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## Control of Concrete Deterioration Due to Trace Compounds in Deicers

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The opinions, findings and conclusions expressed in this publication  
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#### **ABSTRACT**

This report presents the results of research on the influence of trace compounds from rock salt deicers on portland cement mortar and concrete.

An evaluation of the deicers in stock throughout the state showed that about ninety-five percent contained enough sulfate to cause accelerated deterioration of concrete. Of the impurities found in rock salts, sulfate compounds of calcium and magnesium were found to be equally deleterious. Magnesium chloride was found to be innocuous.

Introduction of fly ash eliminated the damage to portland cement mortar caused by sulfates. When used with frost-resistant Alden aggregate in fly ash concrete and exposed to a variety of deicer brine compositions, the concrete did not deteriorate after exposure. With the exception of a high calcium brine, the behavior of the frost-prone Garrison aggregate was independent of deicer treatment; the high calcium brine reduced frost damage with this aggregate.

Two approaches to reducing sulfate deterioration from deicers are suggested as (1) limiting the amount of sulfate to about 0.28 percent, and (2) making concrete sulfate-resistant by using fly ash. Techniques for making existing concrete deicer-sulfate-resistant are essential to a practical solution.

## INTRODUCTION

In 1980, 6.4 million tons of rock salt were used for ice removal on U.S. highways. In Iowa DOT Project HR-271, it was demonstrated that natural rock salt could contain enough sulfate as an impurity to accelerate deterioration of concrete mortar subjected to frost action. Figure 1 reviews the fact that sulfate, as an impurity in sodium chloride brine, can reduce the strength of portland cement mortar to sixty percent of that of specimens subjected to frost action in pure water, and to about forty percent of those in pure sodium chloride.

The mechanism for the destructive nature of sulfate in rock salt deicers was found to be pore structure alteration through the formation of compounds enhanced by the presence of sulfate. A two percent pessimum gypsum concentration caused the most alteration to the pores, and produced the pore structure most vulnerable to frost action. Based on evaluation of data from the literature, it was concluded that rock salt from some natural deposits contains enough sulfate to support the deterioration mechanisms observed in the laboratory. Also, existing specifications for rock salt deicer allow sulfate compounds in sufficient concentration to cause excessive damage.

Previous research was by design a systematic laboratory evaluation in which variables were minimized so damage could be attributed to specific causes. Sulfate, the primary ingredient hypothesized as being detrimental, was introduced as gypsum with sodium chloride in reagent grade. Measures of deterioration were compared with results from specimens tested with water. Although minimization of variables was essential to defining and evaluating deleterious mechanisms, other factors important to field

performance were excluded. Both the influence of other trace impurities known to exist in rock salt, and the interaction between deicing brines and coarse aggregate, could be equally important variables; they are the focus of this project.

### RESEARCH SCOPE AND OBJECTIVES

The objective of this project is to determine how a complex array of variables, including deicer impurities and concrete constituents, interact to the influence of frost action. Applications of this research are improvements in deicer specifications and development of pavement and repair methods more resistant to deicer induced damage. Phase I of this research concentrates on the following goals:

1. Initiate a characterization study for rock salt used in Iowa.
2. Evaluate the influence of other impurities known to exist in rock salt.
3. Determine how coarse aggregate type can influence concrete resistance to deicers.
4. Preliminary evaluation of concrete composition to include use of fly ash.

## DEICER COMPOSITION

### Test Methods

Rock salt composition was evaluated by analytical chemical method; particular attention was given to the potential for error due to interactions among the several ions which can exist in rock salt. Sulfate was measured by gravimetric precipitation with barium. This method involves mixing a rock salt solution with barium chloride and weighing the amount of insoluble barium sulfate produced. The interaction problem stems from the fact that other cations, notably sodium, magnesium, aluminum, and potassium, enter the barium sulfate crystal structure, thus giving a false weight. This coprecipitation error depends on the molecular weight of the foreign ion. An ion which is light compared to barium will cause underestimation of sulfate concentration; the inverse is true for heavy ions.

Coprecipitation can be reduced to an acceptable level with a method called "reverse order precipitation." The amount of foreign cation coprecipitated depends on the concentration of the cation present in the solution at the time of precipitation; higher concentrations of foreign cations mean greater error. Thus, by using small salt samples relative to the quantity of barium chloride, the amount of foreign cations available for interference is reduced to acceptable levels. The term "reverse order" comes from adding a small amount of known salt of solution to the reagent solution of barium chloride, rather than the normal technique of adding a small amount of reagent to the unknown solution containing sulfate. Details of the procedure are in Appendix A.

A quality assurance audit was conducted to determine the precision of sulfate determination. Enough gypsum was added to reagent grade sodium

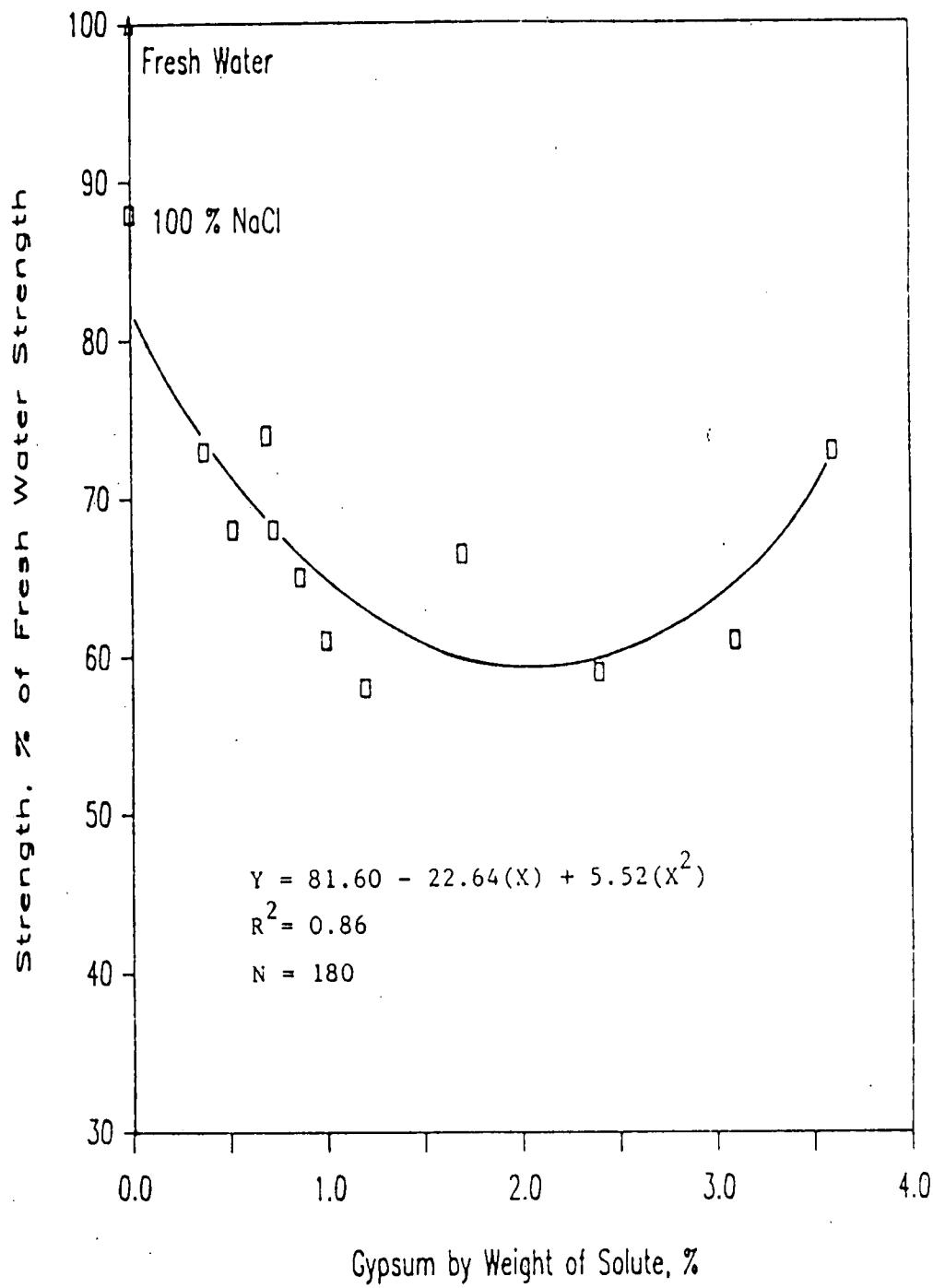


Figure 1. Tensile strength at 88 freeze-thaw cycles [1].

chloride to form a synthetic rock salt sample containing 0.293% sulfate. Sulfate measured by reverse order precipitation was 0.309%, a 0.016 point overestimate, or 105.4% recovery.

Coprecipitation with magnesium in addition to sodium was evaluated with reagent grade sodium chloride specimens with 0.1% magnesium and enough gypsum to produce theoretical sulfate concentrations of 0.283%, 0.285%, 1.364%, and 1.367%. Sulfate recoveries were respectively 98.37%, 98.84%, 100.6%, and 101.6% of the theoretical. Differences among theoretical and measured sulfate concentrations of less than 0.02 percentage points is more than adequate to relate to natural salts having sulfate concentrations on the order of 5 percent.

Other salt components were measured by standard methods after samples were digested with nitric and hydrochloric acids to insure dissolution of gypsum and other water-insoluble materials. The digestate was diluted by a known amount and the calcium and magnesium concentration measured by atomic absorption spectrophotometry. Sodium was measured by flame emission spectrometry. Chlorine content of the solutions were measured by potentiometric titration with silver nitrate solution.

#### Salt Composition

The composition of twenty two rock salt samples provided by the Iowa Department of Transportation are in Table 1. With exception of sulfate presented as gypsum and sulfate presented as the  $\text{SO}_4^{--}$  radical, the ions were combined by order of solubility to form compounds which are presumed to exist in the solid. Sulfate as gypsum is tabulated to allow reference to past work, Figure 1. Sulfate concentration as the radical includes the combined concentration which could come from calcium, magnesium, and sodium sulfate. Sulfate in the radical form is probably the best representation

Table 1. Composition of rock salts used in Iowa.

ID	Sulfate as				
	%GYPSUM	%CaSO <sub>4</sub>	%MgSO <sub>4</sub>	%NaSO <sub>4</sub>	%SO <sub>4</sub> <sup>--</sup>
1	4.381	3.465	0.182	0.050	2.630
2	1.385	1.095	0	0	0.773
3	1.450	1.147	0	0	0.809
4	4.467	3.533	0.197	0	2.650
5	1.407	1.113	0	0	0.785
6	1.156	0.914	0	0	0.645
7	3.410	2.697	0.046	0	1.945
8	2.414	1.909	0.154	0	1.470
9	4.106	3.247	0.249	0	2.490
10	3.781	2.990	0	0	2.110
11	1.693	1.339	0	0	0.945
12	0.568	0.449	0	0	0.317
13	5.326	4.212	0.254	0.074	3.234
14	2.921	2.310	0.200	0	1.790
15	3.329	2.633	0.074	0	1.917
16	7.731	6.114	0.246	0.314	4.764
17	7.044	5.571	0.243	0.140	4.238
18	1.366	1.080	0.026	0.005	0.787
19	5.000	3.954	0	0	2.790
20A	3.582	2.833	0.005	0	2.003
20B	5.928	4.688	0.311	0.125	3.657
20C	3.930	3.108	0	0	2.193
20D	5.025	3.974	0.254	0	3.007
21	0.993	0.785	0	0	0.554
22	0.370	0.293	0	0	0.207

<sup>a</sup>Supplier<sup>b</sup>Site

ID	% MgCl <sub>2</sub>	%CaCl <sub>2</sub>	%NaCl	Source
1	0	0	96.30	Independence Salt Co., Kansas <sup>a</sup>
2	0.013	0.220	98.67	DOMTAR <sup>a</sup>
3	0.007	0.173	98.67	MORTON <sup>a</sup>
4	0.002	0	96.27	Forest City <sup>b</sup>
5	0.062	0.530	98.30	Waterloo <sup>b</sup>
6	0.033	0.371	98.68	West Union <sup>b</sup>
7	0.183	0	97.07	Independence Salt Co., Kansas <sup>a</sup>
8	0.040	0	97.90	Independence Salt Co., Kansas <sup>a</sup>
9	0.009	0	96.50	Independence Salt Co., Kansas <sup>a</sup> , Linn Co. <sup>b</sup>
10	0.163	0.986	95.88	Independence Salt Co., Kansas <sup>a</sup>
11	0.025	0.442	98.19	Rock Island <sup>a</sup>
12	0.009	0.365	99.18	Cargila <sup>a</sup>
13	0	0	95.46	Independence Salt Co., Kansas <sup>a</sup> , Crawford Co. <sup>b</sup>
14	0.003	0	97.49	Independence Salt Co., Kansas <sup>a</sup> , Carroll Co. <sup>b</sup>
15	0.181	0	97.11	Independence Salt Co., Kansas <sup>a</sup>
16	0	0	93.33	Independence Salt Co., Kansas <sup>a</sup> , Calhoun Co. <sup>b</sup>
17	0	0	94.05	Independence Salt Co., Kansas <sup>a</sup> , Calhoun Co. <sup>b</sup>
18	0	0	98.89	Louisiana <sup>a</sup>
19	0.147	0.017	95.88	Unknown
20A	0.387	0	96.78	Independence Salt Co., Kansas <sup>a</sup>
20B	0	0	94.88	Independence Salt Co., Kansas <sup>a</sup>
20C	0.199	0.512	96.18	Independence Salt Co., Kansas <sup>a</sup>
20D	0.101	0	95.67	Independence Salt Co., Kansas <sup>a</sup>
21	0.010	0.102	99.10	Unknown
22	0.363	0.079	99.27	Mexico, Com Kare Group U.S. LTD <sup>a</sup>

and will be used in future research.

In some cases the rock salt sources were not well documented; nonetheless, the data serve the intent of a brief survey of rock salts in stockpile as of Spring 1988. If one would arbitrarily presume to limit damage to 70% of that occurring with freeze-thaw in water, the data in Figure 1 indicate that sulfate expressed as gypsum should be on the order of 0.5 percent or less. It follows from Table 1 that all deicers except the one from Mexico (sample 22) should be eliminated, although bending this rule would allow sample 12 to be used.

The impact of the data is that a reasonable sulfate limit, one which minimizes sulfate damage to pavements, may severely reduce the number of rock salt sources. Obviously this sampling is biased towards salts reportably from Kansas. However, sample 18 from Louisiana suggests what was thought to be a low sulfate source may not always be.

The single sample from Mexico offers an interesting possibility. If this sample is representative of the deposits, return barges from grain shipment may mean an economical supply.

More sampling with better source documentation is necessary for all supply potential regions. The data now available from Kansas sources are from a single company and there are very few data from testing on Louisiana salts. A variety of sulfate concentrations may be available from within each region and possibly from a single mine. If the supplier is aware of a sulfate requirement, it may be possible to produce an acceptable product. However, data available thus far reinforce the presumption that a significant problem exists.

In addition to calcium sulfate, Table 1 shows the presence of significant amounts of sulfates combined with magnesium and sodium. Later in this report, magnesium sulfate is shown to be quite damaging; it is

reasonable to speculate that sodium sulfate will behave in a similar manner. Thus, an appropriate measure of undesirability should be the sum of the water soluble sulfates.

Both magnesium chloride and calcium chloride also are present in several salts at concentrations sufficient to warrant concern. Specific mechanisms for deterioration cannot be postulated but experimental studies have been undertaken to evaluate their impact.

## FREEZE-THAW RESPONSE, OTHER IMPURITIES

### Test Methods

Tests on portland cement mortar subjected to frost action were conducted in the same manner as used in past research, except that the brines were changed to reflect rock salt constituents other than calcium sulfate[1]. Materials for test specimens were Ottawa sand, a low tricalcium aluminate content Type I portland cement, and in some cases, fly ash from the Ames Municipal generating station. The materials were mixed at a 0.45 water/cement ratio and combined to represent the mortar fraction of a typical concrete pavement based on Iowa DOT concrete C-3 mix. A commercial air entraining agent was used to obtain a 9% air content and the mortar was cast in 2-inch diameter by 4-inch long cylinders. The molds were removed after 24 hours of moist curing and then cured in a lime water bath for an additional two weeks. When fly ash was used it replaced 15% of the portland cement by weight. Reagent grades of sodium chloride, magnesium chloride, and magnesium sulfate were used to prepare brines.

To test the effect of freeze-thaw on concrete mortar samples, a modification of "ASTM C 666, Method A" was used. This is the same technique as reported for project HR 271. In brief, the method involves:

Placing nine 2x4 cylinders on end in the freeze-thaw pans with water or a saturated brine maintained at the midpoint of the specimens. Each pan represents a particular treatment subjecting the pan and specimens to between 120 to 150 freeze-thaw cycles at the rate prescribed in ASTM C 666.

Measuring specimen height, weight, and ultrasonic pulse velocity at each 20th thaw cycle .

Testing for splitting tensile strengths at the conclusion of cyclic freeze-thaw in accordance with ASTM C 496.

To reduce the likelihood of subjecting specimens from an exceptionally

good or exceptionally poor batch of mortar to a particular brine treatment, the nine specimens for each treatment were randomly selected from batch sources with equal representation from each batch. Batch source identification was maintained.

### Results

**Magnesium Sulfate.** Results of tests on six sets of nine specimens subjected to freeze-thaw in water, pure sodium chloride brine, and sodium chloride brines with four concentrations of magnesium sulfate are shown in Figure 2. Each data point is for an average of the velocities of the nine specimens, normalized by the average response for saturated specimens prior to being subjected to frost action. Past research indicates that pulse velocity offers an unbiased measure of deterioration as internal fracture slows pulse transmission. Magnesium sulfate concentrations (0.1, 0.5, 1.0, and 2.0 percent) are typical of the concentrations found in natural salts.

These data follow the same pattern previously found to occur with calcium sulfate as the impurity [1]. After about 60 cycles, the pulse velocity decreases when magnesium sulfate is present. A visual observation is that the specimens with pulse velocities reduced to between 50 and 80 percent of the initial values had cracks radiating from the axis of the cylinder. These cracks were limited to the specimen mass maintained below the brine level and are indicative of fracture resulting from internal stress. This fracture pattern is the same as was observed with calcium sulfate.

Results in Figure 3b demonstrate the reproducibility of magnesium sulfate induced deterioration in normal concrete. Results in Figure 3a also show the potential for sulfate resistant effects derived from at least

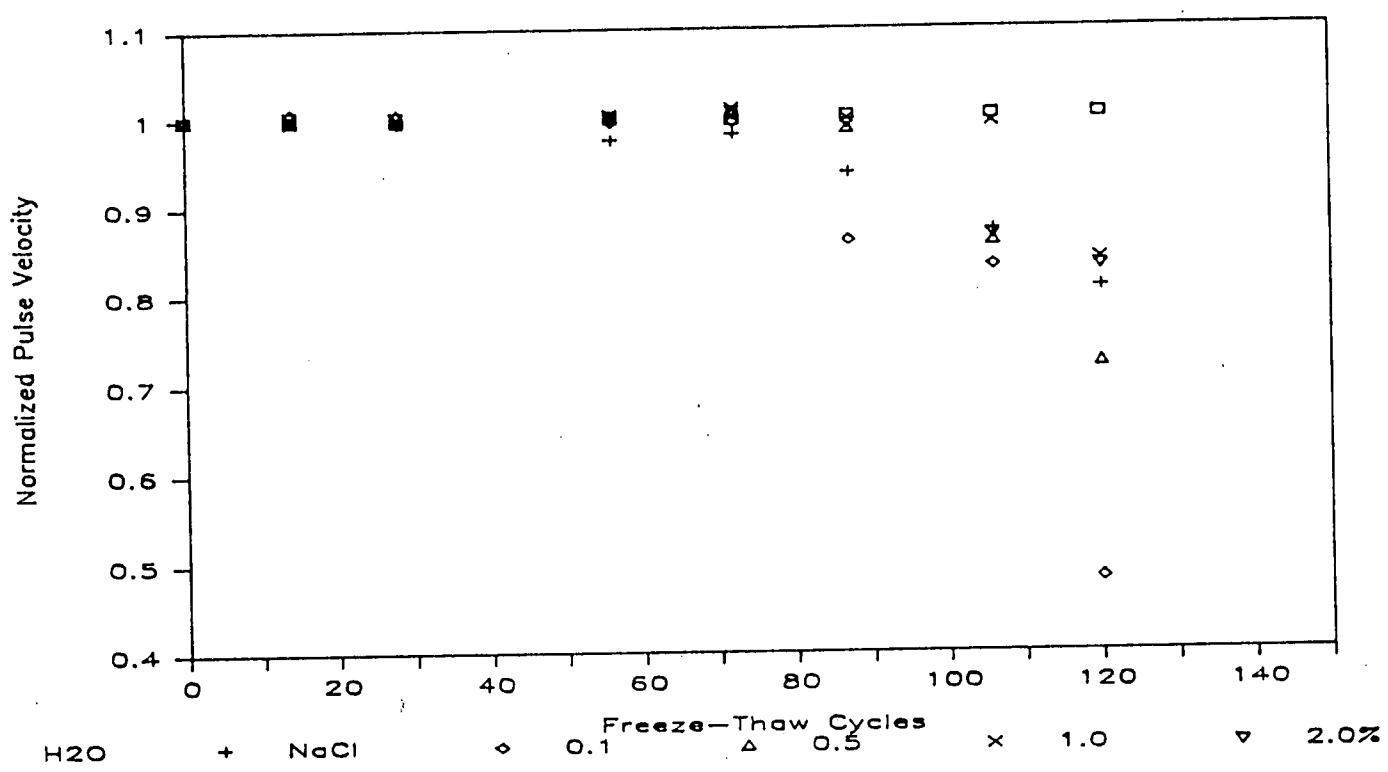
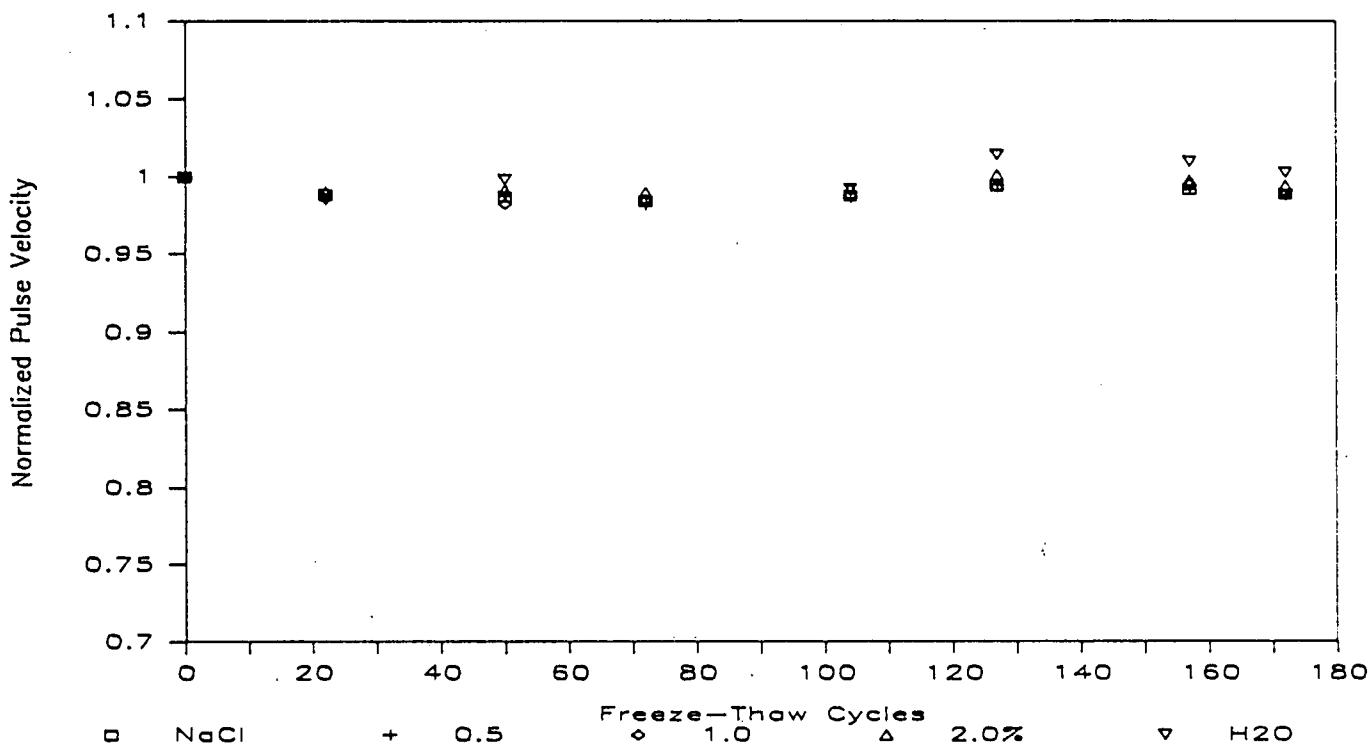
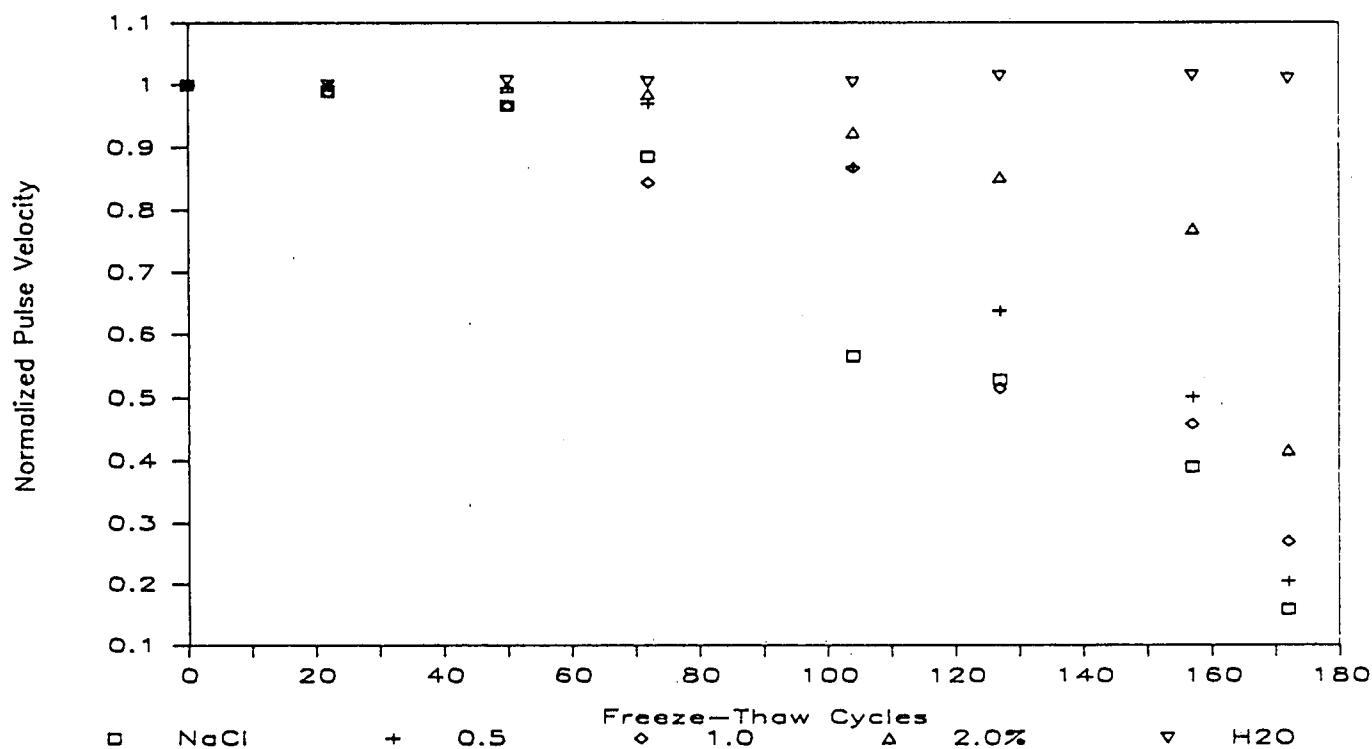


Figure 2. Resistance of a standard mortar to a MgSO<sub>4</sub> brine.  
Pulse velocity data.



(a) Fly ash mortar, 15% Ames fly ash.



(b) Standard mortar.

Figure 3. Resistance of mortar to a MgSO<sub>4</sub> brine.  
Pulse velocity data.

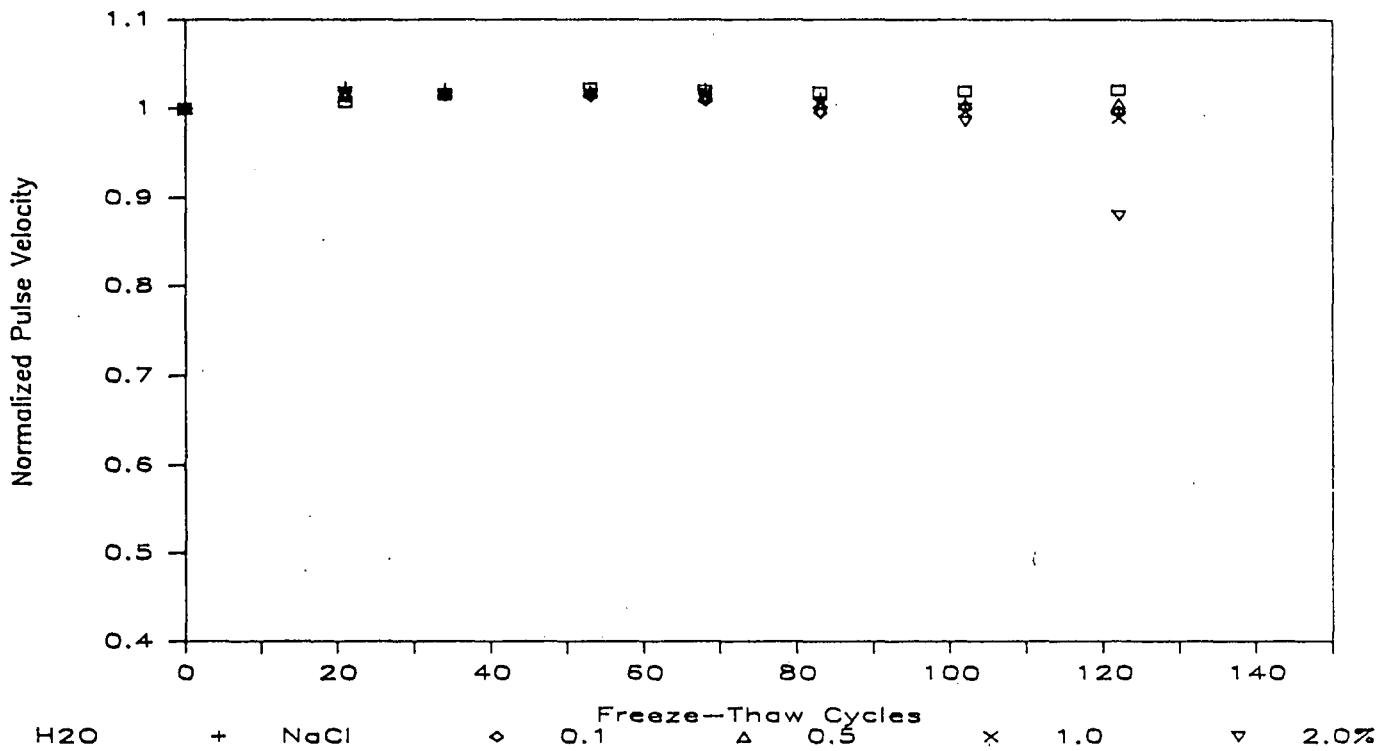
one type of fly ash. It was previously shown that a sample of Neal No.4 fly ash reduced the detrimental effects of calcium sulfate.

Tensile splitting tests are planned for these specimens and the results will be presented in a later report. However, an interim assessment based on experience with pulse velocity indicates that strength on the order of 40 to 60 percent of untreated specimens will result from magnesium sulfate treatment of the normal mortar.

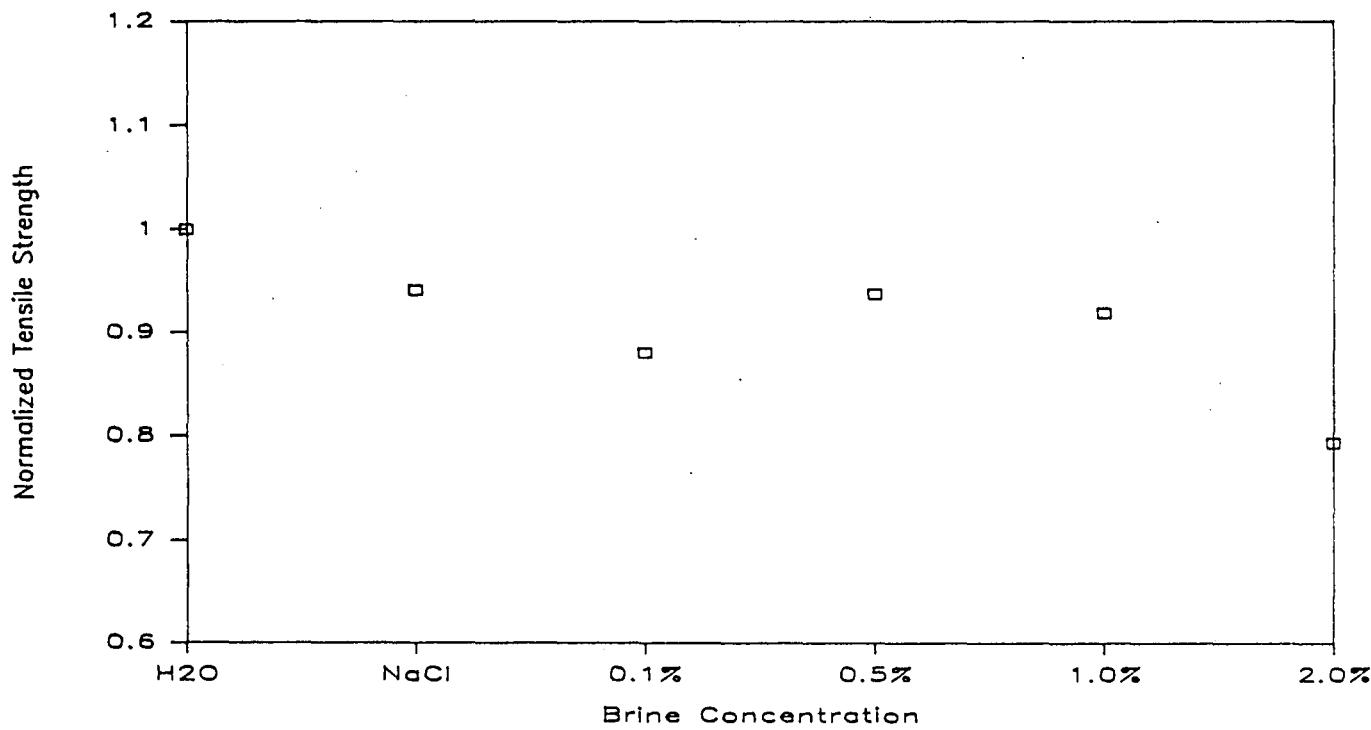
Magnesium Chloride. Results for duplicate experiments of 0.1, 0.5, 1.0, and 2.0 percent of magnesium chloride by weight of sodium chloride in a brine are shown in Figures 4 and 5. A minimal reduction in pulse velocity also is confirmed at 120 or 150 freeze-thaw cycles for more than 90 percent of the untreated specimens. Visual inspection of the specimens revealed competent specimens which showed some minor scaling. Obviously, this did not reduce strength.

Mortar using 15% Ames fly ash was also subjected to 0.1 and 2.0 percent magnesium chloride concentrations to determine whether magnesium chloride interacts with fly ash. To substantiate the benefit of fly ash in resisting sulfate attack, companion specimens were treated with 0.1 and 2.0 percent magnesium sulfate in the brine. Figure 6, a plot of the pulse velocities and tensile strengths obtained, shows magnesium chloride does not interact detrimentally with the fly ash in the mortar and also shows that fly ash arrests magnesium sulfate attack.

Calcium Chloride. Sodium chloride brines containing 0.1, 0.5, 1.0, and 2.0 percent magnesium chloride along with a constant 1.6 percent calcium chloride were concocted to simulate the calcium chloride introduced with combined sand and rock salt deicers. The calcium chloride is added to the sand to keep stockpiles from freezing. The results shown in Figure 7

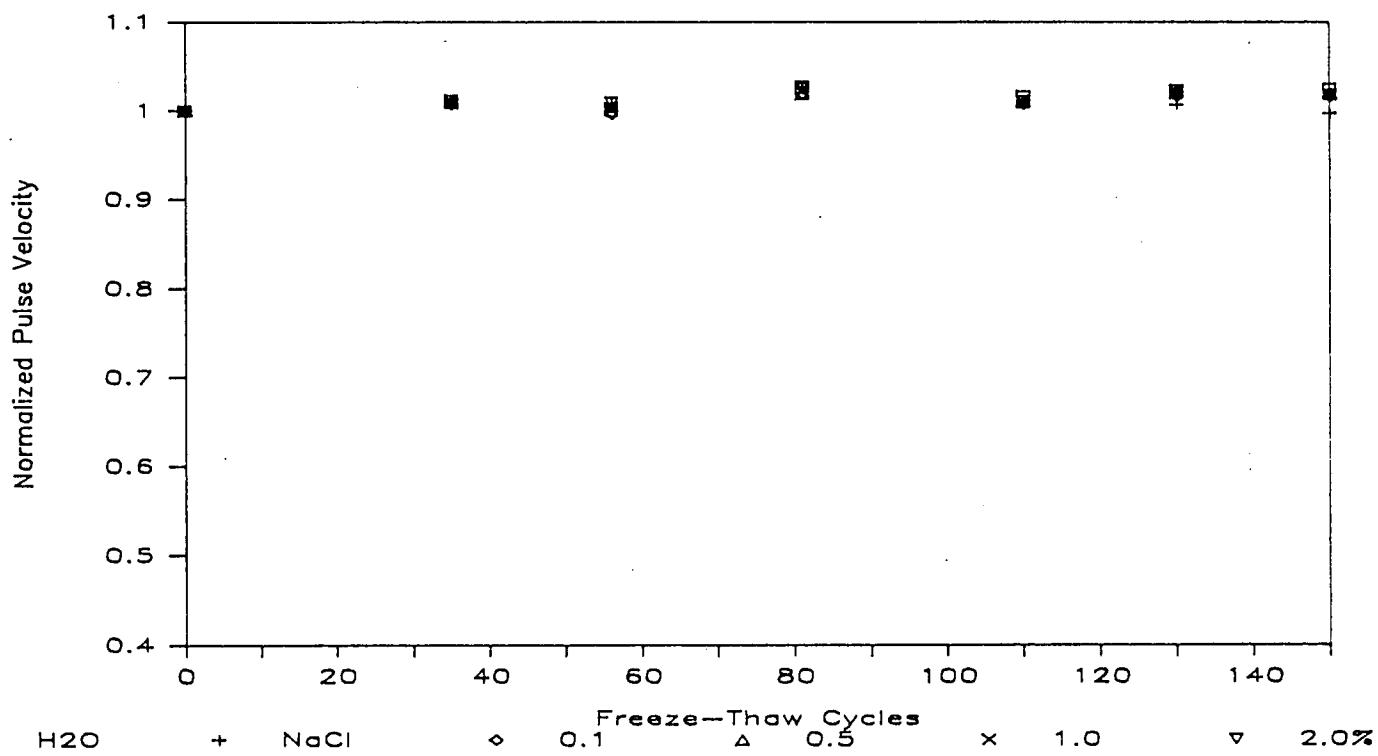


(a) Pulse velocity data.

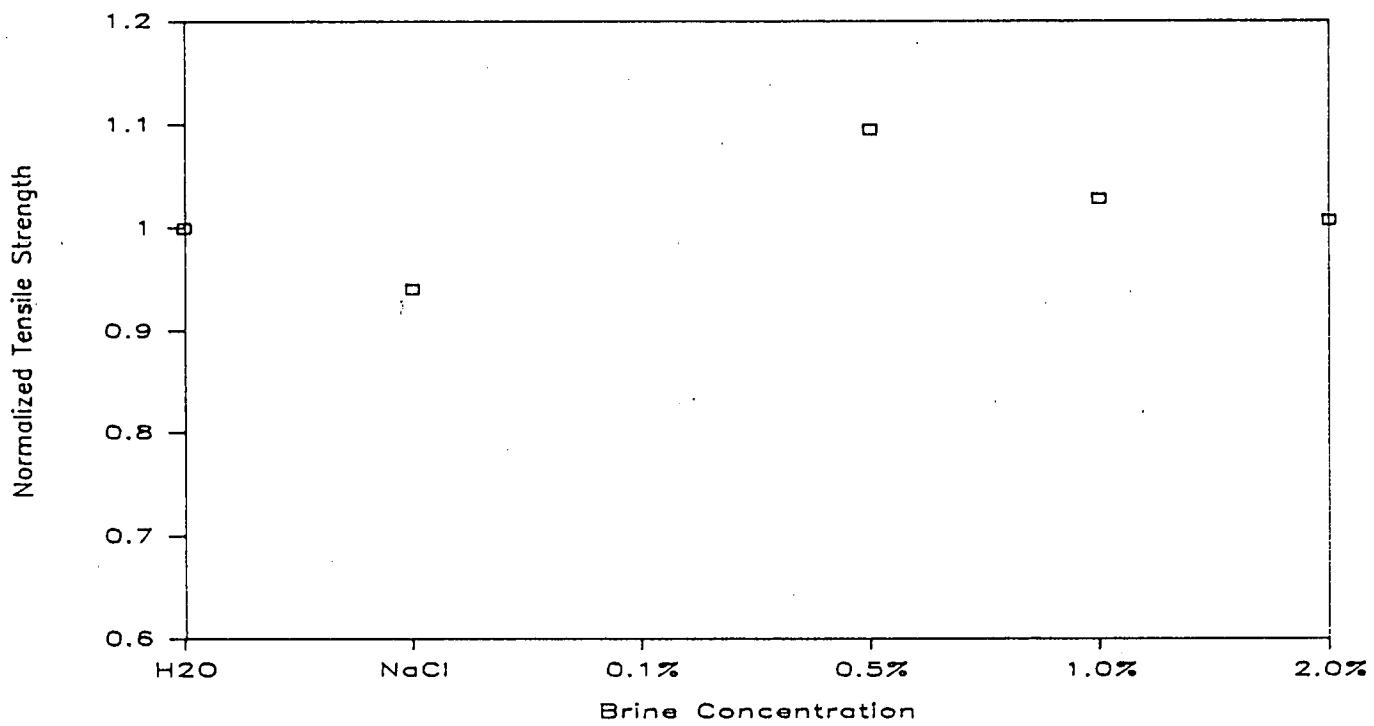


(b) Tensile strength data.

Figure 4. Resistance of a standard mortar to a MgCl<sub>2</sub> brine.

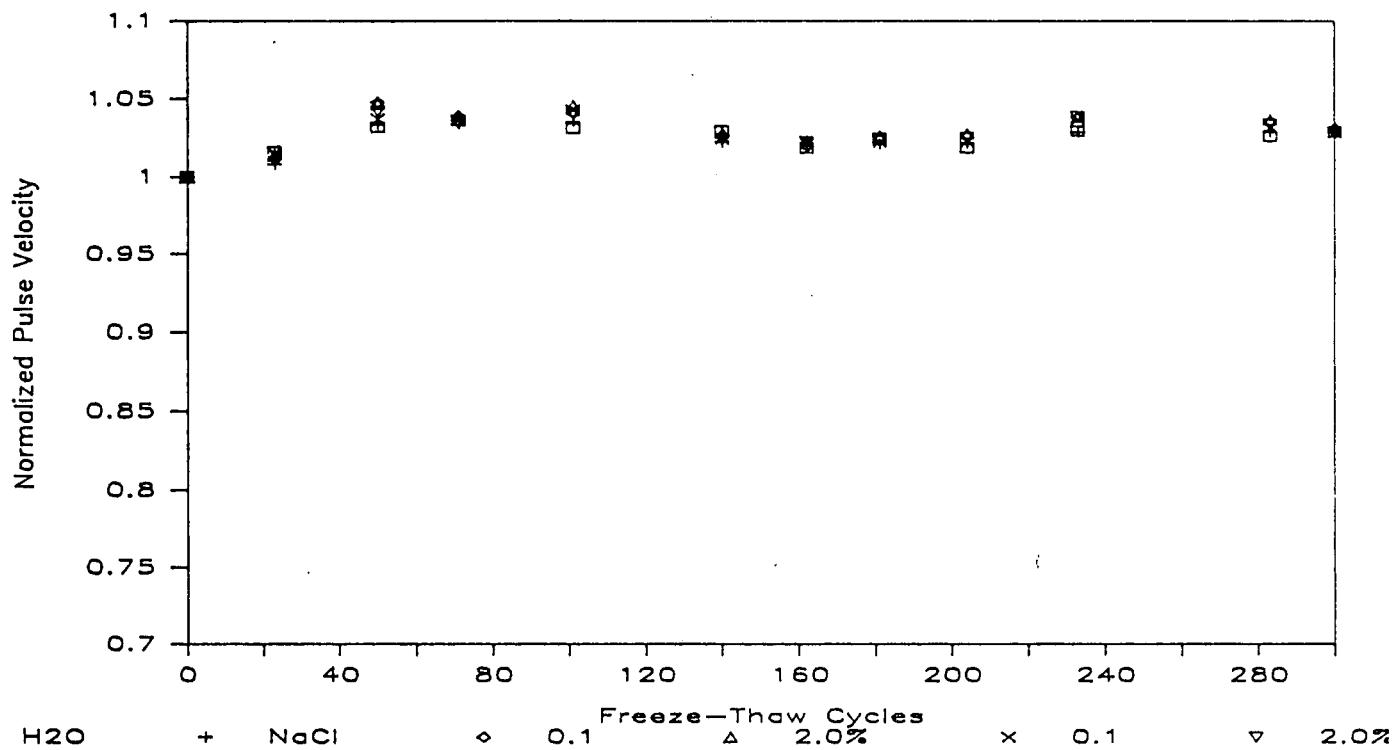


(a) Pulse velocity data.

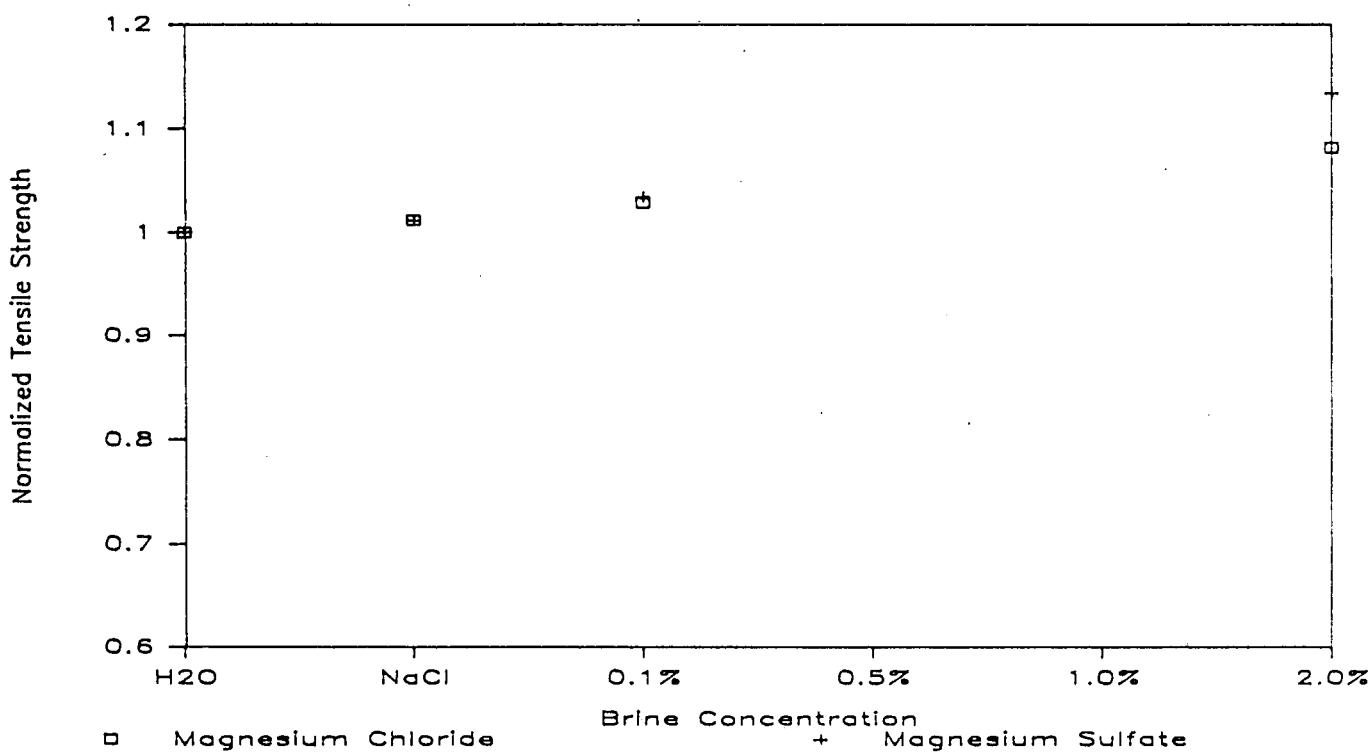


(b) Tensile strength data.

Figure 5. Repeat test on resistance of a standard mortar to a  $\text{MgCl}_2$  brine.

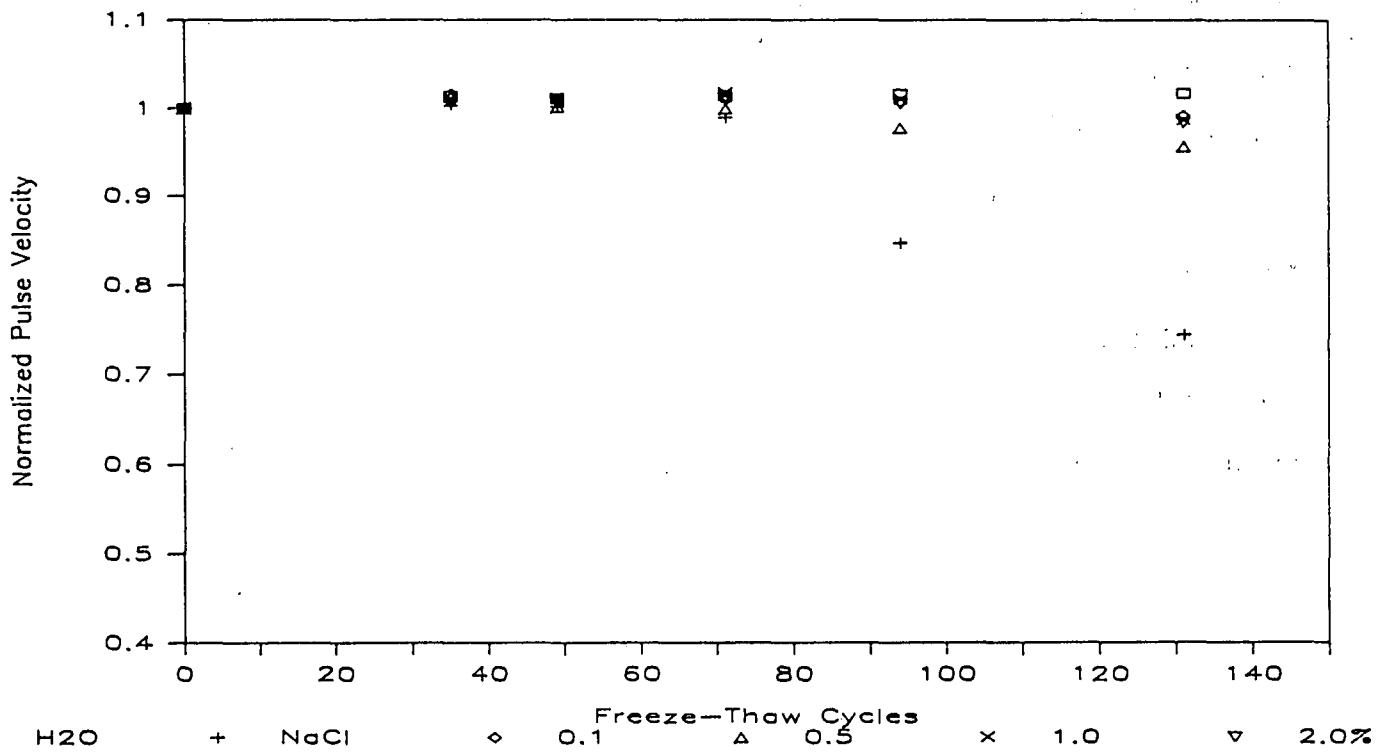


(a) Pulse velocity data.

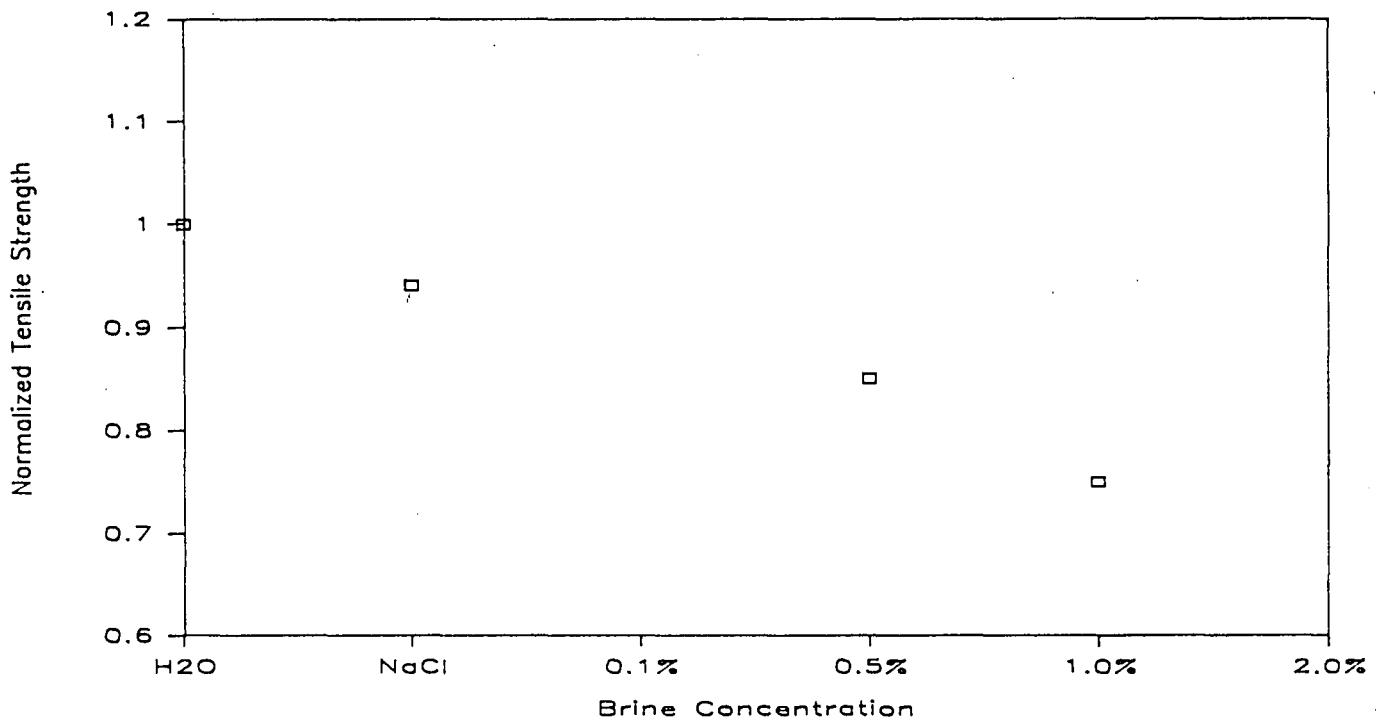


(b) Tensile strength data.

Figure 6. Resistance of a fly ash mortar, 15% Ames fly ash, to both  $MgCl_2$  and  $MgSO_4$  brines.



(a) Pulse velocity data.



(b) Tensile strength data.

Figure 7. Resistance of a standard mortar to a  $\text{MgCl}_2$  brine which included a constant 1.6%  $\text{CaCl}_2$ .

suggest that there may be an undesirable interaction resulting from the combination of calcium chloride and magnesium chloride. Although not severe, strength is reduced to about 75 percent of the control value with 1.0 percent magnesium chloride and the 1.6 percent calcium chloride. This work is being repeated to substantiate its validity.

Tests in Progress. Evaluation of sodium sulfate and realistic combinations of all deicer constituents either are scheduled or are in progress, in addition to those tests previously mentioned.

## DEICERS AND CONCRETE

A presumption of this and previous research on rock salt impurities and their action on mortar is that there exists no interaction between the deicer and the aggregate fraction of concrete. If it can be demonstrated that a mortar similar to that of concrete can be attacked by a deicer, a reasonable extension of this knowledge is that a concrete (regardless of how good its aggregate may be) also will be attacked and the concrete destroyed. Conversely if the mortar can be protected, so can the concrete. One intention of this work is to substantiate this concept.

Further consideration leads to another possibility, namely that the aggregate itself reacts with compounds from a deicer to produce an undesirable result. There is some evidence that some aggregates can themselves be sources of sulfate, which becomes more readily available because of the increased solubility of sodium chloride brines. To evaluate the potential for interaction among aggregate types and deicer compounds, an experimental test was designed in which variations in deicer impurities were tested with three categories of coarse aggregate. The aggregates and their anticipated roles in the experiment are as follows:

1. **Alden:** An aggregate with an excellent service record and good response to laboratory freeze-thaw testing. It is chemically pure calcium carbonate and has a nonporous structure. Sulfate from deicers should cause concrete deterioration because of reactions in the mortar and not in the aggregate.

2. **Garrison:** An aggregate with a poor service record and poor response to laboratory freeze-thaw testing because of an inappropriate pore structure. Both its mineralogical composition, a pyritic dolomite, and its open pore structure make this aggregate suspect for chemical interaction with deicers.

3. **Waucoma:** A chemically inert limestone with an open pore structure and a good service record. Deicer impurities should have the same impact as with the Alden

Table 2. Brine compositions used in concrete freeze-thaw testing.

Solution	NaCl	MgCl <sub>2</sub>	CaCl <sub>2</sub>	CaSO <sub>4</sub>	MgSO <sub>4</sub>
1	100.0 <sup>a</sup>	0	0	0	0
2	98.0	2.00	0	0	0
3	98.0	0	0	2.00	0
4	96.1	0.20	0	3.61	0.09
5	94.6	0.20	1.57	3.55	0.09
6	0	0	0	0	0

<sup>a</sup>weight percent by solute

aggregate unless relative size of aggregate and mortar pore structure plays a role.

ASTM C-666 freeze-thaw specimens were cast from an Iowa DOT C-3 concrete mix, with Ames fly ash replacing 15 percent of the portland cement. The concrete had a water cement ratio of 0.43, a 1.5 inch slump, and 7% air content. Curing was for 28 days, in accordance with ASTM C-192.

Freeze-thaw testing was done in the same manner as was the mortar specimens, in that brines were introduced in the freeze-thaw pans by maintaining the brine level at the beam's mid-height. A measure of durability was made with dynamic modulus of elasticity, per ASTM C215. Six brine compositions were selected to represent a range of natural deicers; these are listed in Table 2.

Results available thus far are for fly ash concrete with Alden and Garrison aggregates. Figure 8, for averages of triplicate specimens, demonstrates that deicing brines have little effect on a fly ash-protected, Alden-aggregate concrete. Tests with the same concrete without fly ash are in progress; it is speculated that different brines will influence the results.

Similar results for the Garrison aggregate, Figure 9, suggest that with exception of solution 5, the effect of brine composition is insignificant. Since fly ash-treated specimens protect the mortar, deleterious action should center on aggregate performance although, obviously, fly ash does not make up for a poor aggregate. However, solution 5 results, which have high calcium concentrations due to the presence of both calcium sulfate and calcium chloride, may indicate the potential for an aggregate-brine interaction. This warrants further investigation.

Concretes without fly ash and concretes with Waucoma aggregate are now being tested.

## ALDEN AGGREGATE

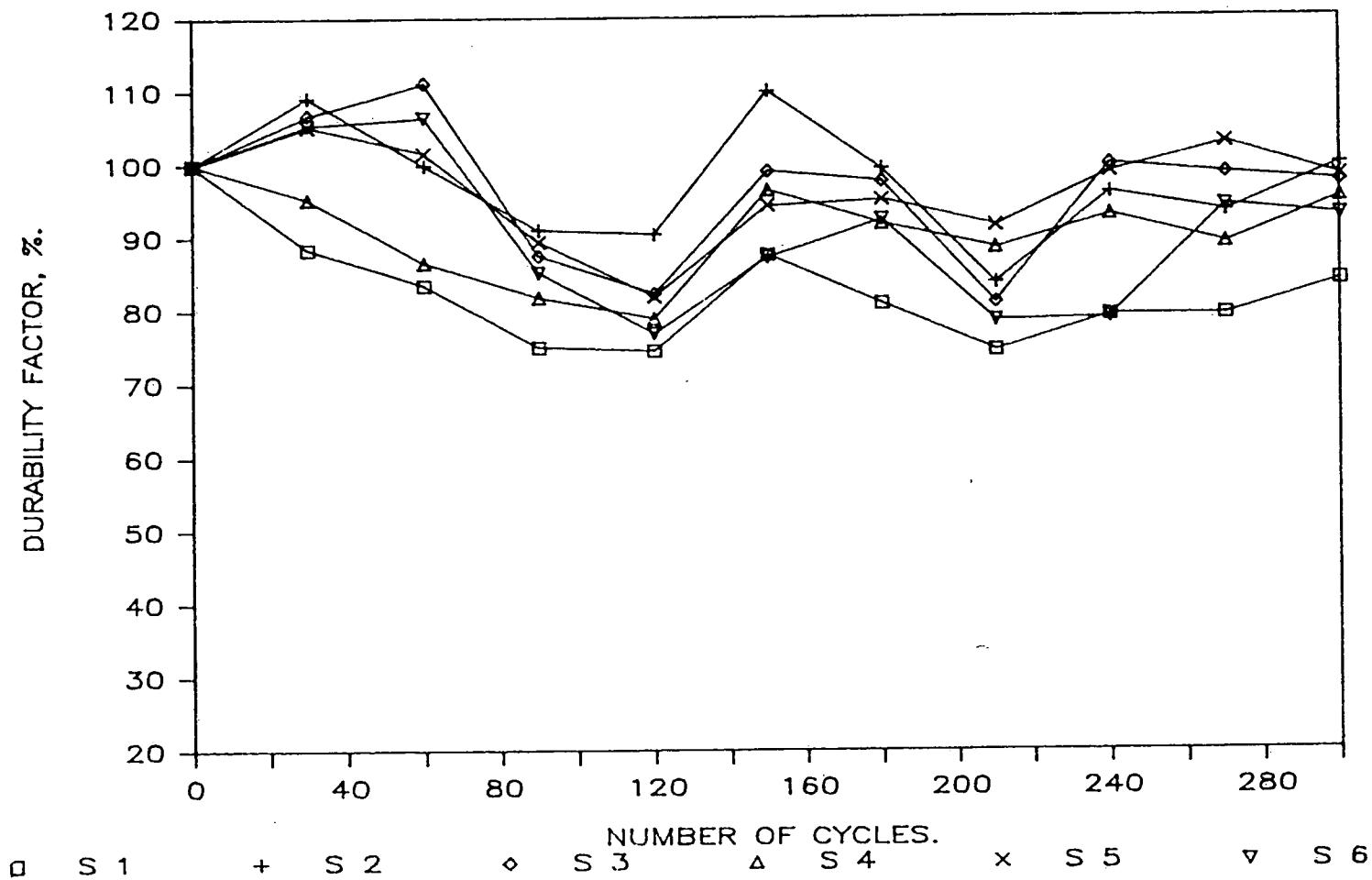


Figure 8. Durability factors of fly ash-protected Alden-aggregate concrete.  
Concrete subjected to six different deicing brines.

## GARRISON AGGREGATE

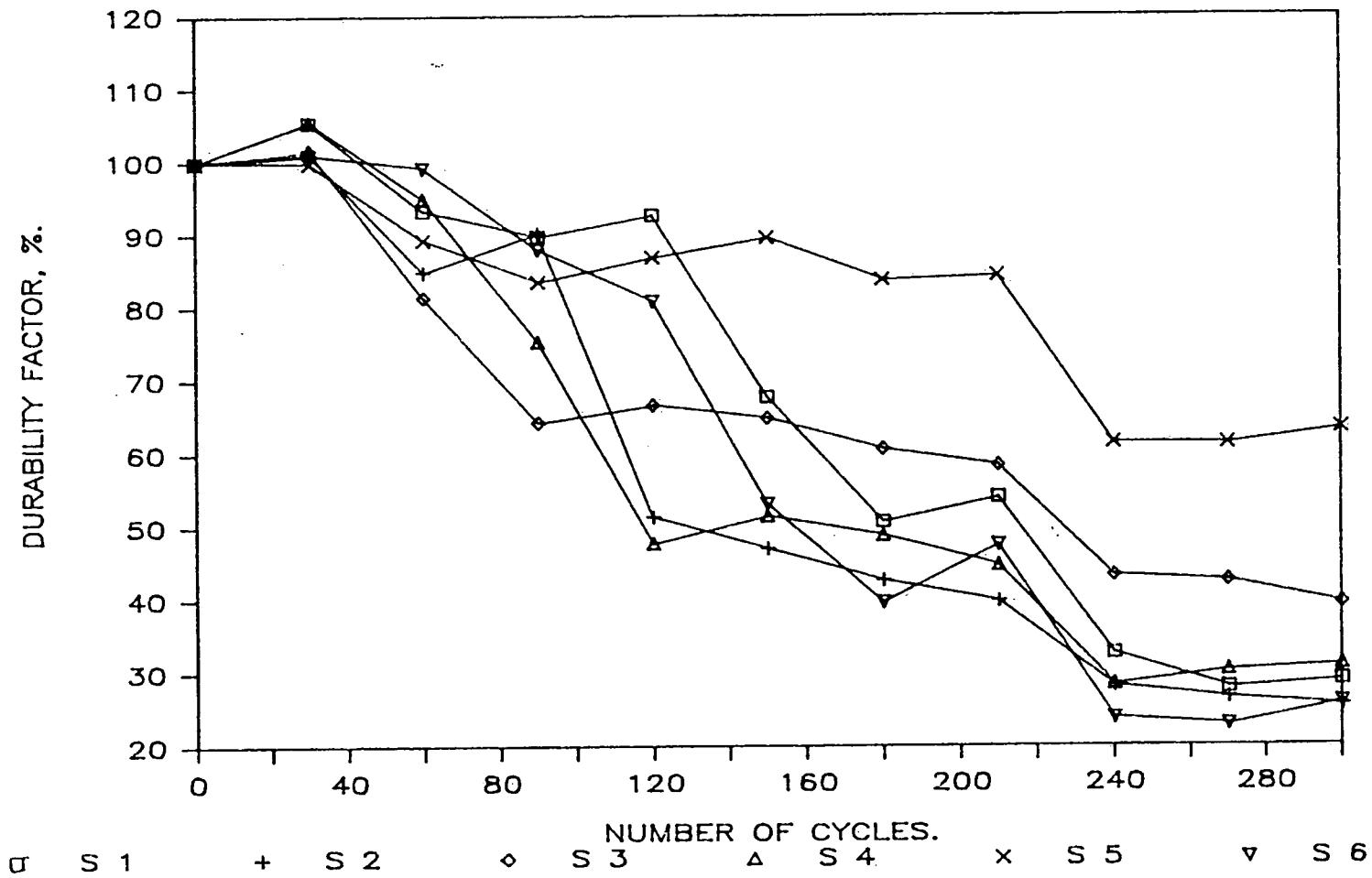


Figure 9. Durability factors of fly ash-treated Garrison-aggregate concrete.  
Concrete subjected to six different deicing brines.

### SUMMARY OF FINDINGS

Based on the research completed thus far, the following conclusions are presented:

1. All but one of the deicers sampled from stockpiles in the state contain enough sulfate to significantly accelerate deterioration of concrete mortar. A deicer sample from Mexico shows promise because of low sulfate content.
2. It appears the compound from which the sulfate radical is derived is not a factor in the deleterious mechanism. This has been demonstrated for calcium and magnesium sulfate. Verification for sodium sulfate is needed. Also, this presumes the sulfate compound is soluble in a sodium chloride brine.
3. Magnesium chloride in concentrations found in natural rock salt does not appear to be deleterious. The destructive action is associated with sulfate alone.
4. Ames fly ash is capable of reducing and possibly arresting the deleterious action of sulfate on portland cement mortar. Reasons for this observation have not been established but a hypothesis is that non-expansive pozzolanic reaction products from fly ash can assimilate sulfate induced reaction products.
5. Action of deicing brine impurities on fly ash concrete with a highly durable aggregate parallels the behavior of mortar. With a poor aggregate thought to be chemically reactive, most combinations of deicing brines produced the same results as freeze-thaw in water. This suggests deterioration of concrete with frost prone aggregate and fly ash protection in the mortar is not influenced by deicer impurities. An exception is for a deicer having a high calcium content.

## CONCLUSIONS AND RECOMMENDATIONS

This research reinforces past work demonstrating sulfate from rock salt is deleterious to the mortar phase of concrete. It also shows that many of the deicers now being used carry more than enough sulfate to cause damage.

There are at least two approaches to solving the problem of sulfate in deicer. The first presumes a continued use of rock salt and leads to a limitation on the amount of sulfate allowed. To this end a decision must be made as to how much sulfate-induced damage is acceptable, because it is unlikely that adequate supplies of rock salt without any sulfate is possible. A requirement based on what is known so far might be to impose a sulfate limitation of 0.5 percent expressed as gypsum. This relates to strength after freeze-thaw of about 70 percent of that for mortar in pure water. One-half percent sulfate as gypsum is the same as 0.28 percent sulfate as the radical.

Caution must be taken when considering sulfate limits in deicers because the research supporting such a decision does not take into account the possibility of accumulating sulfate through numerous applications of low sulfate deicers. Conversely, this work models a continual saturated brine application during the freeze-thaw process. Refinement of salt specifications can be derived from knowledge about chemical dynamics of deicer application and entry in concrete.

A second approach is to make concrete resistant to sulfates. A promising aspect of this work is the improved resistance apparently imparted by fly ash. It is unknown how much it takes or whether all fly ashes work; the two tests using fly ash as a partial (15 percent) replacement for portland cement in concrete mortars show a marked

improvement. While consideration should be given to requiring fly ash for patching concrete and for new paving, this requirement does not protect the good pavement already in place. A treatment for existing concrete, applied at patching joints and possibly structural cracks, would be useful.

In addition to the objectives stated in the original proposal, subsequent phases of this project should also include refining deicer specifications based on the potential for sulfate accumulation, evaluation of significant fly ash sources, and development of concrete treatments.

## ACKNOWLEDGEMENTS

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## APPENDIX A

GRAVIMETRIC DETERMINATION OF SULFATE IN ROCK SALT  
BY  
REVERSE ORDER PRECIPITATION WITH BARIUM

1. Crush or grind rock salt to pass a 30 mesh sieve.
2. Accurately weigh approximately 5g of sample into a 400 ml Griffin beaker.
3. Add 50 ml of 1:5 HCl, cover with a watch glass, and bring to a boil. Immediately add 100 ml of boiling water (ASTM Type II) and boil for about 3 minutes.
4. Filter quantitatively through Whatman #4 filter paper into a 600 ml beaker. Rinse the insoluble residue with portions of hot water. Restrict the volume of filtrate to less than 300 ml.
5. Add 20 ml of 10% BaCl<sub>2</sub> to a 400 ml beaker; bring to a boil along with the filtrate from 4 (above).
6. Using a stirring rod as a guide, slowly add the filtrate to the BaCl<sub>2</sub> solution (this is the reverse-order precipitation). Stir frequently during the addition. Addition should take about 3 minutes.
7. Cover with a watchglass and keep hot (but not boiling) for at least 2 hrs (preferably overnight).
8. Filter quantitatively through Whatman #42 ashless filter paper.
9. Place filter paper into a previously fired and weighed porcelain crucible. Allow to dry at 103°C for about 1 hr.
10. Ash filter paper taking care to avoid high-temperature reducing conditions that may reduce BaSO<sub>4</sub> to BaS. Cool and weigh.
11. % SO<sub>4</sub> = (g BaSO<sub>4</sub>)(41.16)/(g sample)