various brine solutions combined with different brine application techniques, an appropriate laboratory model will be established.

This initial experimentation was also used to establish guidelines and procedures for determining damage mechanisms. Emphasis was placed on finding differences in pore structure of

specimens treated with gypsum compared with untreated specimens. Also, analytical chemistry was used to measure chloride and sulfur concentrations in specimens.

Materials

Ottawa sand, Type I portland cement, and water were proportioned at a 0.45 water-cement ratio to represent the mortar fraction of a typical paving concrete, Iowa Department of Transportation C-3 mix [13]. Table 2 lists the chemical composition of the portland cement where it can be seen that the cement is actually a moderate sulfate resistant Type III. Coarse aggregate was not included in the mix to eliminate influences of aggregate controlled freeze-thaw deterioration. A commercial vinsol resin was used as an air entraining agent to produce 9 percent air in mortar, an equivalency to 6 percent in concrete. Samples were cast as 2 inch diameter by 4 inch long cylinders.

Procedure

To eliminate bias attributed to a particular mortar batch, test groups of seven specimens were assembled by randomly selecting one cylinder from several batches. Specimens were cured 24 hours in a humid room at 70 degrees F, and cured for an additional 13 days in a lime-water bath. After the 14 day curing period, the samples were treated with simulated deicing solutions for 28 days. Solutions consisted of reagent grade sodium chloride and various amounts of calcium sulfate dihydrate (gypsum), see Table 3.

Table 2. Chemical composition of portland cement

Element (or oxide)	Percent by weight	Compound Composition [ASTM C150]	
CaO	63.9	C_3S	61.7
SiO_2	21.1	C_2S	13.9
Al_2O_3	4.35	C_3A	7.7
Fe_2O_3	2.25	C_4AF	6.8
SO_3	1.96		
MgO	2.91		
K_2O	0.49		
TiO_2	0.22		
Na_2O	0.25		
P_2O_5	0.03		
Loss on Ignition	2.07		
Insoluble Residue	0.47		
Total	100.00		

The solutions in Table 3 will be referred to in this report as the fresh-water solution, the sodium-chloride-only solution and solutions containing various amounts of gypsum will be referred to by gypsum content. For example, the solution containing sodium chloride and 2.41 percent gypsum will be referred to as 2.41 percent gypsum. Unless otherwise mentioned, sodium chloride is present in all solutions except the fresh-water-only solutions.

Table 3. Experimental brine compositions
[from Madgin and Swales (8)]

Solution #	Sodium Chloride ($g/100gH_2O$)	Gypsum ($g/100gH_2O$)	Gypsum (% by weight of Solute)
1	0	0	-[a]
2	35.7	0	0[b]
3	35.7	0.441	1.22
4	35.7	0.569	1.57
5	28.5	0.705	2.41
6	23.5	0.753	3.10

[a] Fresh water only.

[b] Sodium chloride only.

Four methods of brine application were evaluated during this portion of the research. This was done to provide data over a range of conditions that could occur at pavement joints. As pavement joints could undergo several moisture conditions, the following methods were considered:

Method 1: Sample immersed in solution to midpoint for 28 days to simulate brine collecting in a joint.

Method 2: Brine applied for 28 days to an indentation measuring 1 inch diameter by 1/4 inch deep in the top of the specimen. The brine was replenished every 4 days. This was to simulate brine accumulation in depressions.

Method 3: Cyclic 4-day submersion in solution and 3-day drying over 28 days, a total of 4 cycles, to observe influence of drying.

Method 4: Complete submersion in brine for 28 days, representing continously wet pavement.

After treatment, rapid freeze-thaw tests were conducted according to ASTM C666 procedure A, rapid freezing and thawing in water.

Specimens were monitored during freeze-thaw testing with ultrasonic pulse velocity measurements (ASTM C597). Pulse velocity is a non-destructive test method used as an indicator of sample durability The time it takes for an ultrasonic pulse to travel the length of the specimen is measured and compared to velocities measured before freeze-thaw testing. Travel time will increase as the freeze-thaw test progresses and the cement matrix starts to develop cracks. After freeze-thaw testing was concluded, splitting tensile tests (ASTM C496) were used to evaluate specimen strength. Tensile strength was considered to be important in that rigid pavement design and behavior are dependent on this parameter.

Pore structure was evaluated using a Quantachrome SP2000 mercury intrusion porosimeter. Pressures of up to 60,000 psi were used to force mercury, a non-wetting liquid, into smaller and smaller size pores as the pressure increases. The volume intruded is recorded and plotted over the range of pore sizes. One of the major limitations of porosimetry is the assumption of constant pore geometry. It cannot compensate for a pore connected to the surface with a bottleneck. Thus, the entire volume intruded for that particular pore is recorded

in connection with the bottleneck size, regardless of pore size beyond the bottleneck.

Another disadvantage is that the drying procedure required to eliminate water from pores for testing could also affect the pore structure. This is especially pertinent in this case where it is speculated that ettringite is being formed. High temperatures can drive off some of the water in ettringite resulting in partial collapse of the crystal structure. Keeping these limitations in mind, porosimetry can be a effective tool for evaluating and comparing pore structure changes.

Chloride and sulfur trioxide contents of specimens were also measured. Chloride concentrations were determined using hydrochloric acid dissolution techniques outlined in ASTM C114. Six repetitive trials on a random sample showed precision to be:

Chloride (as Cl^-) = 0.354 % (by weight of mortar)

Standard deviation = 0.0093 % (by weight of mortar)

Coeff. of variation = 2.6 %

This precision was deemed adequate for this project.

Sulfur trioxide concentrations in the mortar specimens were measured with the knowledge that sulfur can be present from two sources: (1) as a retarder in the portland cement and (2) as induced by a deicing brine. Measurements of sulfur trioxide for this research include all sulfur.

Determination of sulfur trioxide by ASTM C114 guidelines produced results from 6 repetitive trials as:

Sulfur (as SO_3^{-2}) = 0.7048 % (by weight of mortar)

Standard Deviation = 0.066 % (by weight of mortar)

Coeff. of variation = 9.2 %

This large variation could mask the phenomenon of interest. A second attempt to determine sulfur concentrations was made using a Dietert sulfur analyzer. Specimens are heated to 2700 degrees F in pure oxygen whereupon any sulfur present is converted to sulfur dioxide. Gases containing sulfur dioxide are dispersed into an iodine solution where sulfur is determined by measuring the amount of iodine reduced to iodide by the sulfur dioxide. Six repetitive trials on the same sample resulted in:

Sulfur (as SO_3^{-2}) = 0.7048 % (by weight of mortar)

Standard deviation = 0.015 % (by weight of mortar)

Coeff. of variation = 2.1 %

This precision was deemed adequate and most testing was done with the sulfur analyzer.

Results

No physical damage to the specimens was noted after 28 days of room-temperature exposure to the different brines, regardless of application method. However, after a few freeze-thaw cycles, differences in application methods became apparent. Some specimens were subjected to Method 1 treatment for an additional 13 weeks and still showed no evidence of physical damage.

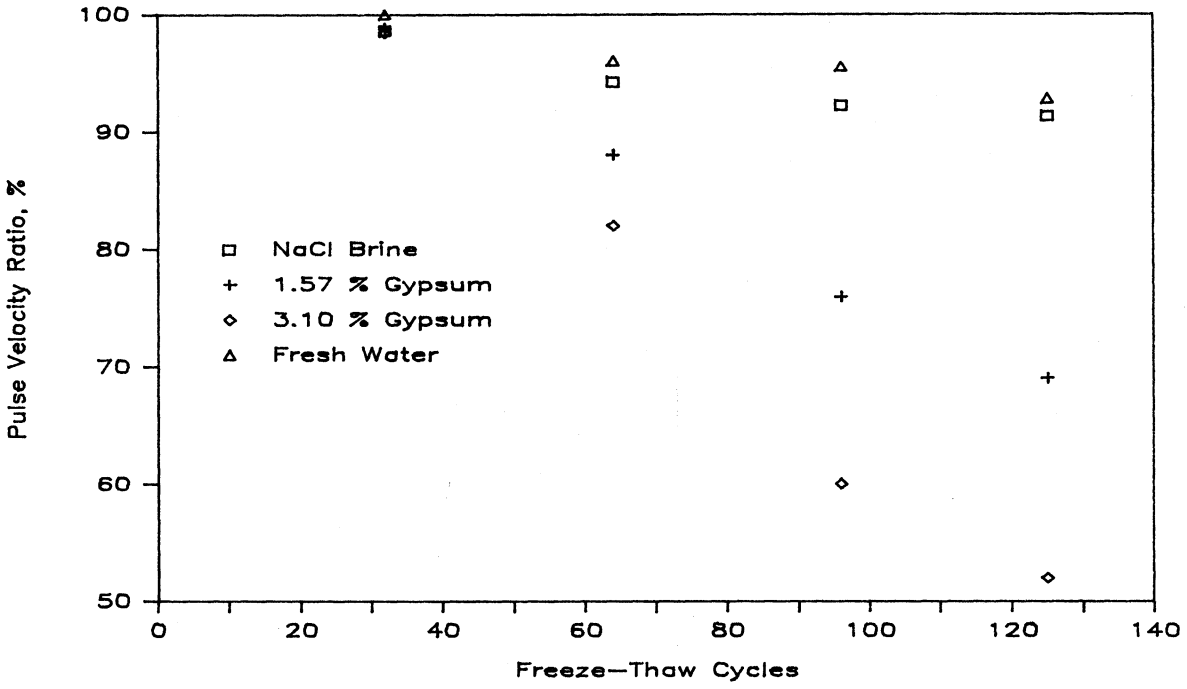

Figure 2. Pulse velocity ratio, Method 1

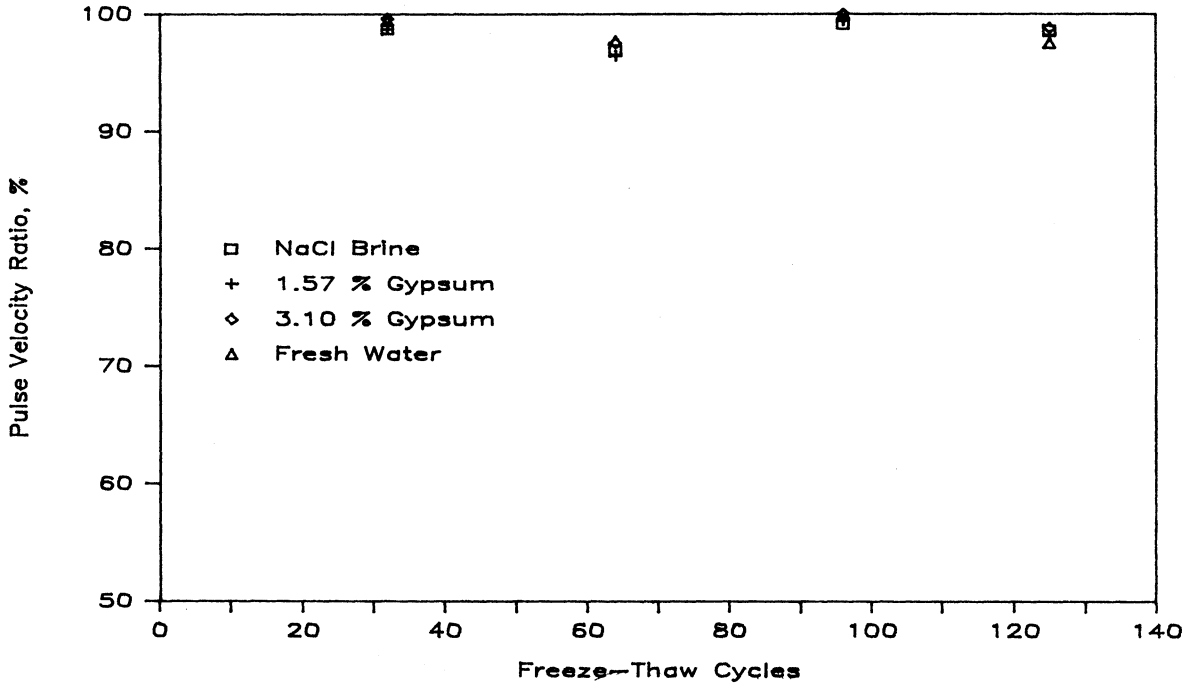

Figure 3. Pulse velocity ratio, Method 2

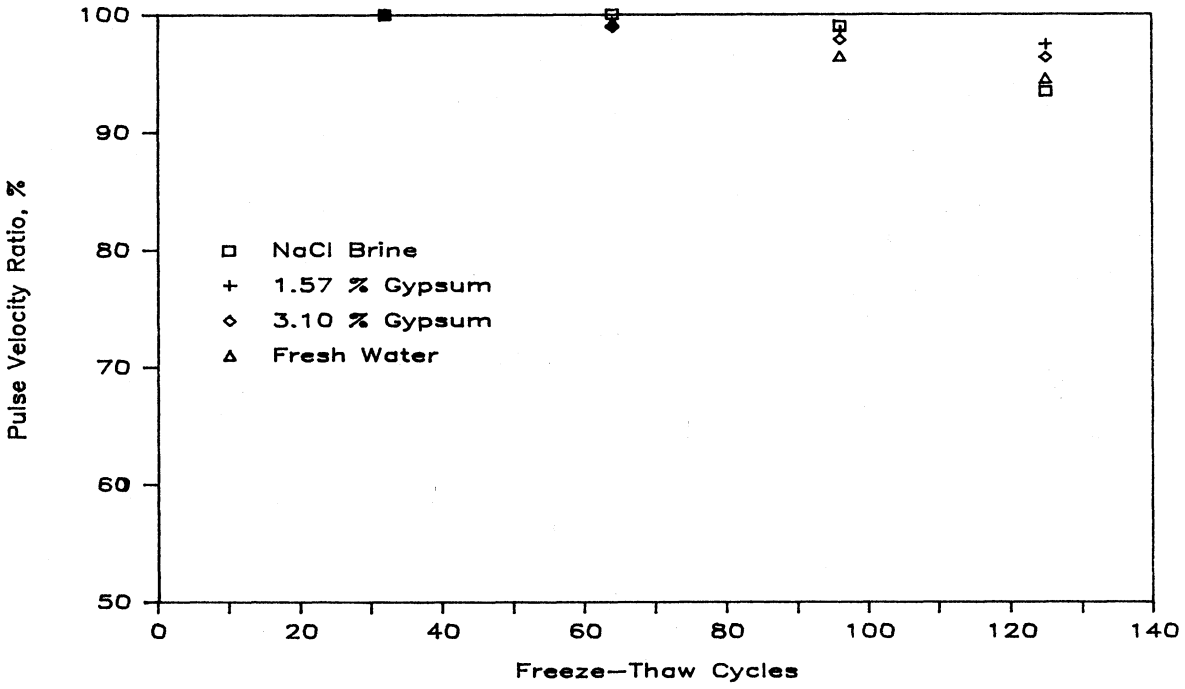

Figure 4. Pulse velocity ratio, Method 3

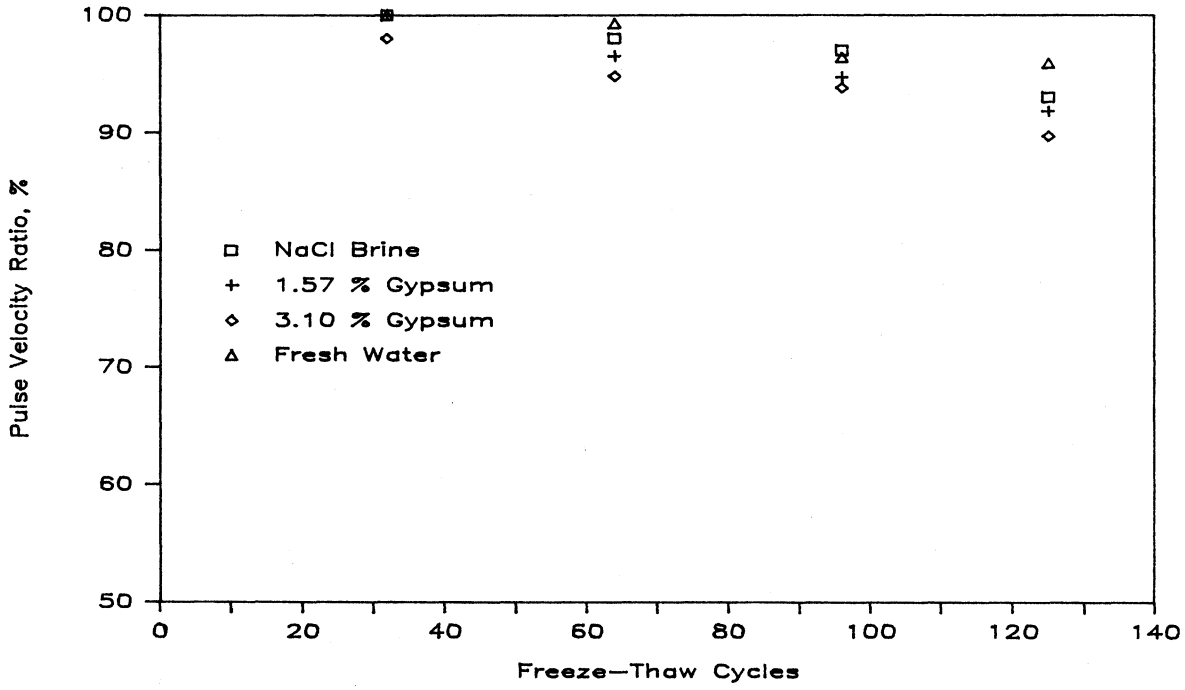

Figure 5. Pulse velocity ratio, Method 4

Figures 2 through 5 show the progression of damage during the freeze-thaw test and compare the different brine application techniques. Pulse velocity ratio is defined as pulse velocity measured at a specified number of cycles of a specimen divided by the initial velocity of that specimen expressed as a percent. Each point represents an average for 7 specimens.

Application Method 1 resulted in a sharp decrease in pulse velocity for the gypsum treatments as compared to the groups treated with water, as a control, and with sodium chloride brine treatment. Cracking was observed below the brine solution level on the lower half of the specimens for both 1.57 and 3.10 percent gypsum treatments. No cracking was seen on specimens treated with the other solutions. The test was terminated at 122 cycles.

The influence of brine application in Methods 2 through 4 was far less pronounced and, with some reservations, it may be concluded that gypsum, when applied through these techniques, had little or no influence on mortar deterioration. The reservations are that the wetting and drying process was for only four cycles and the brine dripped in an indentation produced visible damage but was limited to a small volume of the specimens and was not reflected in the gross measurement.

Tensile splitting tests were performed on Method 1 specimens and the data are shown in Figure 6. The data are plotted as percent strength of the fresh water specimens treated similarily in the freeze-thaw test. Each point represents an average of 7 specimens

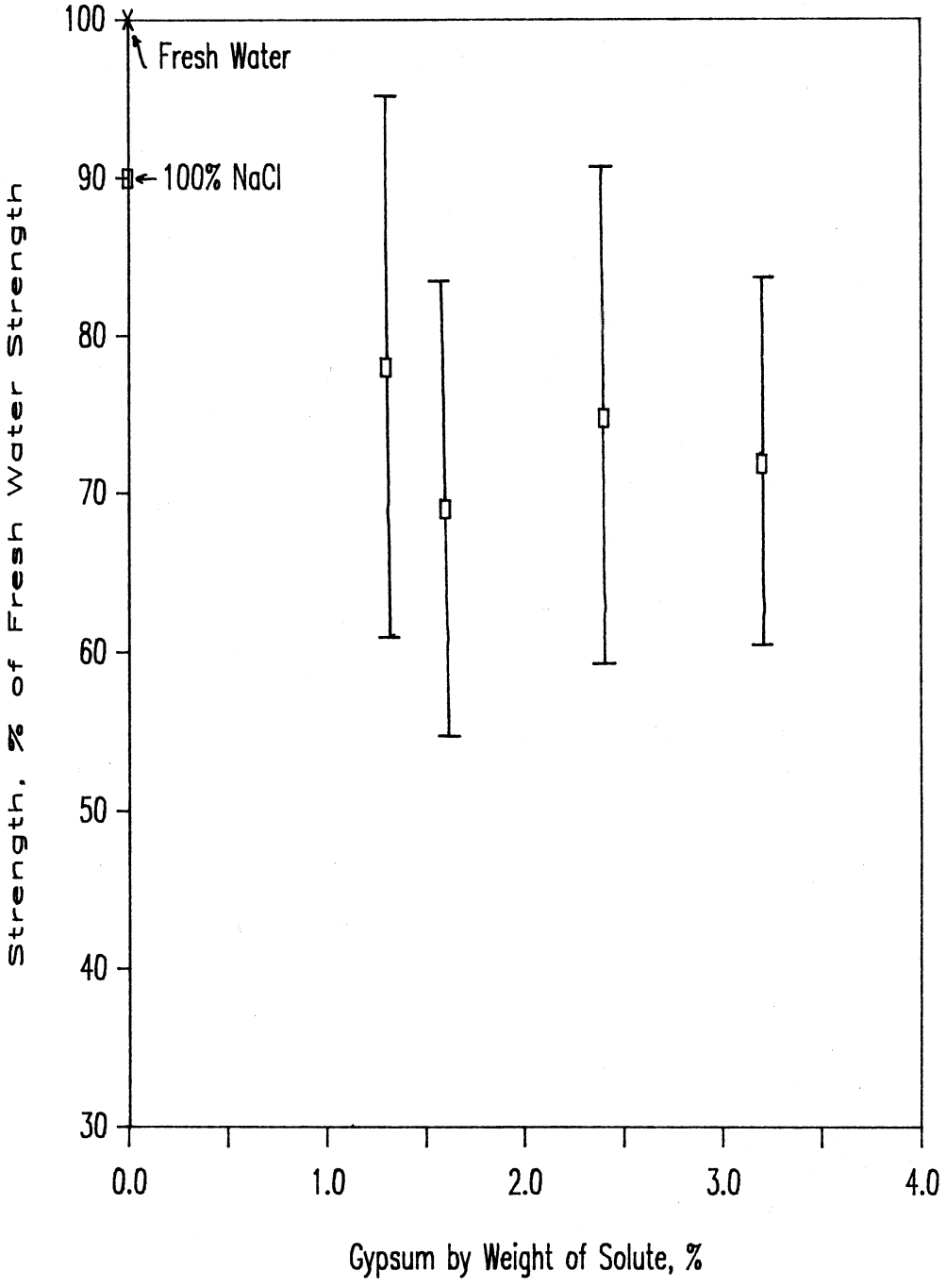

Figure 6. Tensile strength, Method 1

and one standard deviation for each point is also shown. Specimens treated with sodium-chloride-only showed a 10 percent strength loss. Strength losses for the gypsum treatments were much more severe even for the 1.22 and 1.57 percent concentrations. It appears that loss of strength occurs quite rapidly in the initial portion of the curve and is more constant after gypsum levels reach about 2 percent.

Pore structure of Method 1 specimens was examined from two sets of intrusion tests; one with a sodium chloride only specimen and one with a specimen treated with 3.10 percent gypsum. Samples of the specimens were taken from the upper portion of the specimen above the solution level, from the midpoint of the specimen at the solution level, and from the lower portion of the specimen below the solution level. Figures 7 through 10 show percent pore volume intruded plotted against pore size for the different treatments. Figures 7 and 8 show results for large capillaries from 53,300 to 889 angstroms, a pressure range of 0 to 1200 psi. Figures 9 and 10 show results for capillaries from 533 angstroms to 18 angstroms, a pressure range of 0 psi to 60,000 psi.

One notable difference between sodium-chloride-only and the gypsum treatment is seen in Figures 7 and 8. The pore volume at the sample midpoint is greater for the gypsum treatment, suggesting pore enlargement. In contrast, the gypsum treatment reduced pore size above and beneath the brine level. This suggests compound formation and deposition or simply dissolution and redeposition. Regardless of the mechanism, a clue as to the cause for deterioration may be in the

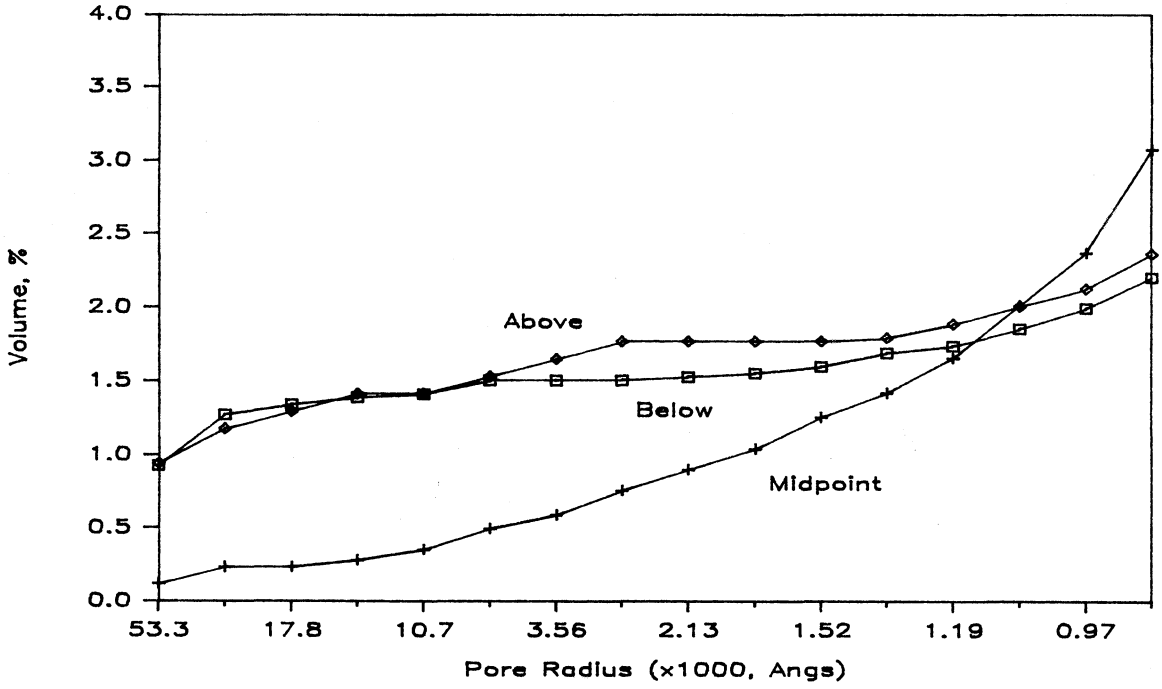

Figure 7. Mercury intrusion porosimetry, sodium chloride only (large pores)

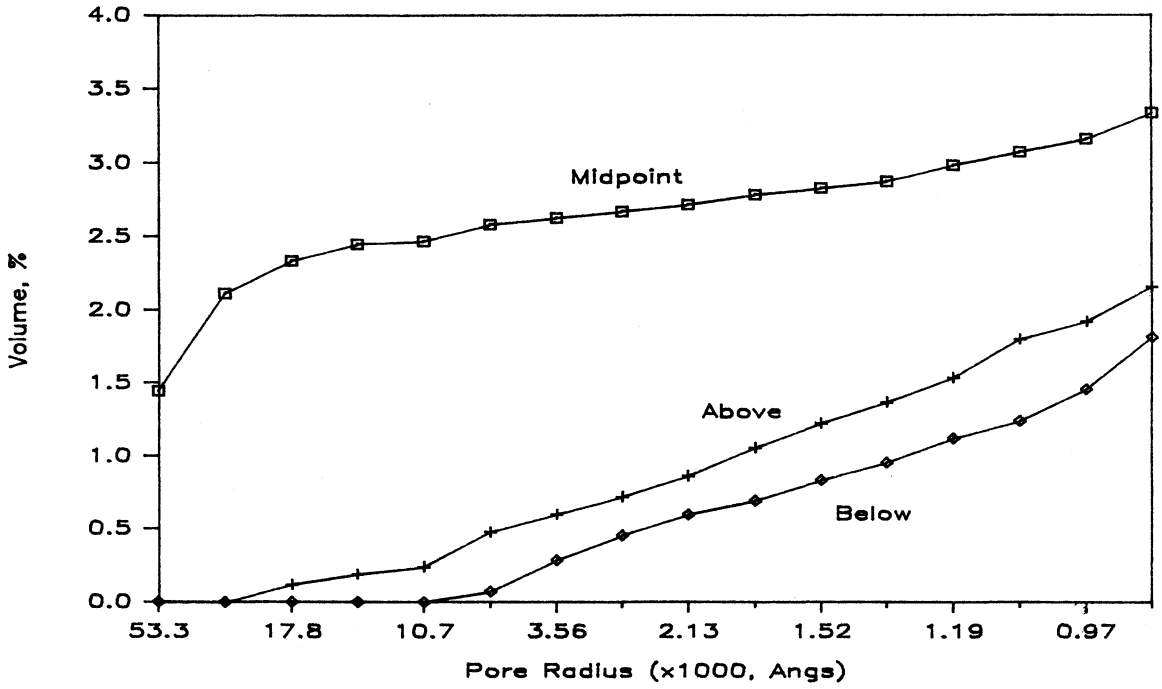

Figure 8. Mercury intrusion porosimetry, 3.10% gypsum (large pores)

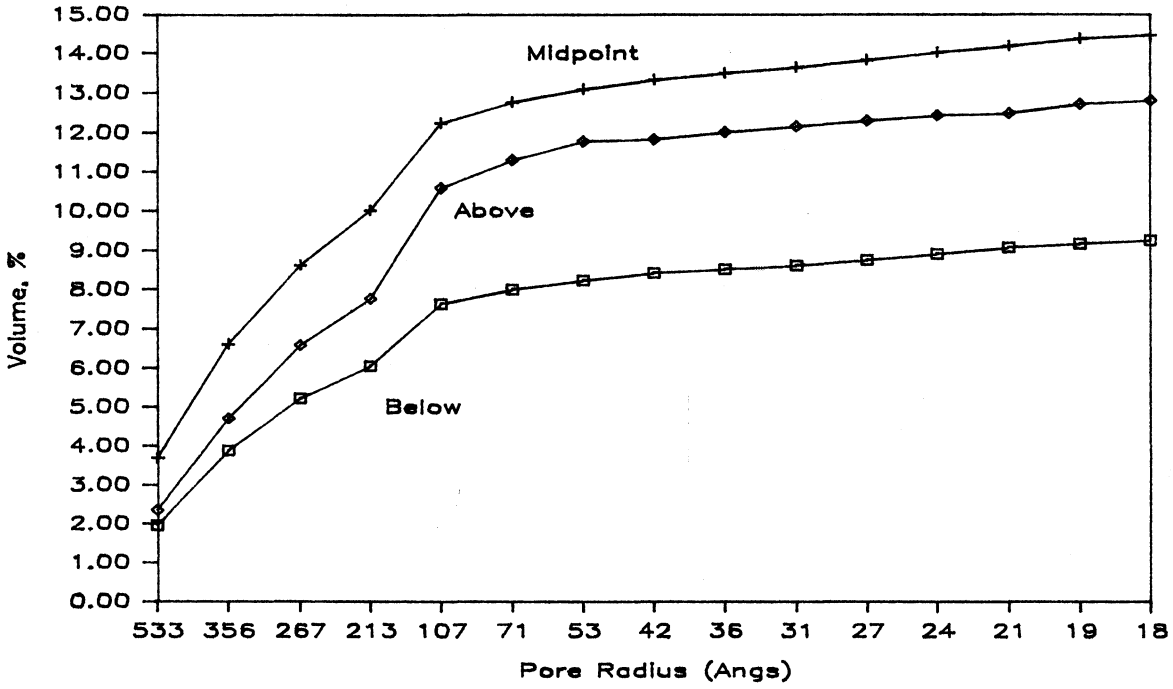

Figure 9. Mercury intrusion porosimetry, sodium chloride only (small pores)

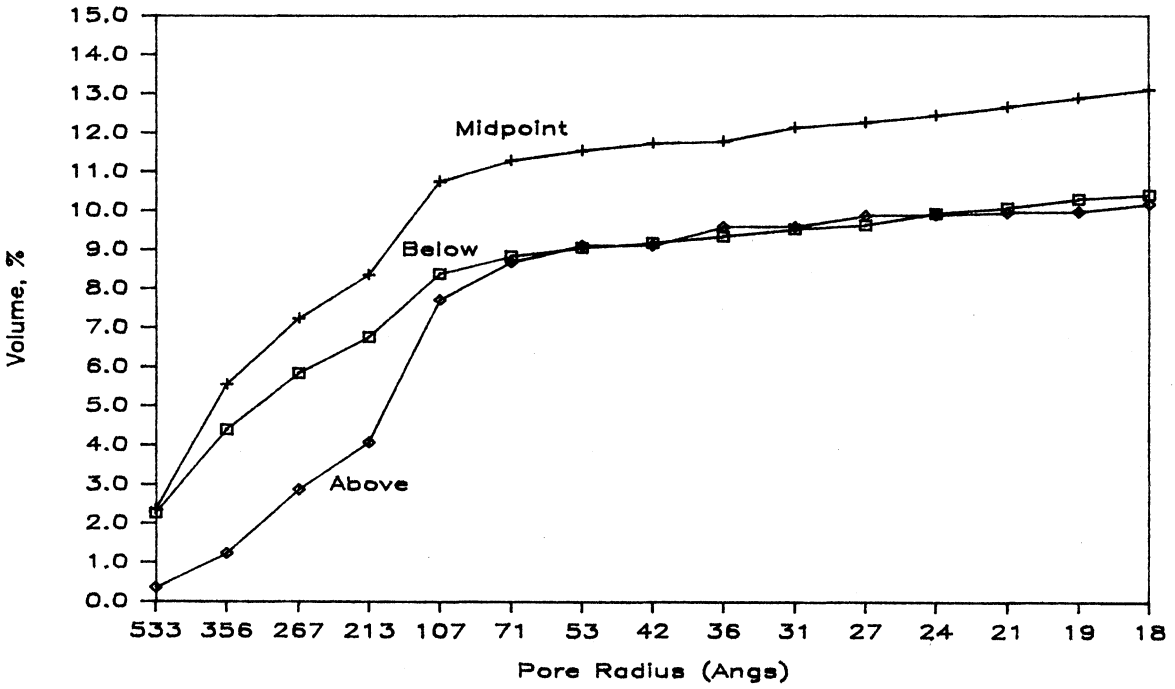

Figure 10. Mercury intrusion porosimetry, 3.10% gypsum (small pores)

observation that damage occurred beneath the brine level. The reduced pore sizes may have made the mortar more vulnerable to freeze-thaw. Although sulfate treated mortar above the brine level has a similar structure, it was not inundated during freezing and thawing.

The differences in pore structure in the smaller pore size range shown in figures 9 and 10 are not as pronounced. The midpoints in this size range do not appear to be affected by the different treatments. Treatment at room temperatures before freeze-thaw testing does not seem to affect the pore structure significantly in this size range.

Chloride and sulfur (as sulfur trioxide) concentrations in the specimens after being subjected to freeze-thaw are listed in Table 4. All values are averages for three specimens and the base level chloride concentration (water treatment) was found to be 0.03 percent. Chloride concentration was increased by all treatment methods with Method 3 showing the greatest accumulation. This method allowed salt crystalization to occur on the specimen surface where samples were taken for analysis. These data are consistent with chloride measurements made by others on concrete samples subjected to deicers in the field. Clear and Hay (16) report chloride concentrations at reinforcing steel levels as ranging from 1.5 to 14 pounds per cubic yard or 0.1 to 1.0 percent by weight of mortar. This brackets the concentrations measured in this research and suggests saturated brines used in this research are appropriate.

Table 4. Chloride and sulfur trioxide concentrations

	Gypsum,%	Cl^-,%	percent change	SO_3^{-2},%	percent change	SO_3^{-2},%
Method 1 (1/2 immersed)						
above	0	0.363		0.503[a]		0.72[b]
solution	1.22	0.494	36.1[c]	0.554	10.0	0.81
level	1.57	0.300	-17.4	0.616	22.5	0.78
	2.41	0.446	22.9	0.674	34.0	0.75
	3.10	0.354	- 2.5	0.615	22.3	0.82
midpoint	0	0.450		0.594		0.75
solution	1.22	0.349	-22.4	0.711	19.7	0.79
level	1.57	0.355	-21.1	0.664	11.8	0.75
	2.41	0.355	-21.1	0.693	16.7	0.81
	3.10	0.353	-21.6	0.652	9.8	0.79
below	0	0.412		0.485		0.77
solution	1.22	0.503	22.1	0.688	41.9	0.79
level	1.57	0.484	17.5	0.620	27.8	0.76
	2.41	0.483	17.2	0.654	34.8	0.80
	3.10	0.484	17.5	0.610	25.8	0.80
Method 2 (indentation)						
	0	0.665				0.76
	1.22	0.674				0.76
	1.57	0.685				0.78
	2.41	0.764				0.76
	3.10	0.661				0.75
Method 3 (cyclic wet-dry)						
	0	0.928				0.76
	1.22	0.840				0.77
	1.57	0.745				0.77
	2.41	0.813				0.93
	3.10	0.706				0.78
Method 4 (completely immersed)						
	0	0.587				0.78
	1.22	0.571				0.77
	1.57	0.498				0.80
	2.41	0.526				0.79
	3.10	0.385				0.77

[a]Sulfur trioxide measured using Dietert sulfur analyzer.
[b]Sulfur trioxide measured using ASTM C-114.
[c]Amount of increase or decrease from NaCl only treatment.

Specimens with the most damage, Method 1, show some interesting results. First, Method 1 chloride concentrations are lower than those of Methods 2 through 4. Two explanations are possible: (1) chloride did not accumulate during treatment; (2)it was in a more soluble form and was leached away during freeze-thaw. Regardless of what happened, an important observation from this experiment is that chloride concentration in mortar may not correlate to damage. The most physical damage occurred with Method 1 treatments; so did the lowest chloride concentrations.

For the Method 1 treatments there is evidence of some chloride migration, particularly in the presence of gypsum. At the solution level, the specimens treated with the gypsum showed a decrease in chloride concentration from the specimens treated with sodium chloride only. This decrease is tabulated in the percent change column in Table 4. The measurements taken below the solution level show an increase in chloride concentration. It seems that chloride concentrations are lower at the location of the solution level and increase with the addition of gypsum to the saturated sodium chloride solutions.

Another interesting trend in chloride concentration occurs above the solution level. This portion of the specimens never came into direct contact with the solutions but significant increases in chloride concentration still occurred. This is evidence of the amount of ion movement that is occurring during treatment.

The sulfur trioxide concentrations shown in Table 4 were

determined from ASTM C114 and also the Dietert sulfur analyzer. The results from ASTM C114 are listed in the table only as a matter of record and were not considered further because of poor precision. Because deterioration occurred on Method 1 specimens, Dietert sulfur analyzer results were performed for this brine application method only. The base level of sulfur was determined to be 0.698 percent from the samples treated with water only. This comes from the portland cement hydration products as noted earlier.

Only one specimen group (midpoint at 1.22 percent gypsum)showed an increase in sulfur concentration from the base level even though additional sulfur was supplied to the system from the brine. This suggests the chloride treatments have a leaching effect on the sulfur present in the mortar samples. Also, the concentrations at midpoint have a lower percent increase compared to increases seen from the sample portions from below solution levels. This trend is similar to that for chlorides. It is possible that freezing processes at the solution-air-sample interface cause a leaching phenomenon thereby lowering concentrations.

Summary

Initial results indicate that brine application technique is critical and directly influences deterioration. Specimens immersed to midpoint in the brine solutions, Method 1, showed the most severe damage when subjected to cyclic freezing and thawing. Deterioration was not observed at the time of brine application but occurred soon after the specimens were exposed to frost action. Experimental evidence suggests that this condition creates a capillary potential that transports ions through the cement matrix. This could also explain the increases in sulfate and chloride measured above the solution level in the portions of sample that never came into direct contact with the brines.

The portions of the specimens below the solution level showed extensive cracking indicating an expansive failure mechanism. Measurements of pore structure indicated an increase in pore volume for large capillaries near the solution level and a decrease in volume of these pores above and below the solution level. Pore structure data from the smaller pore sizes were not as conclusive. Chemical analysis showed increases in chloride concentration below the midpoint of the specimens caused by addition of gypsum to the brine solutions. The concentration of sulfur in this area was slightly lower than the base level but increased with the addition of gypsum to the brine solutions.

EXPERIMENTAL DESIGN II

Objective

One of the objectives of this portion of the project was to test the Method 1 application procedure with the brine present during frost action. This seems a more reasonable simulation of frost action on pavement joints than freeze-thaw in fresh water. As before, specimens were exposed to various brine solutions with the exception that treatments coincided with freeze-thaw tests. Field conditions dictate exposure of pavement joints to deicing solutions over a wide range of temperatures. Lower temperatures could have several effects on deterioration processes such as:

1) Increased capillary action from higher surface tensions of water due to lower temperatures [14].

2) Change in gypsum solubility with temperature [14].

3) Change in calcium hydroxide solublility at lower temperatures (enhancing gypsum corrosion) [9].

4) Sulfate damage more severe at lower temperatures [12].

Another objective was to further define damage mechanisms. Methods used included pore structure investigation using porosimetry and measuring of chloride and sulfur similar to the previous section. X-ray diffraction was used to identify changes in sample composition.

The initial portion of this project established a trend for deterioration in strength as related to brine composition. This work was intended to refine this relationship, particularly at gypsum concentrations below 1.5 percent. The intent was to determine a

minimum amount of sulfate required to cause damage.

Materials

All materials used are identical to those as described in Experimental Design I.

Procedure

Test group selection and specimen procedures were not changed. Sample treatment, however, was conducted simultaneously with the freeze-thaw test. Specimens were placed in plastic bags with enough brine added to immerse the samples to midpoint. The bags were then sealed to prevent evaporation during freeze-thaw testing. Brine compositions used are listed in Table 5.

Specimen progress during testing was monitored every 15 cycles with ultrasonic pulse velocity measurements. Also, a procedure was developed to evaluate and record visual damage. The specimens were inspected at the same time as pulse velocity and the following rating scheme was applied:

Damage Rating	1	2	3	4	5
Number of Cracks	None	1	2-3	4-5	> 5

The ratings provide a numerical description of the extent of the deterioration.

Table 5. Experimental brine compositions
[from Madgin and Swales (8)]

Solution No.	NaCl ($g/100gH_2O$)	$CaSO_4 \cdot 2H_2O$ ($g/100gH_2O$)	Gypsum (% by weight of Solute)
1	0	0	- (Water Only)
2	35.7	0	0 (NaCl Only)
3	35.7	0.134	0.375
4	35.7	0.188	0.523
5	35.7	0.250	0.695
6	35.7	0.261	0.730
7	35.7	0.313	0.868
8	35.7	0.361	1.000
9	35.7	0.419	1.160
10	35.7	0.615	1.700
11	28.5	0.705	2.410
12	23.5	0.753	3.100
13	20.6	0.765	3.580

Tensile strength, pore structure, chloride and sulfur concentrations were measured in the same manner as before. In addition, x-ray diffraction was used to evaluate sample composition.

Results

As the freeze-thaw test progressed, it became apparent that sample deterioration was much faster when the specimens were exposed to the brine solutions in the freeze-thaw cabinet. Original plans were to run the test to 122 cycles and compare results to earlier testing. When it became evident that specimens would not last, the test was terminated at 88 cycles.

The pulse velocity ratio and the best fit representation based on correlation coefficient is shown in Figure 11. This parameter was selected as a measure of durability, and defined as the percentage ratio between velocity after 88 freeze-thaw cycles and an initial velocity for each specimen. Data points represent an average result for nine specimens. Using fresh water as a base, these data suggest a 2.8 percentage point loss in pulse velocity ratio due to NaCl alone and a maximum 4.2 percentage point loss due to 2.4 percent gypsum in the brine. The regression analysis indicates a minimum in pulse velocity at 2.5 percent gypsum.

Visual damage ratings at 88 cycles are plotted in Figure 12. Cracks first appeared below the solution level perpendicular to the longitudinal axis of the cylinders. As deterioration proceeded, the pattern of crack orientation became less obvious. The cracks did, however, remain below the solution level. Figure 12 shows average visual ratings for the nine sample groups plotted against gypsum concentrations, each point representing nine specimens.

Damage ratings correlate well with the velocity measurements. Specimens treated with fresh water had no cracks; those treated with sodium chloride had a damage rating of 1.3, indicating few cracks. The number of cracks increased as gypsum percentage increased and samples at 2.41 percent gypsum had an average of 5 or more cracks per sample. An interesting trend becomes apparent at the high gypsum concentrations, 3.10 and 3.57 percent: contrary to expectations, deterioration seems less severe. This same trend is seen in the

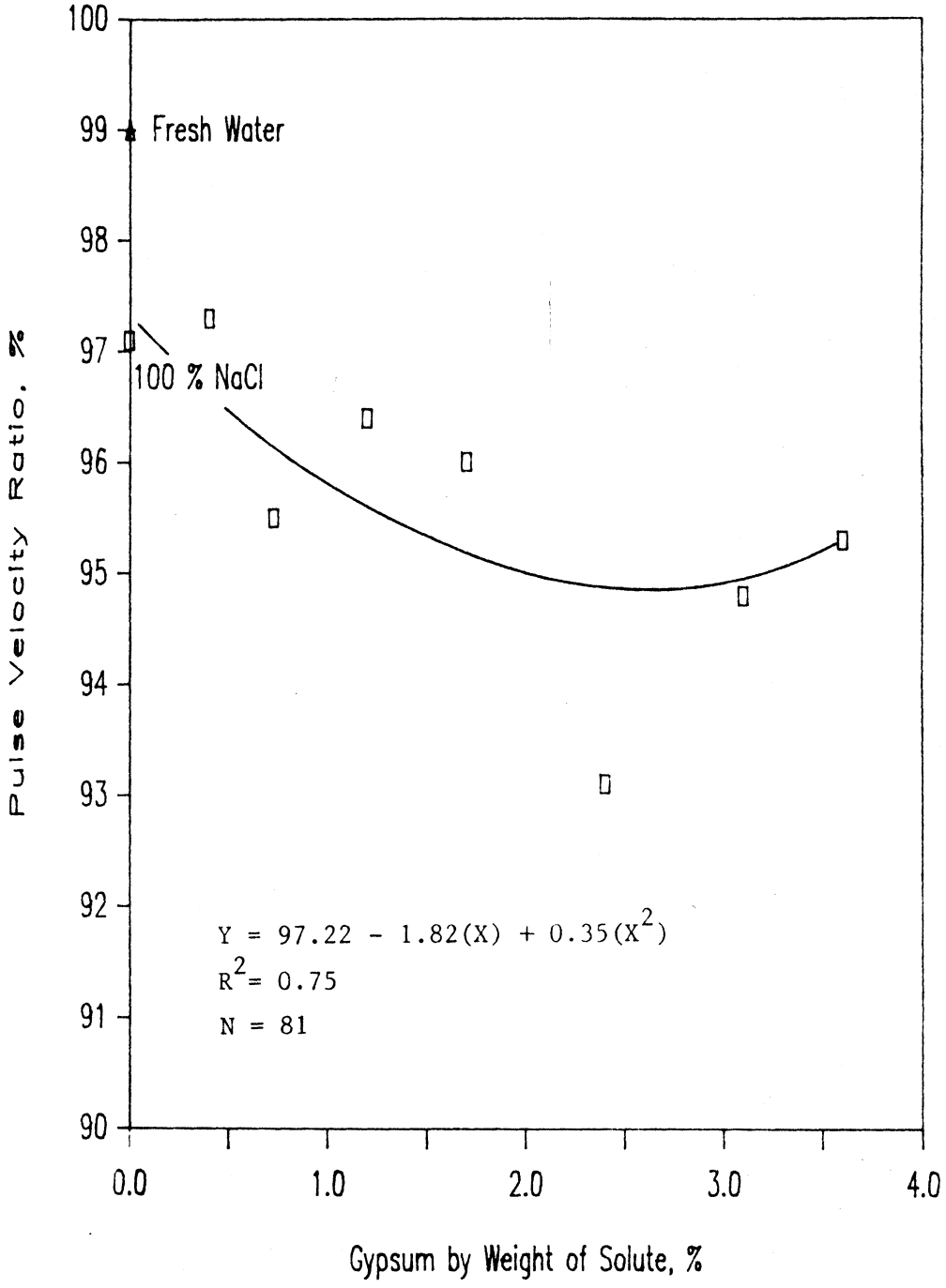

Figure 11. Pulse velocity ratio, Method 1 application during freeze-thaw test

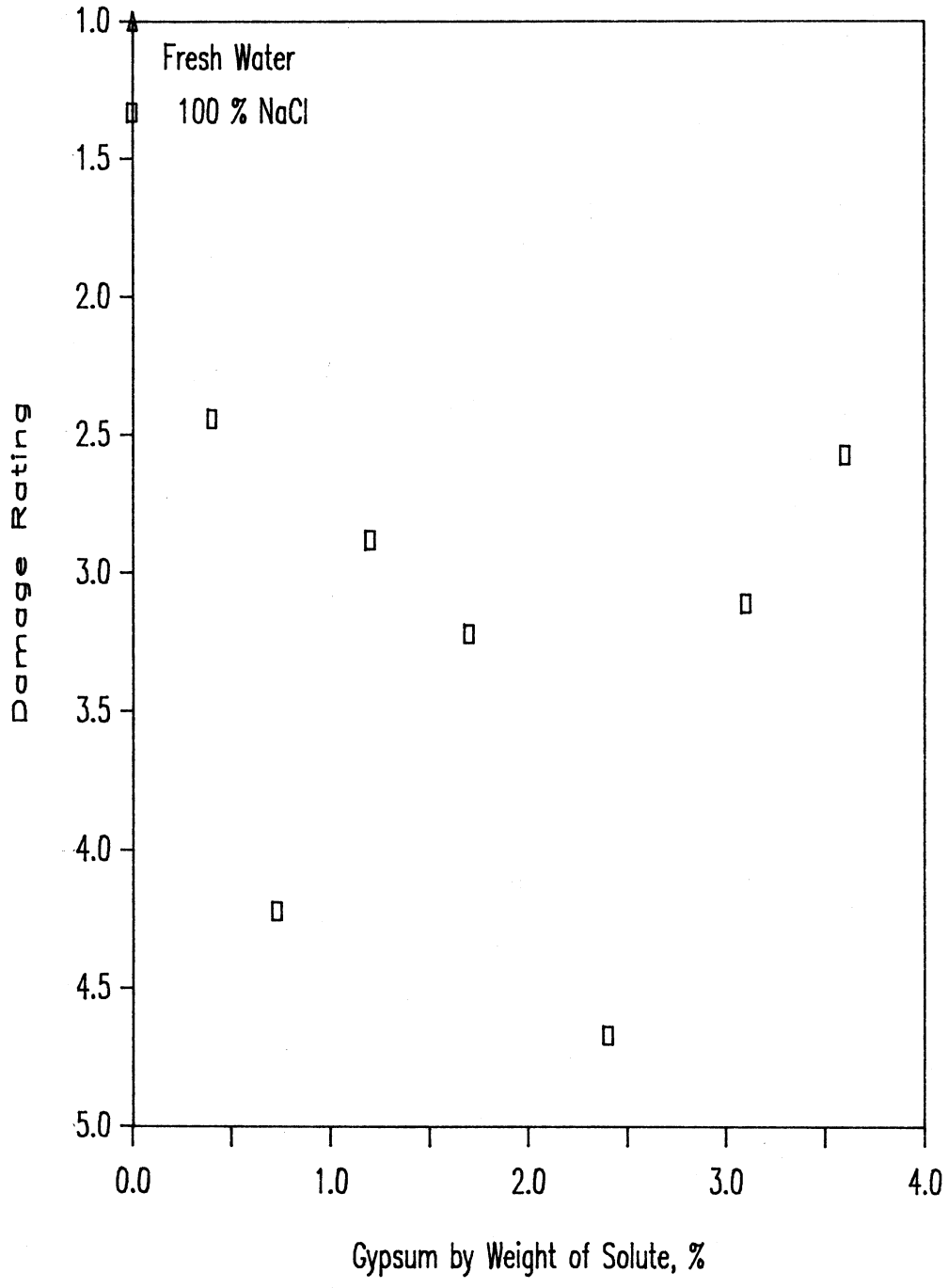

Figure 12. Visual damage rating at 88 freeze-thaw cycles

velocity data.

As tensile strength is a key element of pavement behavior, it is considered the most significant of physical parameters measured in this study. Average tensile splitting strength ratios (based on fresh water strength) and expected values from a least squares polynomial regression are shown in Figure 13: the minimum strength occurs at two percent gypsum. Based on strength of fresh water treatment, NaCl alone reduced expected values for strength slightly more than 12 percentage points. At the most damaging sulfate concentration, a 40 percent loss in expected strength is observed. When compared to natural rock salt compositions, significant damage occurred over a range of sulfate concentrations possible from all but one of the commercial sources in Table 1.

Although the statistical regression results in Figure 13 suggest the existence of a relation between strength after freezing and thawing and sulfate concentration in a brine, the validity or lack of validity in experimental results can be assessed through analysis of variance and significance tests. Average values for strength and their standard deviations are presented in Table 6. A significance test can be formulated with the null hypothesis being: calcium sulfate in a NaCl brine does not reduce strength. The alternate hypothesis may be stated as: calcium sulfate in the brine reduces strength. This formulation places the burden of proof on the proposed phenomena. Test statistics computed from experimental data and

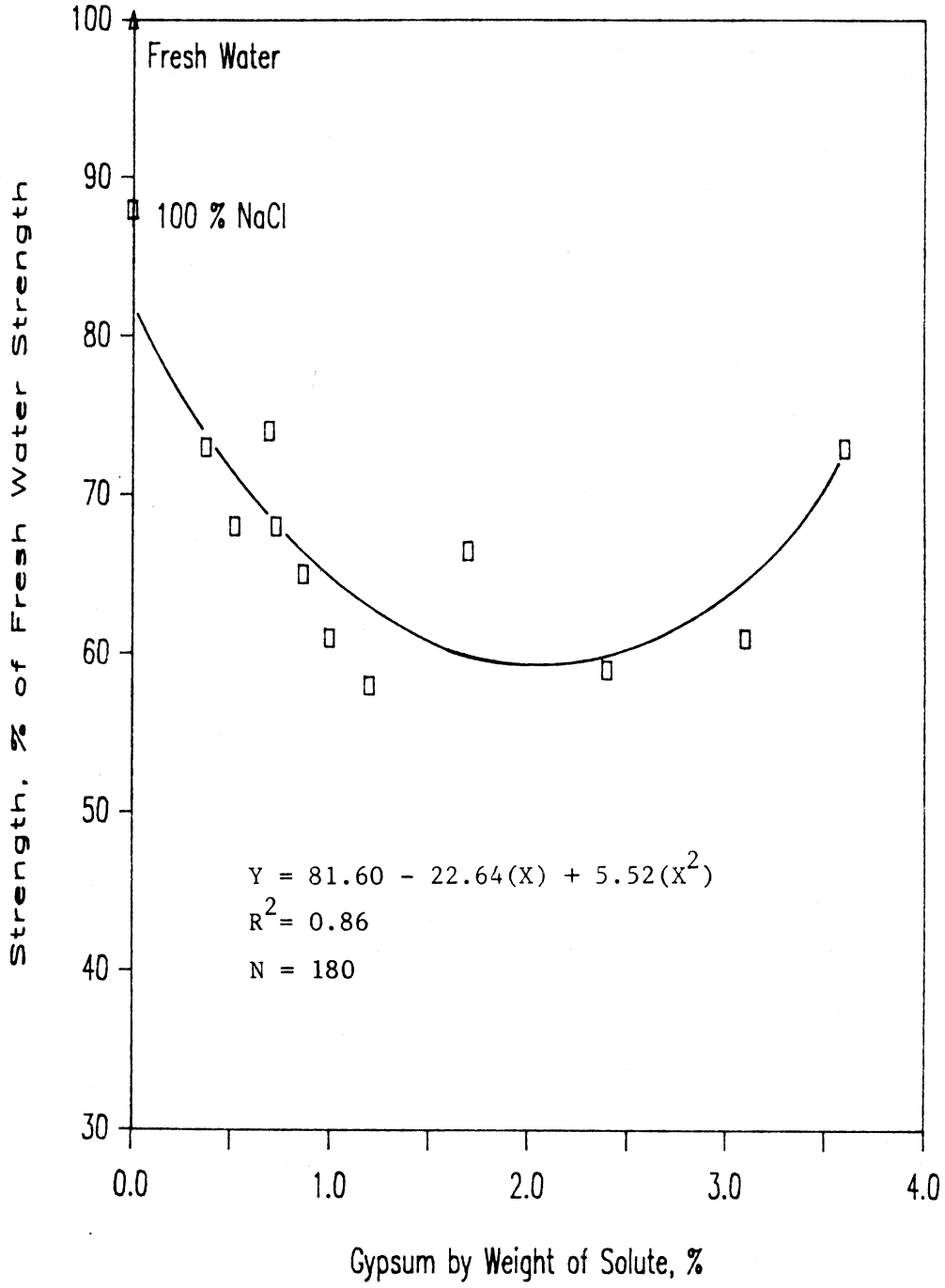

Figure 13. Tensile strength at 88 freeze-thaw cycles

Table 6. Analysis of Tensile Strength Data

Gypsum (%)	Strength Mean ($\bar{y}$)	St. Dev. (s)	Number of Observations (N)	Test[a] Statistic	t-parameter	Confidence Level (%)
0.0[b]	87.9	16.7	27			
0.375	72.7	16.7	27	3.34	2.40	99.0
0.523	67.8	14.4	9	3.22	2.44	99.0
0.695	73.8	20.2	9	2.08	2.44	97.5
0.730	67.9	16.3	18	3.99	2.42	99.0
0.868	65.1	15.5	9	3.61	2.44	99.0
1.000	61.2	12.2	9	5.56	2.44	99.0
1.200	58.2	24.9	18	3.80	2.42	99.0
1.700	66.3	21.6	18	2.98	2.42	99.0
2.400	58.9	13.6	18	4.83	2.42	99.0
3.100	60.9	16.5	18	4.22	2.42	99.0
3.600	73.2	14.2	18	2.42	2.42	99.0

[a]From methods outlined in reference 17.

[b]Gypsum in saturated NaCl brine.

Student's t-distribution parameters are also in Table 6. A test statistic larger than the t-distribution parameter means that, at a particular level of confidence, there is evidence that the null hypothesis or the presumption that calcium sulfate does not reduce strength is untrue. Thus the alternate hypothesis can be accepted. In Table 6 it can be seen that in all but one case the null hypothesis is rejected at the 99 percent or higher confidence level. The deviation suggests a 97.5 percent confidence level. Thus, sulfate in this experimental environment produced significant reductions in strength.

Pore structure was evaluated on samples taken from below the solution level, where the deterioration was most severe. Figure 14 shows the intruded percent of pore volume plotted against pore radius for fresh water, NaCl, and three gypsum percentages. A significant difference in intruded volume occurs between fresh water and brine treated specimens. More pores are present in the fresh water mortar. A less dramatic but still noticeable difference also is evident between two treatment pairs, (NaCl and 0.73% gypsum) and (1.70 and 2.41% gypsum); this pore filling pattern correlates to strength. Sodium chloride and a 0.73% gypsum produced an intermediate strength reduction when compared to that for higher sulfate concentrations.

In Figure 14, it is observed that most differences in pore structure occurred in the 100 to 500 angstrom range. By one classification [9] these are small to medium sized capillary pores

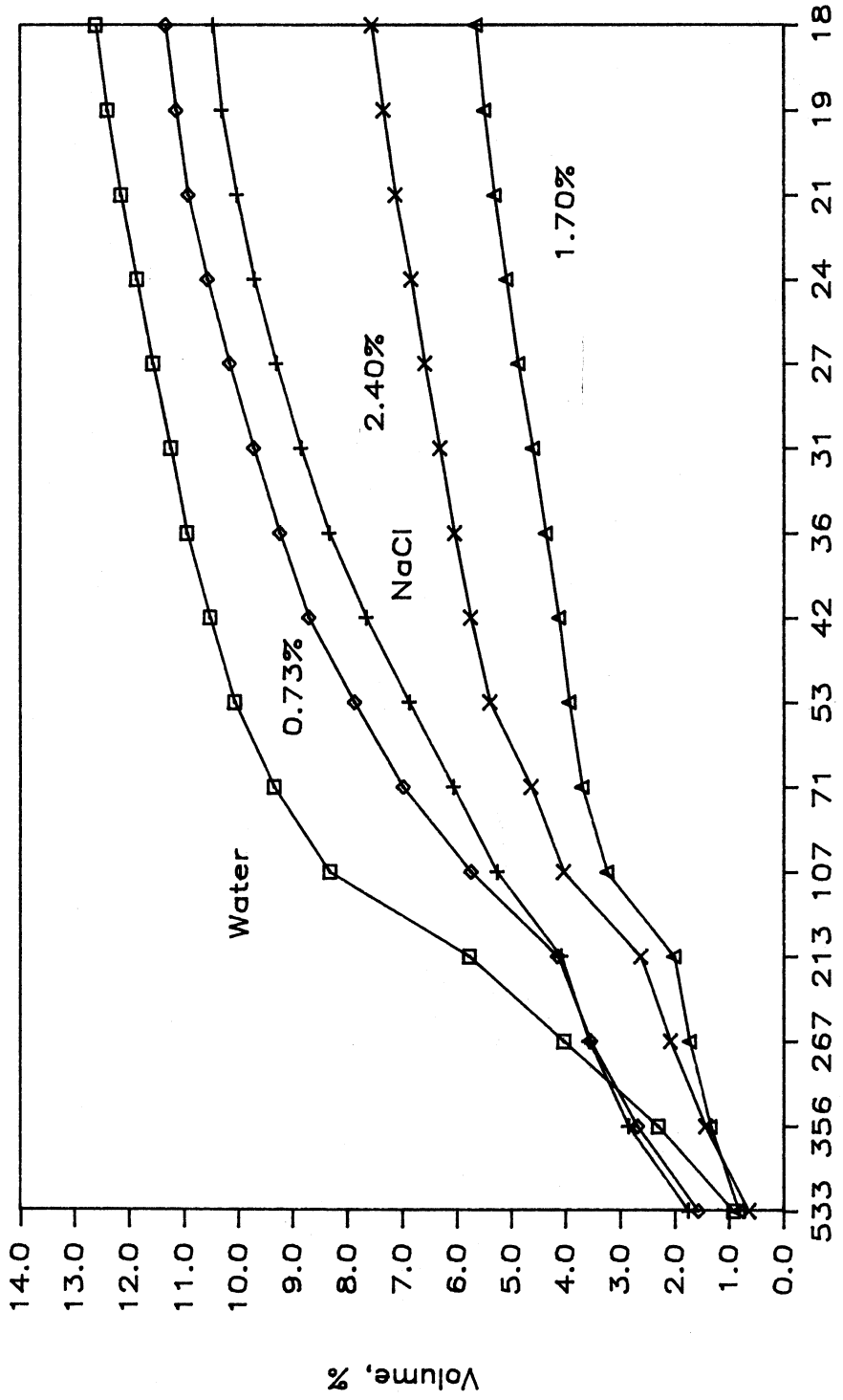

Figure 14. Mercury intrusion porosimetry at 88 freeze-thaw cycles

known to influence mechanisms for frost action.

X-ray diffraction charts for samples from specimens subjected to freezing and thawing in water, in sodium chloride brine, and in sodium chloride with 2.4% gypsum are presented in Figures 15 through 17. These results are similar and are as anticipated for a mortar hydrate; ie. the specimens are highly amorphous but do exhibit peaks for crystalline compounds: calcium hydroxide, quartz, ettringite, and calcium carbonate. The latter compound is attributed to atmospheric carbonation. Differences attributed to the treatments can be seen in intensity of ettringite peaks and the occurrence of a new compound identified as Friedel's salt, $3CaO.Al_2O_3.CaCl_2.10H_2O$, a tricalcium aluminate hydrate involving chloride [11]. Friedel's salt was identified from diffraction peaks at 7.87, 4.70 and 3.81 angstroms. Diffraction peaks at 9.73, 5.61, and 3.88 angstroms identified ettringite.

Table 7 summarizes diffraction data in regard to relative compound quantities as estimated from peak intensities. These data suggest ettringite formation is enhanced by sodium chloride alone and, as is expected, further enhanced by gypsum. Friedel's salt, not present from fresh water treatment, is promoted by sodium chloride and further enhanced by gypsum [15]. Compounds formed as a result of NaCl and gypsum are thought to be responsible for void filling measured by mercury porosimetry.

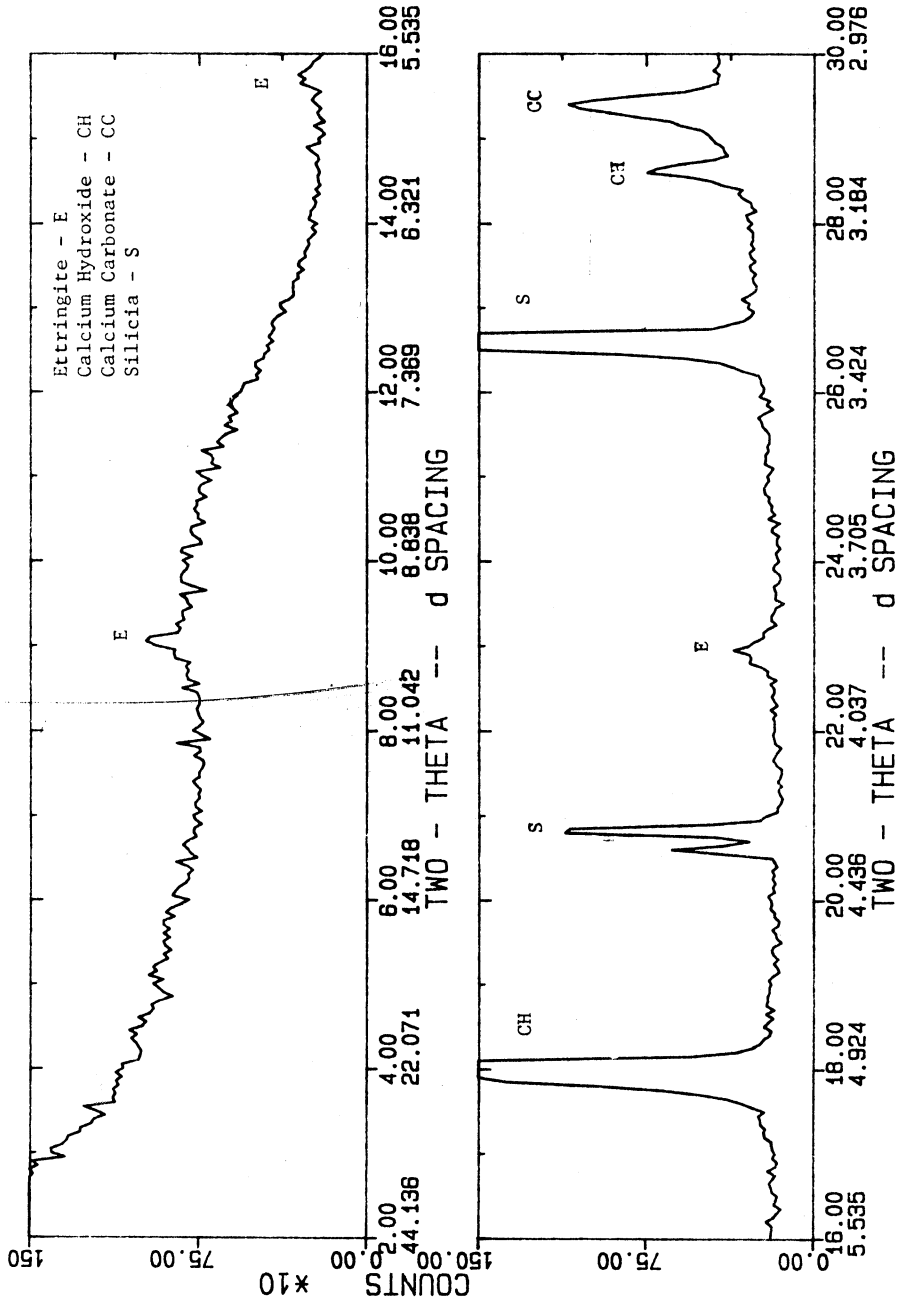

Figure 15. X-ray diffraction, fresh water sample

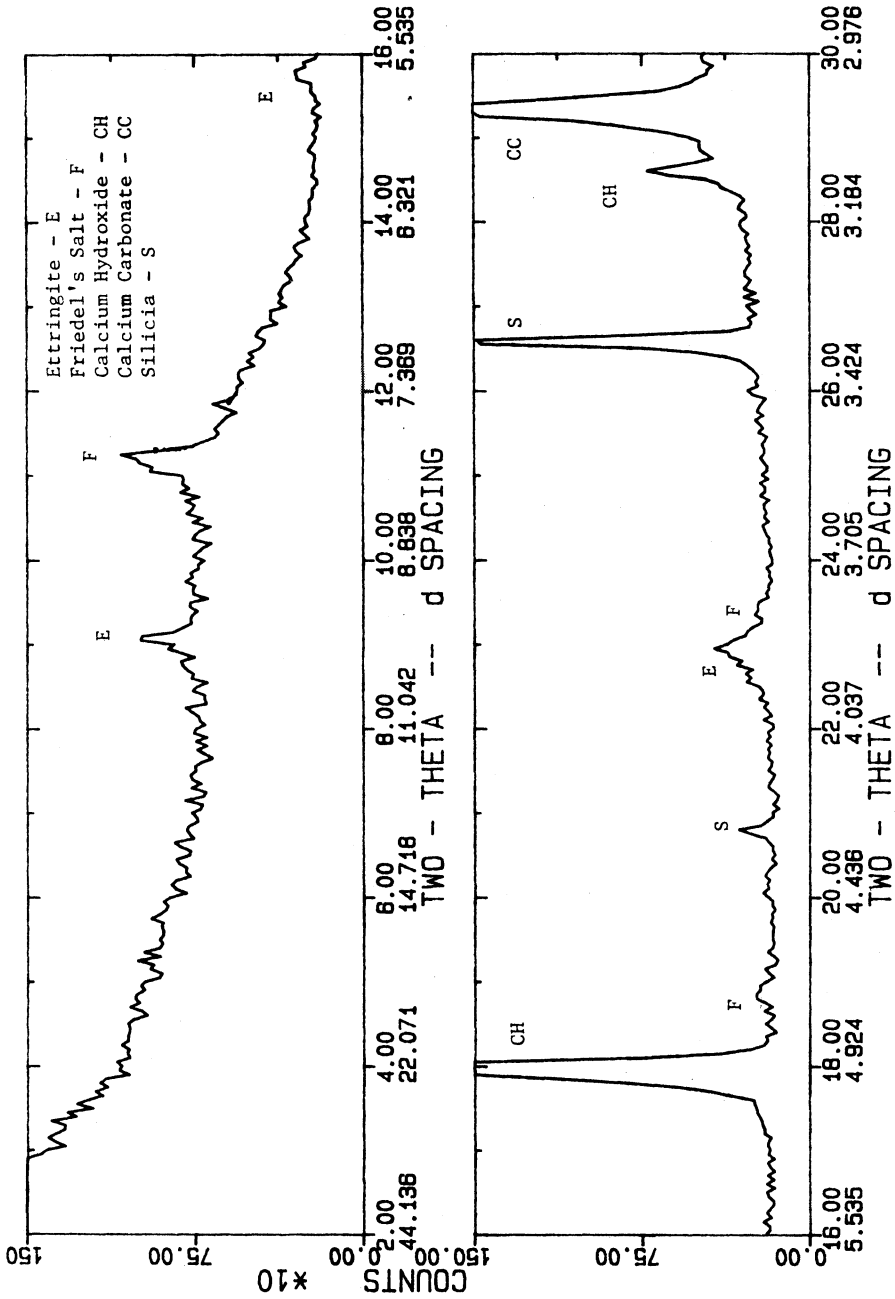

Figure 16. X-ray diffraction, saturated sodium chloride brine

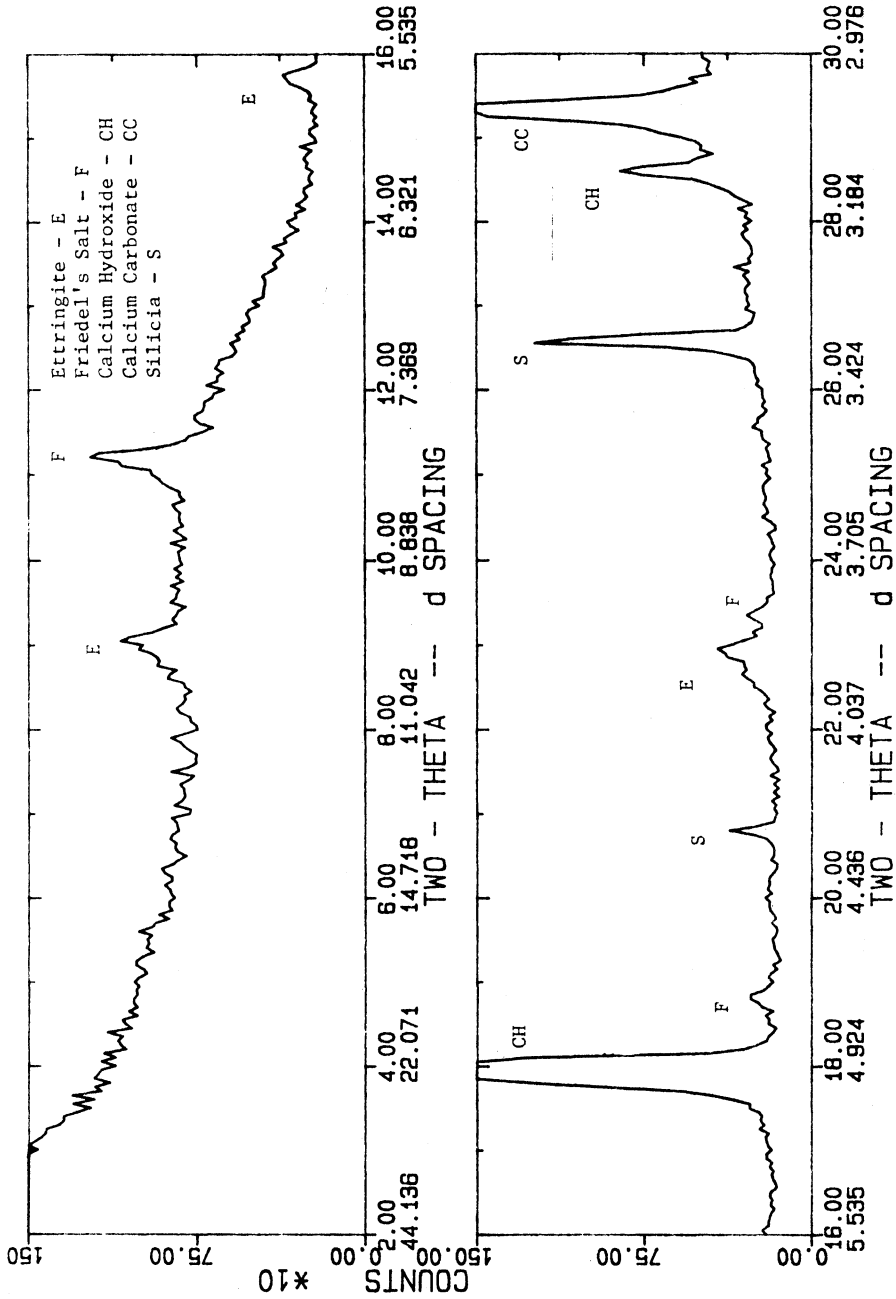

Figure 17. X-ray diffraction, 3.10% gypsum by weight of solute

Table 7. Summary of diffraction data

Treatment	Maximum Intensity Counts for 100% peak	
	Ettringite	Friedel's Salt
Water	216	Not Present
NaCl	260	479
NaCl+Gypsum	304	496

Chloride and sulfur trioxide measurements and regression results for mortar specimens subjected to different brine treatments are in Figure 18. As anticipated, brine treatments cause a substantial increase in chloride concentration, thus supporting the observation that some chloride is tied up in Friedel's salt. These data also suggest a maximum chloride concentration near 2 percent gypsum, a gypsum concentration that corresponds reasonably well with: (1) minimum pulse velocity (2.6%), (2) minimum visual rating (2.0 %), (3) minimum strength (2.1 %), and (4) maximum amount of void filling.

Sulfate concentrations measured in the specimens after undergoing freeze-thaw testing decreased slightly and nearly linearly as gypsum in the brine increased. To be consistent with pore filling, this evidence suggests the primary participant in the filling is Friedel's salt, because it does not contain the sulfate radical found in ettringite.

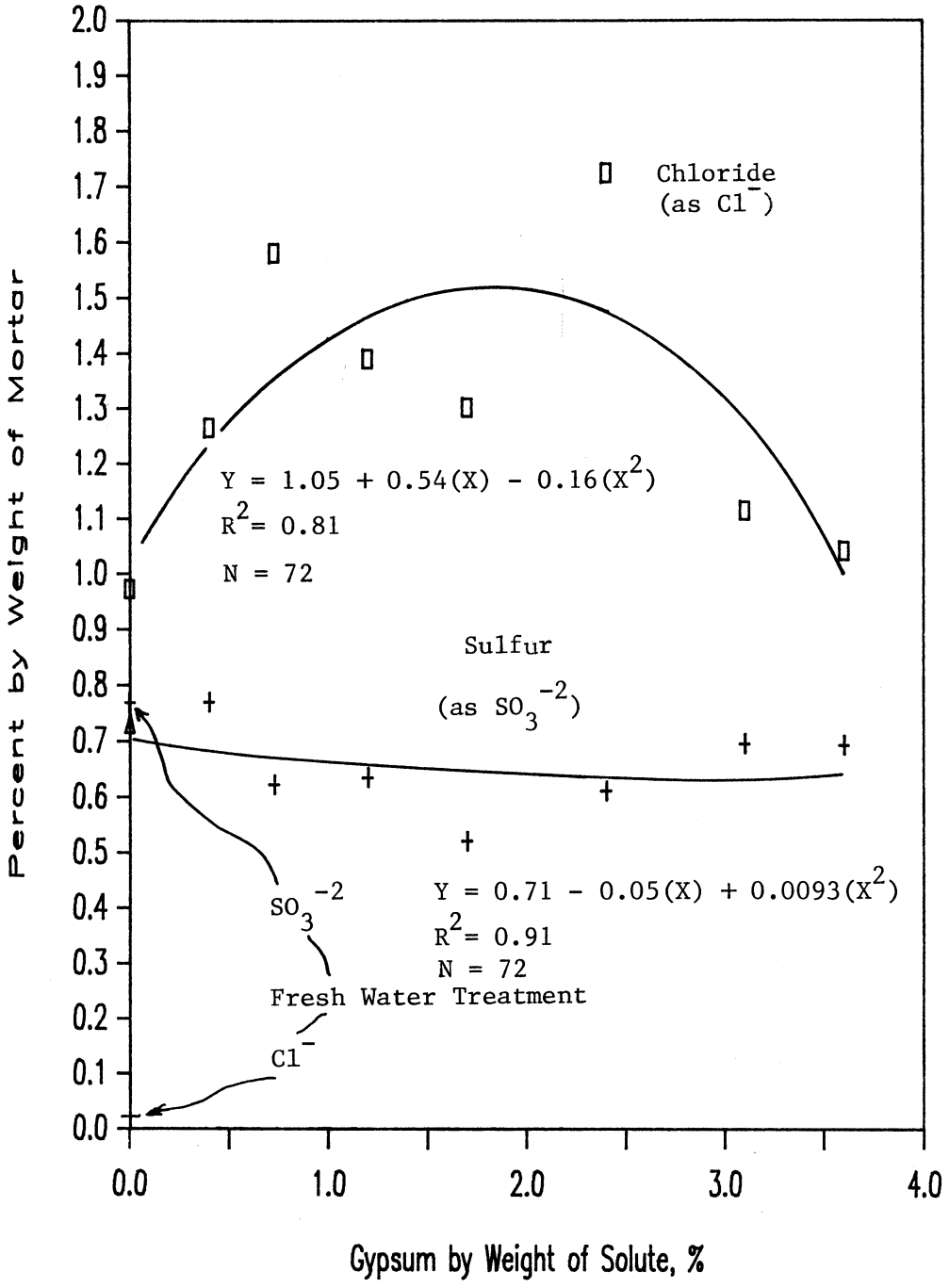

Figure 18. Chloride and sulfur trioxide contents of mortar

Summary

Brine treatment coincident with freeze-thaw testing resulted in a much faster deterioration rate than any of the four methods used in the first experiment. It is reasoned that coincident brine application more closely represents field conditions. Cracking occurred below the solution level, which is evidence of an expansive fracture mechanism resulting from a combined influence of sulfate brine treatment and frost action.

Experimentation demonstrated that small amounts of sulfate (less than 0.5 percent) in deicing brines can be detrimental to durability of concrete mortar, regardless of the physical parameter being measured. Deterioration in terms of tensile strength was maximum at 2 percent gypsum and corresponded to a loss of nearly half the fresh water freeze-thaw strength.

Mechanisms for sulfate enhanced chloride deterioration are thought to be void filling from formation of Friedel's salt and possible additional ettringite. Formation of Friedel's salt also appears to be enhanced by sulfates. This mechanism is different from the classic views of individual sulfate or chloride attack, both from the standpoint of chemistry and the physical response. Different compounds are involved and the process proceeds at a much faster rate.

FIELD TESTING

Objective and Scope

The objective of this portion of the research was to relate laboratory testing to an actual pavement deterioration problem. The field investigation was conducted on Story County Road E-29 near the U.S. Highway 65 intersection. This pavement had extensive D-cracking near the intersection, but damage decreased to the east of the intersection, until at a distance of 300 to 400 feet, there was no visible damage. It was speculated that the D-cracking may have been the result of deicers tracked from U.S. 65 and occasional salt application at the intersection by Story County. Very little, if any, deicing was applied away from the intersection on this secondary pavement.

The pavement was built in 1966 using Iowa Highway Commission Standard Specifications, 1964. The pavement was constructed with a 6 inch thick, B-3 mix with 6 percent air entrainment. The fine and coarse aggregate used were from Hallets of Ames. Pavement between stations 0+12 to 0+50 was constructed using a different mix and was not included in the study.

Three-inch diameter cores, taken from station 0+50 to station 5+00, were obtained adjacent to joints, and at the midpoint between joints. Several cores were also taken adjacent to structural cracks that had developed visible D-cracking. Chloride concentrations were measured using ASTM C-114; sulfur trioxide concentrations were

measured using the Dietert sulfur analyzer.

Results and Discussion

Chloride and sulfur trioxide concentrations are shown in Figures 19 and 20. Sulfur trioxide concentrations were determined using the Dietert sulfur analyzer. All results were converted to a percentage by weight of mortar. Comparison with Table 4 and Figure 18 suggests the use of saturated brines in the laboratory was appropriate.

Chloride concentrations measured at the joints decrease with distance away from the intersection, suggesting that chemical contamination is occurring. The concentrations found at the joints was much higher than concentrations found at the midpoint of the slabs, reinforcing the hypothesis that joints act as reservoirs collecting deicing solutions. Chloride concentrations found adjacent to structural cracks was somewhat less than at the joints. This could be the result of less exposure time if the cracks occurred several years after construction.

Sulfur trioxide concentrations are shown in Figure 20. With exception of three high values, possibly outliers due to pyrite particles known to be in the sand, sulfate concentration tends to increase with distance from the intersection. This is consistent with the inverse relationship observed in Experiment II, Figure 18 in that slightly lower sulfate concentrations were measured in the mortar as the sulfate in the brine increased. Thus more deicer near the intersection should mean the combined sulfate-chloride reaction should be enhanced.

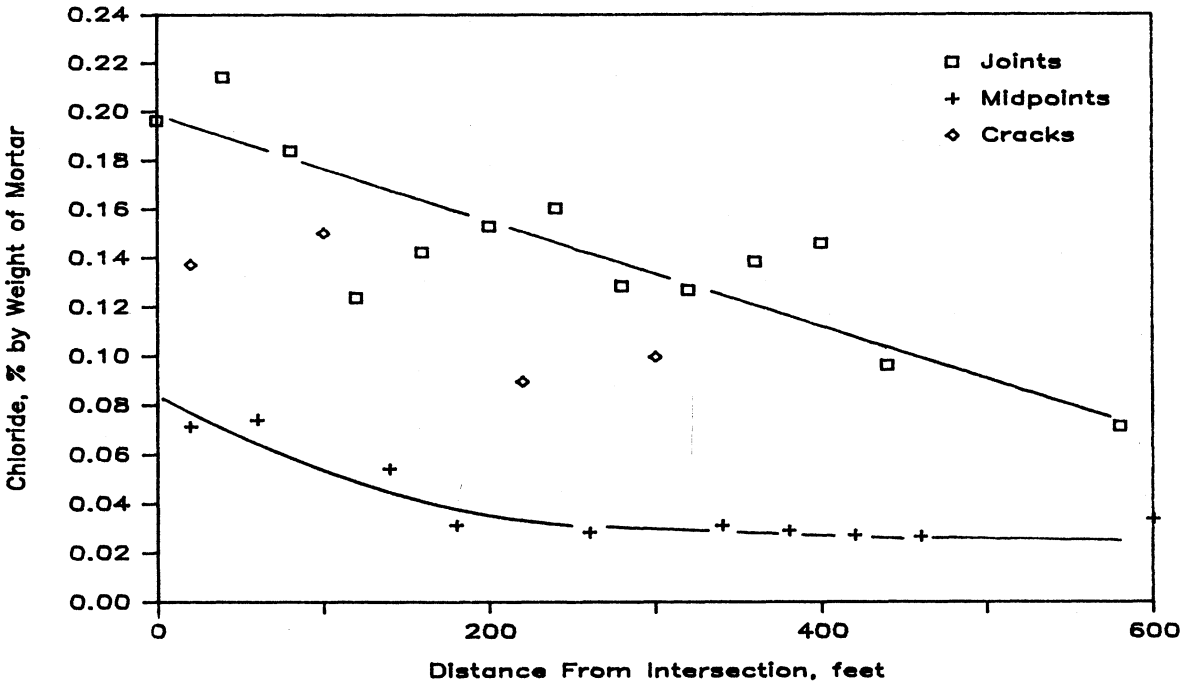

Figure 19. Field testing, chloride concentrations

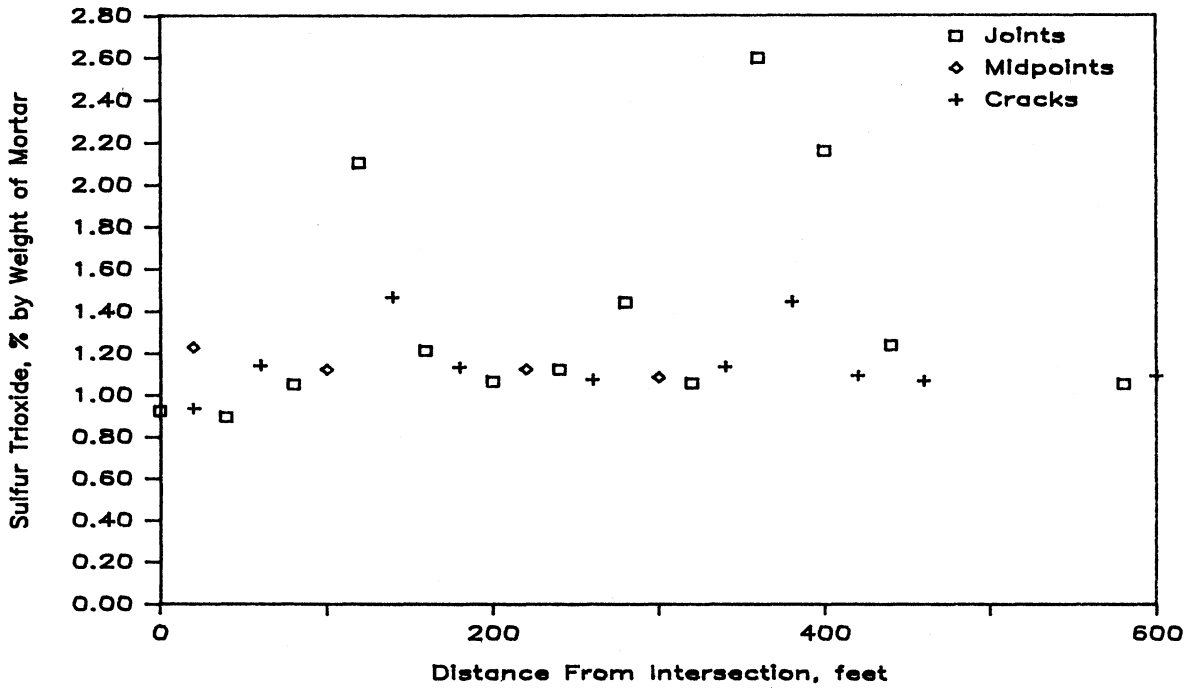

Figure 20. Field testing, sulfur trioxide concentrations

POSSIBLE SOLUTIONS

Objective

Potential methods of correcting sulfate contamination are considered in this section. Remedies might be applied to several aspects of the problem: specifications limiting the amount of sulfate impurities in rock salt, admixtures to concrete for patching and new pavements, treatment of existing pavements, or treatment of deicing salt before application.

Salt Specifications

The simplest solution to the problem would be to set limits on the amount of sulfate impurities in allowed in deicing salt. This research shows that significant damage occurs at levels as low as 0.5 percent gypsum in halite. Unfortunately, specifications limiting calcium sulfate impurities to below this level may have the adverse effect of eliminating several rock salt sources. If Table 1 data is indicative of salt quality and availability, two of the three sources, Kansas and Michigan, would be eliminated. A technically appropriate limit on sulfate could promote more selective mining and processing methods but the cost (now an unkown) would have to be balanced against the damage the sulfates are causing. Also, this solution would not eliminate problems caused by previous deicing.

There is still the question of gypsum accumulation in the joints with time. Sulfate deposits could occur from rock salt containing

less then 0.5 percent calcium sulfate impurities through evaporation and depositional processes which, after a period of time, result in concentrations sufficient for sulfate induced deterioration. If this is the case, then salt specifications will only postpone the problem.

Fly Ash Replacement

Fly ash is a pozzolanic material and, when used as a partial replacement for portland cement, has been shown to alter pore structure through reactions between calcium hydroxide and the reactive silicates [10,12]. Thus a 20 percent fly ash replacement to the C-3 mix was evaluated on the chance that such pore alteration might reduce the damage from sulfate/chloride attack. Table 8 gives the origin and chemical composition of the Class C fly ash used in this preliminary study.

Test results shown in Figures 21 and 22 indicate that fly ash has potential for reducing sulfate/chloride damage. Pulse velocity and strength losses were notably less than found in the earlier results. Some deterioration did occur from treatments of 2.41 percent gypsum and higher. Comparison of this strength loss, 10 to 14 percent, is much less then the 40 percentage point loss noted earlier.

Table 8. Chemical composition of Neal No. 4 fly ash

SiO_2	34.75
Al_2O_3	15.47
Fe_2O_3	6.31
SO_3	3.55
CaO	25.76
MgO	5.82
Na_2O	1.57

Treatment of Existing Pavements

Results from Experiments I & II indicate severity of deterioration is dependent on the environment at brine application. Thus, one tactic to eliminate the problem is to upset the balance or remove an element essential for the destructive process. This research demonstrates an air/brine boundary to be such an element. Mortar specimens inundated with brine did not deteriorate. Thus keeping concrete saturated at all times may be a solution, although not very practical. An opposite approach is to eliminate the boundary by keeping concrete dry. Isobutyl trimethoxy-silane (silane) is a compound that bonds to the silica in hydrated portland cement causing it to become hydrophobic, thus keeping it dry. Silane is a liquid and has potential for being sprayed on existing joints.

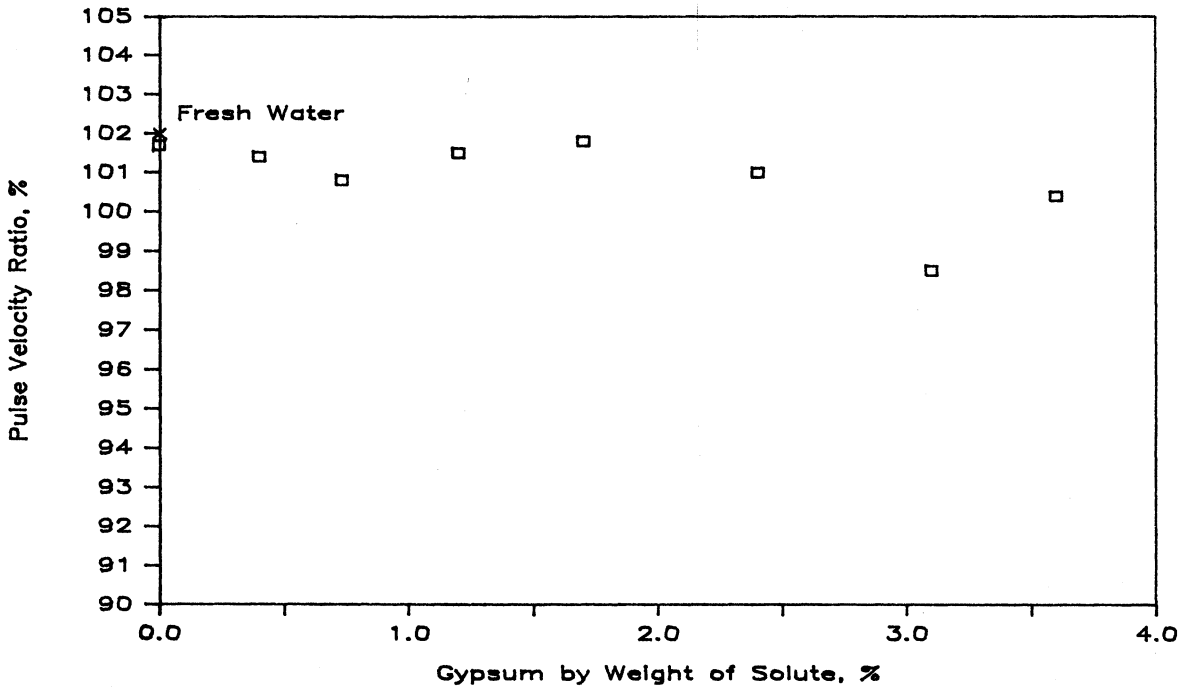

Figure 21. Pulse velocity ratio, 20% fly ash

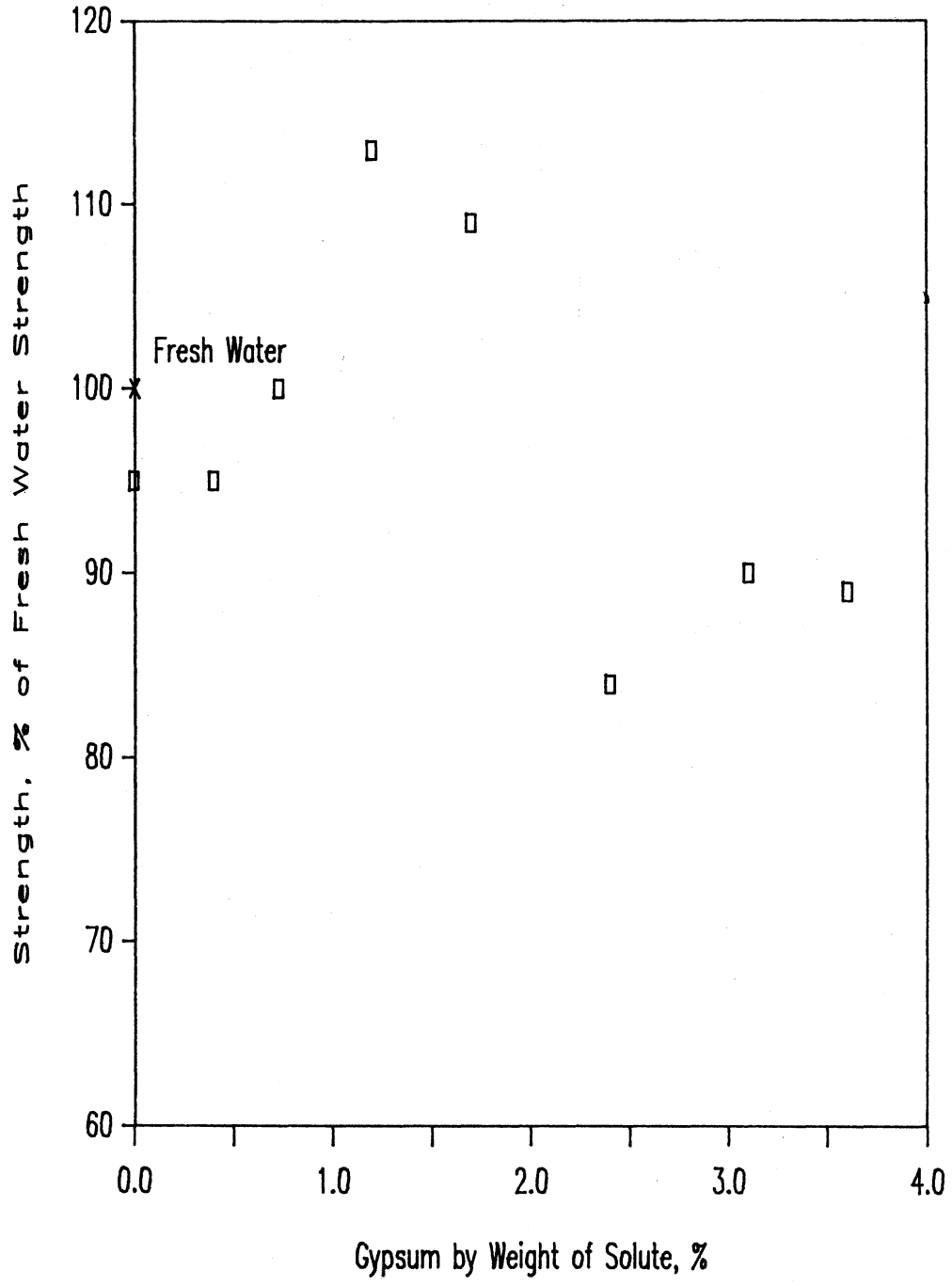

Figure 22. Tensile strength, 20% fly ash

To evaluate the potential of silane treatment, fourteen day old mortar specimens were treated and then allowed 48 hours reaction time before being subjected to freeze-thaw in brines, as was done in Experiment II. Figures 23 and 24 show that deterioration was virtually nonexistent. With the exception of a two percentage point loss in strength ratio for the highest gypsum concentration, pulse velocity and strength results were equal to or greater than those for water treated specimens.

It is proposed that this type of treatment could be selectively applied to areas susceptible to deicing contamination by spraying, thus greatly improving concrete durability. One source quoted a price of $30 per gallon which will cover 100 to 125 square feet. Thus, material costs will be approximately $10 to $15 per joint.

Treatment of Deicing Salt

Another approach which may reduce the undesirable influence of sulfates in rock salt is to treat the salt with the intent of immobilizing the problem ion. This is theoretically possible by adding a highly soluble compound which reacts with the sulfate radical to produce a very insoluble product. Barium chloride and barium hydroxide are two salts which should react with the sulfate to form barium sulfate, a compound 1000 times less soluble than calcium sulfate.

Brine treatments with 1.70, 2.41, and 3.10 percent gypsum were used with barium added in the form of barium chloride or barium

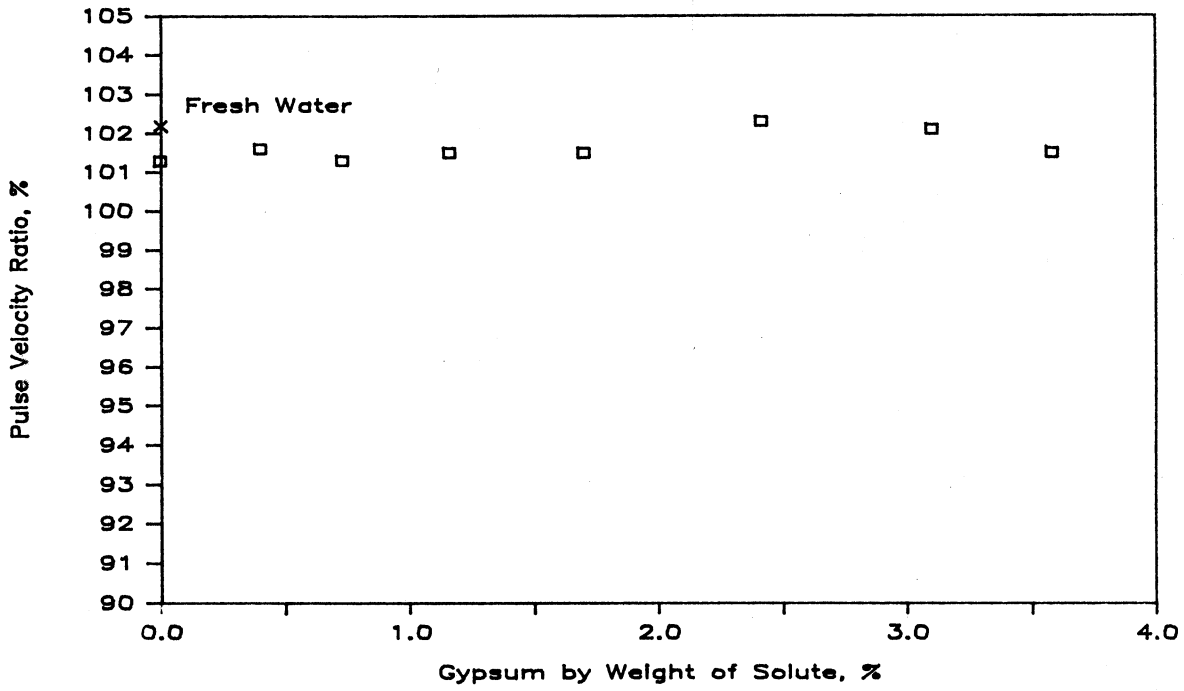

Figure 23. Pulse velocity ratio, silane treatment

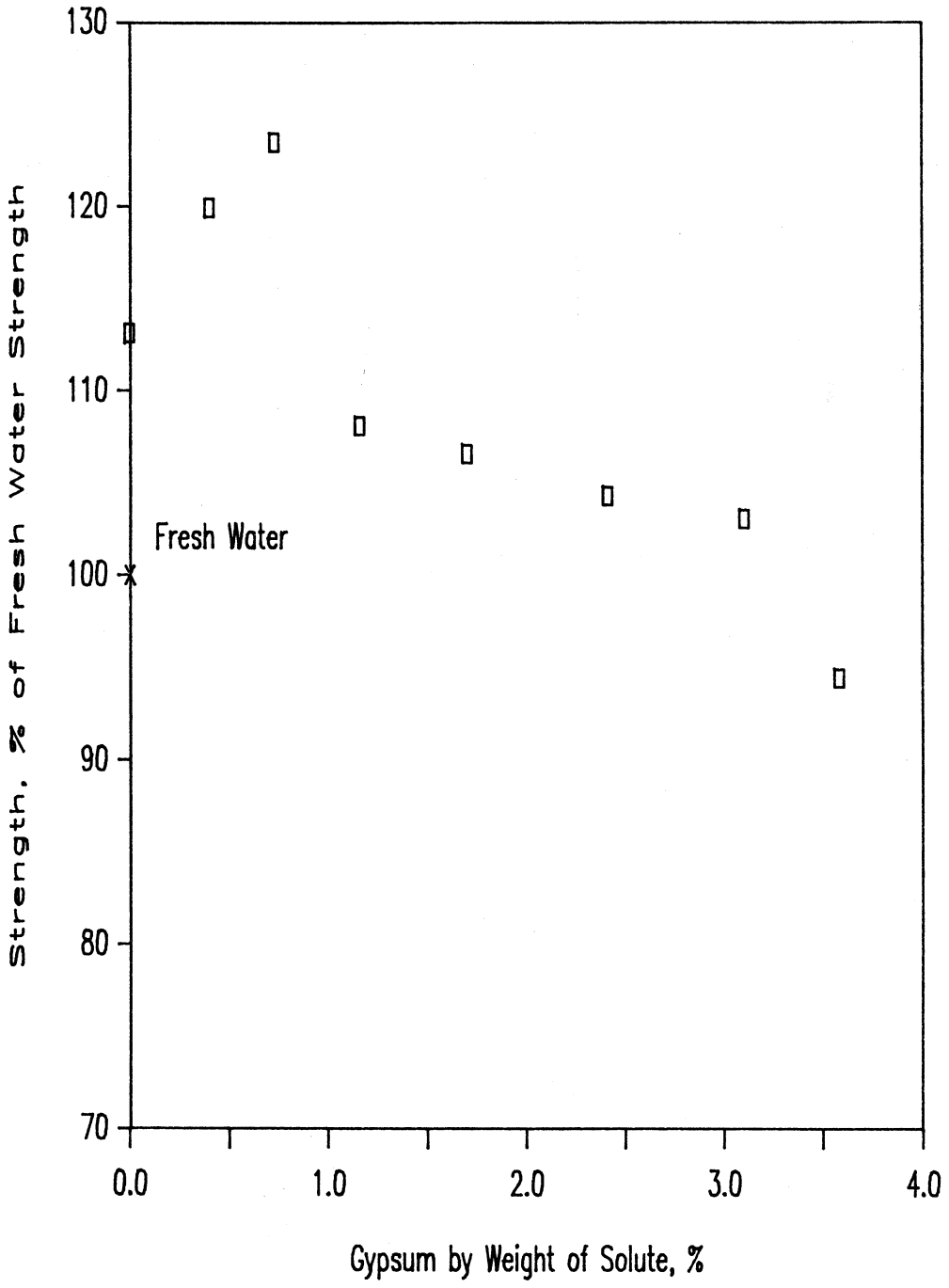

Figure 24. Tensile strength, silane treatment

hydroxide in amounts theoretically sufficient to react all the sulfate with the barium. The resulting solutions were then applied in the same manner as in Experiment II.

The results, shown in Figures 25 and 26, were not very encouraging. Gypsum caused reductions in both pulse velocity and strength. No apparent difference was seen between the barium chloride or barium hydroxide treatments. It is not completely understood why deterioration was so severe. This idea may be worth further investigation with other additives.

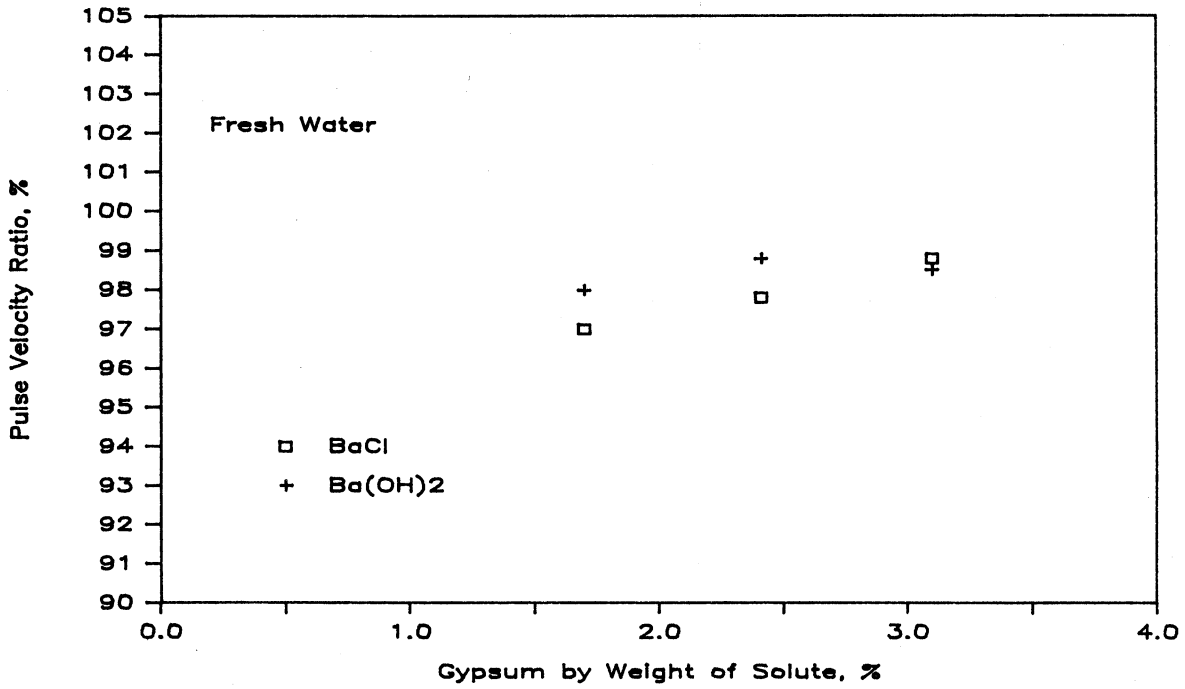

Figure 25. Pulse velocity ratio, barium treatment

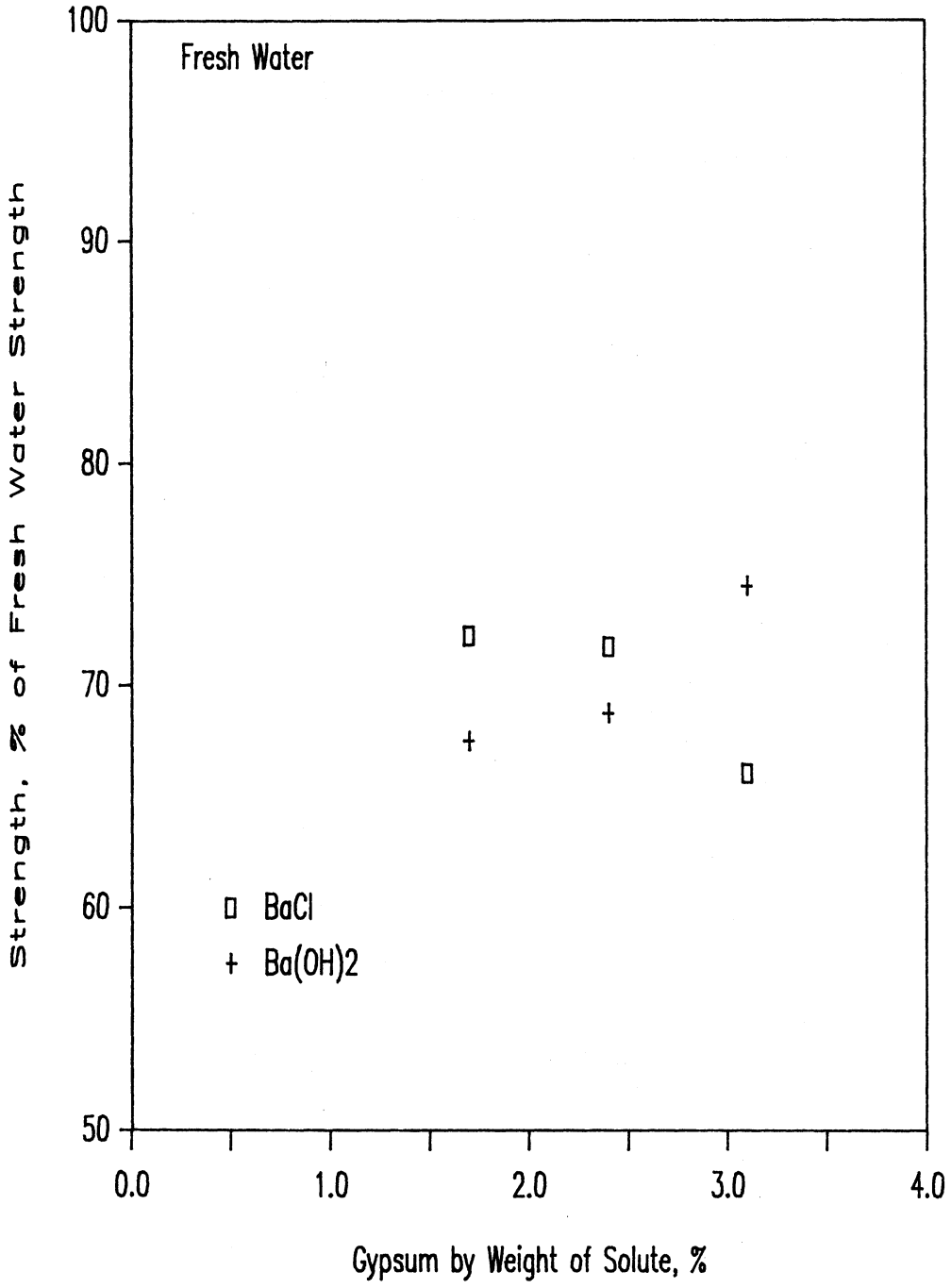

Figure 26. Tensile strength, barium treatment

CONCLUSIONS

This research investigated the hypothesis that trace amounts of calcium sulfate occurring naturally in halite deposits used for deicing can be detrimental to portland cement concrete pavements. The following conclusions are made:

1. Sulfate introduced as gypsum with sodium chloride in deicing brines can have detrimental effects on portland cement mortar. Under certain conditions of application, tensile strength of mortar can be reduced by nearly half after as few as 88 cycles of freeze-thaw.

2. The concentration of sulfate required to render a brine destructive was found to be as low as one-half percent of the solute. Commercial rock salts may easily exceed this limit.

3. Conditions of brine application are critical to specimen durability. Specimens half immersed in brine solutions during frost action proved the least durable. Specimens half immersed in brine prior to being subjected to frost action and subjected to freeze-thaw in fresh water were damaged, but less severely. Specimens completely immersed or subjected to cyclic wetting and drying showed little or no deterioration.

4. Mechanisms for deterioration are due to pore filling resulting from compound formation and deposition. Ettringite and Friedel's salt are the compounds thought to be responsible. Ettringite forms in a secondary reaction from tricalcum aluminate hydrates and sulfates. Freidel's salt, a tricalcium aluminate

chloride hydrate, does not contain sulfate but its formation appears to be enhanced by presence of gypsum. The pore filling that occurs is not in itself sufficient to destroy the mortar. It does however make mortar more vulnerable to frost action.

5. There appears to be a pessimum gypsum concentration in sodium chloride brine with regards to strength, pulse velocity, and visual indexing of cracks. This concentration is on the order of 2 percent by weight of solute in the brine.

6. A field evaluation of deteriorating joints suggests the sulfate phenomona demonstrated in the laboratory also operates in the field. Sulfate and chloride concentrations in mortar from field cores were in reasonable agreement with measurements on laboratory specimens.

7. Preliminary evaluation of remedies includes: limits on sulfates, fly ash admixtures, treatment of existing pavement, and salt treatments.

RECOMMENDATIONS FOR FURTHER STUDY

Areas requiring further investigation are:

1. More detailed study of actual pavement joints, including: evaluation of deicer meltwater samples over an extended period to define actual brine concentrations and evaluation of temperature and moisture conditions within concrete near joints to determine number of freezing cycles coincident with a brine interface.

2. Study of how concrete materials (eg. aggregate and cement type) and maturity may influence the sulfate/sodium chloride deterioration process.

3. Correlation of laboratory performance to field deterioration. This might be accomplished by adapting the visual index system of this research for field observation. Field measurements may be linked to laboratory specimens of equivalent quality but with a known history of deterioration. This may allow prediction of additional joint life if any.

4. Investigate and evaluate the value of corrective methods. This should include: portland cement compositions, physical construction of joints (ie. drainage and sealants), joint treatments such as silanes, portland cement admixtures, salt treatments, and the economic impact of establishing sulfate limits.

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ACKNOWLEDGEMENTS

This research was conducted through the Engineering Research Institute of Iowa State University and sponsored by the Iowa Highway Research Board of the Iowa Department of Transportation as HR-271 The authors are grateful to Dr. Robert Lamb for his evaluation of rock salt distribution, Mr. James Gaunt for his chemical analysis, and Mr. Jerry Amenson for his assistance with x-ray diffracton. Mr. David Robson is greatly thanked for his editorial and design assistance.