

interference with normal snowplow operations. Specifications for an installation contract of snowplowable markers could allow for use of any of these three markers (Stimsonite 96, Dura-Brite, and recessed), but considering available cost data, the recessed marker should provide the lowest cost.

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## Evaluation of the Effect of Natural Brine Deicing Agents on Pavement Materials

RONALD W. ECK, MUMTAZ A. USMEN, WILLIAM A. SACK, IRFAN ARAR, AND ALI ATEFI

Laboratory tests were conducted to analyze and compare the effects of natural brines and traditional deicing chemicals on bituminous concrete, portland cement concrete, and two types of steel. The effects of 100 freeze-thaw cycles on bituminous concrete immersed in distilled water, a sodium and calcium chloride solution, and a natural brine solution were evaluated by testing specimens for Marshall stability, flow, and weight changes. Two separate 100-cycle freeze-thaw experiments—a surface degradation test, and compressive strength and pulse velocity tests—were conducted to evaluate the effects of distilled water, a sodium and calcium chloride solution, and a natural brine solution on concrete performance. A 100-cycle wet-dry immersion test, where specimens of A-36 and SAE-1010 steel were subjected to a sodium and calcium chloride solution and a natural brine solution, was used as an accelerated corrosion test. Corrosion was measured by weight loss. In general, the effects of natural brines on bituminous concrete were no different than the effects of traditional deicing agents. In terms of the surface deterioration of portland cement concrete, natural brine performed slightly better than traditional deicing agents. Potential discoloration of concrete from brines with high iron content was indicated. The effect of natural brine on concrete compressive strength was no different from that of water or sodium and calcium chloride deicing agents. Specimens of automobile-body steel demonstrated less corrosion in natural brine than in a sodium and calcium chloride solution; however, specimens of structural steel demonstrated opposite results.

As expenditures for snow- and ice-control materials continue to increase, highway agencies are seeking ways to minimize the use of traditional deicing materials and, where possible, are substituting less-costly deicing agents for sodium and calcium chloride. The use of naturally occurring salt brines, which are by-products of oil and gas production, as deicing agents is either a reality in some locations or is being studied in a number of locations. Natural brines are widespread geographically; their existence is not limited to oil and gas fields. The oil and gas industry considers brine as a waste product because there is no apparent use for the liquid, which may be several times stronger than sea water.

The major ions found in most brines are sodium, calcium, magnesium, and chloride. Lower levels of constituents such as potassium, iron, sulfate, and bicarbonate are also usually present. In addition, brines may contain a number of minor or trace ionic

species, including bromide, iodide, barium, lead, arsenic, zinc, cadmium, and chromium.

Brines are difficult to dispose of in an environmentally acceptable manner; thus they represent a major problem for the oil and gas industry. For example, more than 100 million gallons of brine are produced annually in West Virginia. Several large brine producers make use of injection wells for brine disposal. In addition to being an expensive disposal method, there is the possibility that increased concern about groundwater contamination may result in legislation that will limit deep well injection. An unknown but significant quantity of waste brine is discharged directly onto the ground or into surface waters, which results in contamination. Eck and Sack (1) have presented a more detailed discussion of brine characteristics and current disposal practices.

The use of natural brines for deicing purposes would appear to solve several problems simultaneously. The oil and gas industry could dispose of an unwanted by-product, and highway agencies could acquire a deicing material at minimal cost. However, before advocating a major deicing program that uses natural brines, a number of issues need to be evaluated. For example, the quantity of brine available for highway deicing in a given geographical area must be assessed. Brine quality from the major producing formations must be determined, including both the major salts and the minor trace elements, in order to assess potential water pollution problems. It would be desirable to compare various brines with commercial deicing agents relative to melting, skid resistance, and refreezing of roadway surfaces. Also, the transportation and storage costs of brine must be estimated. Similarly, comparisons are needed as to the relative effect of brines and commercial deicing agents with respect to corrosion of steels as well as the deterioration characteristics of portland cement concrete (PCC) and bituminous pavement.

A comprehensive research project is in progress at West Virginia University (WVU) to address these

Table 1. Chemical analysis of brine from Chemung Formation, Lewis County, West Virginia.

Item	Value
Ions (mg/L)	
Total dissolved solids (TDS)	215 240
Sodium	57 780
Calcium	23 010
Magnesium	3 116
Potassium	450
Chloride	136 143
Sulfate	198
Iron	210
Barium	4.85
Lead	3.86
Cadmium	0.869
Zinc	0.680
Arsenic	0.231
Chromium	<0.050
pH	4.00

questions. The study includes both laboratory and field testing programs. The procedures used and the results obtained in a laboratory evaluation of the effects of natural brines on three common transportation materials--bituminous concrete, PCC, and steel--are presented in this paper. Other aspects of the project, although important in assessing the overall feasibility of natural brines as deicing agents, are beyond the scope of this paper. Results of a field testing program, where brine was applied to actual roadways, are described elsewhere (1).

#### BACKGROUND AND OBJECTIVES

There is a wealth of information in the literature describing the effects of sodium and calcium chlorides on transportation materials. The detrimental effects of commercial sodium and calcium chloride deicing agents on PCC and steel have been well documented in many studies. Several recent surveys of these efforts are available in the literature (2-4). The effect of these agents on bituminous concrete has received less study. This is probably because the few studies that have been performed (5,6) indicated that deicing salts had no significant effect on bituminous concrete mixes. Because the large number of constituents in natural brines makes them different from commercial deicing agents, previous research findings about the effects of commercial agents on transportation materials are not necessarily transferable to natural brines.

The effects of deicing agents on the corrosion of metals have received much attention. Two recent reviews (2,3) have assessed the effects of deicing chemicals on metals. It is concluded that chloride deicers accelerate the corrosion of motor vehicles and metal highway structures.

The literature dealing with natural brine as a deicing agent is limited. Although a number of state, county, and local highway agencies have used or are using natural brines (7-9) as deicing agents, they have not, in general, evaluated or monitored the impacts associated with brine use. The environmental aspects of using Arkansas brine for highway purposes have been examined (10), although the study did not include a field evaluation. Laboratory studies were used to determine the effect of brine on concrete, metal corrosion, soil properties, and runoff water quality. The study concluded that the effects of Arkansas brine on metal corrosion rates and concrete strength were not significantly different from those of an equivalent sodium chloride solution.

No published literature could be located relative

to the effects of brines from Appalachian oil and gas fields on transportation materials. Because brine composition varies from one location to another, research with different brines appeared warranted. Thus the overall goal of the research described herein was to analyze and compare the effects of West Virginia brines and traditional deicing chemicals on bituminous concrete, PCC, and two types of steel.

#### EXPERIMENTAL PROCEDURES

##### Brine Characteristics

The brine used was taken from the Chemung Formation in Lewis County, West Virginia. A chemical analysis of the brine is given in Table 1; the analysis reveals that the major constituent ions are sodium, calcium, magnesium, and chloride. Lower levels of ions such as sulfate, potassium, and iron are also present, along with trace-level concentrations of heavy metals such as barium, lead, and zinc. Sulfate levels are of particular interest with respect to the attack of concrete. Sulfate levels in brine vary widely but are usually less than 700 mg/L. For example, an analysis of nine West Virginia brines revealed an average sulfate concentration of 126 mg/L, with a range of 3 to 547 mg/L. In a recent study Pierce (11) concluded that sulfate levels of 150 mg/L or less would result in a negligible attack on concrete, whereas levels of 150 to 1500 mg/L would cause a positive degree of attack, and above 1500 mg/L the degree of attack would be severe. Based on these considerations, the sulfate level in most brines would not be expected to contribute significantly to concrete deterioration.

Trace metal levels in certain brines may be of environmental concern. In the brine used in this study, lead and barium were present at concentrations of 4 to 5 mg/L, whereas other trace elements were measured at less than 1 mg/L. Although a complete discussion of this issue is beyond the scope of this paper, it should be noted that conventional dry deicing agents analyzed as part of the overall project at WVU were also found to contain trace metals at levels comparable to those found in brine. It should also be noted that, when considering the potential impacts of constituents such as trace metals or sulfate, considerable dilution of the brines will occur during melting and runoff after application.

##### Bituminous Concrete

In designing the bituminous concrete mixture, an aggregate gradation and an asphalt cement representative of those used in wearing courses in West Virginia were used. Asphalt Institute Mix Type IVb, which is dense graded and has a maximum nominal size of 0.5 in., was chosen. Materials were acquired from local sources that furnish asphalt mixes for West Virginia Department of Highways (WVDOT) projects. An AC-20 viscosity graded asphalt cement, which had a specific gravity of 1.03 and conformed to the requirements of AASHTO M-226, was used. The aggregates--limestone sand and No. 67 coarse limestone aggregate--were obtained from the same supplier.

The Marshall method (12) of mix-design performed in the study encompassed the fabrication of replicate specimens at varying asphalt contents by using 50 blows of drop hammer compaction and subjecting these specimens to bulk specific gravity, Marshall stability, and flow tests as well as a density-voids analysis. An optimum asphalt content of 6.2 percent was established by using the Marshall mix-design

criteria. The mix, as designed, had an average Marshall stability of 2,500 lb, a flow value of 0.18 in., a unit weight of 147.5 lb/ft<sup>3</sup>, 3 percent air voids, and 15 percent voids in mineral aggregate (VMA). Note that the flow value, although somewhat high, was still in the acceptable range.

The bituminous mixture just described was used in the preparation of 50 standard Marshall specimens. These specimens were divided into a control group and three treatment groups (immersion in distilled water, a sodium and calcium chloride solution, and a natural brine solution), and each was divided into three subgroups (exposure to 10, 50, and 100 freeze-thaw cycles), such that a total of 10 groupings of 5 replicate specimens each were generated (50 specimens overall). Groupings were established such that the difference between the mean bulk specific gravity of each group was less than 0.010.

Group 1 specimens were for control purposes and received no treatment in the form of immersion or exposure to freezing and thawing. Specimens in group 2 were immersed in distilled water and were subjected to the specified number of freeze-thaw cycles. Group 3 specimens were immersed in a 100 000 mg/L total dissolved solids (TDS) solution of sodium and calcium chloride, which had a 50:1 ratio of sodium to calcium. This solution was prepared by dissolving in distilled water carefully weighed quantities of dry sodium chloride and calcium chloride that were obtained from WVDOH stockpiles. Although the two salts are no longer normally used in combination in West Virginia, the rationale behind choosing this solution was to devise a possible worst case that could occur on a roadway or bridge treated with both salts at different times.

Specimens in group 4 were immersed in a 100 000 mg/L TDS solution of natural brine that had been diluted with distilled water. The original concentration (TDS) of this brine was 215 240 mg/L, as noted in Table 1. It was diluted to achieve a concentration equivalent to that of the sodium and calcium chloride solution used in the treatment of the group 3 specimens. This was necessary for drawing meaningful comparisons between results obtained from the two groups. The TDS of 100 000 mg/L was selected for use in the study because it appeared to be a convenient midrange of deicing-agent concentrations found in a comprehensive review of previous research and practice. However, it should be noted that the brine applied to roadways would be used straight and not prediluted. Diluted brine was applied to bare concrete to account for the fact that, in practice, deicing agents are diluted by the accumulation of snow and ice on the pavement.

The specimens were placed in cylindrical 5-in.-diameter and 6-in.-high containers that were fabricated by wrapping several layers of heavy-duty aluminum foil around a hardware cloth (0.25-in. mesh) frame and sealing the base with paraffin. These containers had been previously used in related research at WVU and provided a flexible, yet watertight container capable of holding sufficient quantities of solutions to cover the specimens. The containers with the specimens were then placed in a programmable environmental chamber.

Temperature limits for the freeze-thaw tests were 0° and 40°F. Each cycle consisted of 2 hr of exposure at 40°F, followed by a gradual decrease in temperature to 0°F during a 2-hr period; exposure at this temperature for another 2 hr; and finally a gradual increase in temperature to 40°F during a 2-hr period, for a total of 8 hr. With the aid of the automated chamber, three such cycles could be accommodated per calendar day. The specimens remained in the chamber during the entire investiga-

tion; daily observations were made during this period.

The effect of different treatments on the performance characteristics of bituminous concrete was evaluated by testing the grouped specimens for Marshall stability, flow, and weight changes. The specimens in group 1 were weighed and subjected to Marshall stability and flow tests (ASTM D-1559) immediately after fabrication. The initial weights of all other specimens were also recorded before treatments. When the appropriate number of cycles in each treatment (10, 50, or 100 cycles) were reached, specimens were removed from the environmental chamber and allowed to warm to room temperature. Critical visual observations were then performed on the specimens. Finally, the specimens were photographed, weighed, and tested for Marshall stability and flow.

#### Portland Cement Concrete

Two separate tests were conducted to evaluate the performance of concrete: (a) a surface degradation test and (b) compressive strength and pulse velocity tests. Both tests were conducted on specimens prepared from a PCC mix typical of that used for highway pavements in West Virginia. The concrete mix data indicated a water-cement ratio of 0.41; fine aggregate made up 41 percent of total aggregates. Enough Daravair air-entraining agent was added to give average strength. The mix yielded a slump of 1.75 in., and the air content was 8.75 percent.

Specimens for each test were allowed to cure at room temperature for 24 hr under a plastic cover. The molds were then removed and specimens were moist-cured (100 percent relative humidity) for 14 days at an average temperature of 70°F. They were then air-cured at 73°F for another 14 days.

The solutions of natural brine and traditional deicing agents used in the test were identical to those used in the bituminous concrete experiment. Characteristics of the solutions were presented in the preceding section.

#### Surface Degradation Tests

Test specimens were divided into five groups. Specimens in group 1 were subjected to freezing and thawing in distilled water. Those in group 2 underwent freezing and thawing with a sodium and calcium chloride solution. Group 3 specimens were subjected to freezing and thawing with natural brine. Groups 4 and 5 underwent wet-dry cycles while exposed to sodium and calcium chloride and natural brine solutions, respectively.

Two different procedures, freeze-thaw and wet-dry, were selected to simulate field conditions existing when deicing chemicals are applied. Five specimens were fabricated for each group. ASTM C-672 (Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Salts) was followed.

A 10-in.-diameter polyvinyl chloride (PVC) plastic sewer pipe was cut into 3.15-in. sections to serve as molds for the concrete. Each section was then slit to ensure ease of removal of the cured specimen. Wire was wrapped around the perimeters of the pipe sections to keep them from opening during placement of the concrete. These pipe sections were then clamped to sheets of plywood. Concrete was placed and finished in accordance with ASTM C-672. As specified, specimens were surface-roughened by brushing them with a medium stiff brush to simulate the finish on a highway pavement.

The pipe sections, used previously as molds, were retained for use as dikes. This was accomplished by

slipping the pipe sections over the cured specimens with about 1 in. protruding above the concrete surface as a dike. Wire was wrapped around the pipe section to hold it secure during the test. Caulk was applied to the crack formed by the pipe around the perimeter of the specimen to prevent leakage of the solution.

Freeze-thaw concrete specimens were alternately stored in two small temperature-controlled rooms. One room had a nominal temperature of 0°F, and the other was at 50°F. Because the rooms were at constant temperature, it was necessary to move the specimens twice daily (by using a cart) between the rooms to produce the freeze-thaw cycles.

Specimen groups 1, 2, and 3 were subjected to daily cycles of freezing at 0°F for 16 hr and thawing at 50°F for 8 hr, with 0.25 in. of the appropriate solution covering the surface of each specimen. All specimens were kept in the freezer during weekends. As evaporation occurred, distilled water was added to maintain a 0.25-in. depth of the solution. The testing period for these groups was 100 cycles.

Specimen groups 4 and 5 were subjected to wet-dry cycles. In the wet portion of the cycles each specimen was covered with 0.25 in. of the appropriate deicing solution for 24 hr. The dry phase of the cycle started after the salt solution was washed from the specimens with distilled water; specimens were then allowed to dry for 24 hr. Therefore, for groups 4 and 5, one complete cycle required 48 hr. The entire cycle was performed in the laboratory at essentially constant room temperature (about 72°F). The test continued for 100 cycles.

At the end of every five cycles the surfaces of all specimens were rinsed with distilled water, visually inspected, and rated for scaling by using the 0 to 5 subjective rating scale specified in ASTM C-672. Photographs were taken of specimen surfaces after every five cycles.

#### Compressive Strength and Pulse Velocity Tests

Specimens were divided into four groups, with each group consisting of four cylindrical (4 x 8 in.) specimens. After curing the cylinders were placed in plastic containers with sufficient solution to cover them completely. Specimens in group 1 were tested for pulse velocity and compressive strength immediately after curing. Group 2 specimens underwent freezing and thawing while completely submerged in distilled water, whereas specimens in group 3 were exposed to freezing and thawing while completely submerged in a sodium and calcium chloride solution. Specimens in group 4 were subjected to freezing and thawing while completely submerged in natural brine. The pulse velocity test was used in this study to obtain periodic evaluations of concrete quality.

Cylinders in groups 2, 3, and 4 were tested for pulse velocity while completely submerged in appropriate solutions, and then were subjected to daily cycles of freezing at 0°F for 16 hr and thawing at 50°F for 8 hr. Tests were conducted in the same chambers described previously for the surface degradation tests. At the end of every five cycles the cylinders were wiped dry with a towel and the pulse velocity was measured and recorded for each specimen by using procedures outlined in ASTM C-597. Specimens were then resubmerged in the appropriate solution and subjected to additional freeze-thaw cycles. Both pulse velocity and compressive strength were measured at the end of 100 cycles.

#### Steel Corrosion

A wet-dry immersion test, where metal specimens were

alternately immersed and removed from salt solutions, was used in this study as an accelerated corrosion test. Corrosion was measured by weight loss. The corrosion test essentially followed ASTM G-31 (Laboratory Immersion Corrosion Testing of Metals) and G-1 (Preparing, Cleaning, and Evaluating Corrosion Test Specimens).

Two types of steel were tested: A-36 steel was chosen to represent the steel used in highway construction and SAE-1010 steel was selected as being representative of that used in automobile bodies. Coupon specimens 2 in. wide by 4 in. long were used. A-36 steel specimens of these dimensions had been cut from 2-in.-wide by 0.25-in.-thick hot-rolled bar stock by a shear blade at the factory. Although it would have been desirable to use a thinner gauge for testing purposes, the 0.25-in. thickness was the minimum size available locally. The SAE steel was obtained in 4-in.-wide by 12-in.-long sheets of 24 gauge (nominal thickness 0.0239-in.) cold-rolled steel. By using a shear blade in the laboratory, the sheets were cut into 2 x 4 in. specimens. Forty-eight specimens from each of the two types of steel were used in the test. With two different solutions and six time periods, this meant there were four replications for each test condition.

Four 50-L plaster picnic coolers were used to hold the test solutions and metal coupons. In addition to having the desired capacity, the coolers had attached lids that made convenient covers to keep out dust and other contaminants. A drain in the bottom made it possible to expose the coupons to air simply by lowering the solution level rather than by lifting the specimens out of the solution and disturbing them. The solutions drained from the coolers were stored in plastic bottles. Coolers were refilled by placing the plastic bottles at a higher level than the coolers and letting the solutions flow back to the coolers. Wooden spring-loaded clothespins were placed over glass rods positioned across the top of the cooler; the metal specimens were suspended from the clothespins into the solutions. The sodium and calcium chloride solutions used in the corrosion test were identical to those used in the bituminous concrete and PCC tests described earlier.

Specimens were subjected to daily cycles of immersion for 16 hr and drying for 8 hr. Both immersion and drying took place in the laboratory at room temperature (about 73°F). During the wet phase of the cycle specimens were immersed completely in the appropriate solution. The dry phase was achieved by lowering the solution level 0.5 in. below the bottom edge of the specimens. At the end of the 8-hr dry phase the coolers were refilled with the same solutions. On weekends the specimens remained in the immersed state. Every 2 calendar weeks the solutions in the coolers were replaced with fresh solution of the same concentration as the original.

Specimens were prepared in 4 groups of 24 specimens each. The coupons were cleaned according to ASTM G-1. The A-36 steel specimens were wet sanded under running distilled water; this step was not necessary for the SAE steel coupons. All specimens were rinsed thoroughly in running distilled water and scrubbed with a stiff fiber-bristle brush using a bleach-free scouring powder. Specimens were then pickled in an acid bath, rinsed in distilled water, and placed in an acetone bath. Finally, the specimens were weighed and photographed before being placed in the appropriate cooler.

After the designated number of wet-dry cycles, the appropriate group of specimens was removed, photographed, and visually evaluated. They were then cleaned according to ASTM G-1. Loose corrosion products were removed by carefully scraping the



specimen with a razor blade. Any stubborn corrosion was removed with a fiber-bristle brush. Specimens were dipped in a pickling bath, the solution was stirred vigorously, and specimens were rubbed with a nonabrasive rubber implement. Specimens were rinsed with distilled water and bathed in acetone before being weighed and photographed.

## RESULTS

### Bituminous Concrete

Results obtained for the bituminous concrete performance characteristics studied are shown in Figures 1-3. The mean Marshall stabilities presented in Figure 1 for bituminous concrete specimens tested immediately and then after 10, 50, and 100 freeze-thaw cycles indicate that the specimens exposed to distilled water all experienced a reduction in Marshall stability, whereas all but one of the specimens exposed to salt solutions had higher stabilities than the control value. The differences between the specimens subjected to rock salt and natural brine solutions were not significant. The results obtained from Marshall stability tests after 100 freeze-thaw cycles in the laboratory do not indicate a serious degradation of specimens on exposure to any of the solutions.

The mean flow values shown in Figure 2 for specimens tested immediately after curing and then after 10, 50, and 100 cycles reveal that, with the exception of those subjected to 10 cycles of freezing and thawing in rock salt solution, all specimens pro-

Figure 2. Marshall flow test results for bituminous concrete specimens subjected to freeze-thaw cycles of water, rock salt solution, and natural brine.

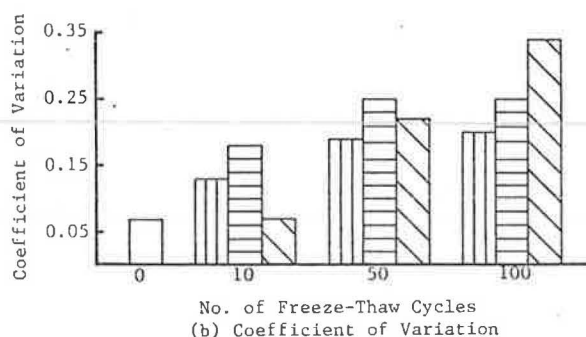
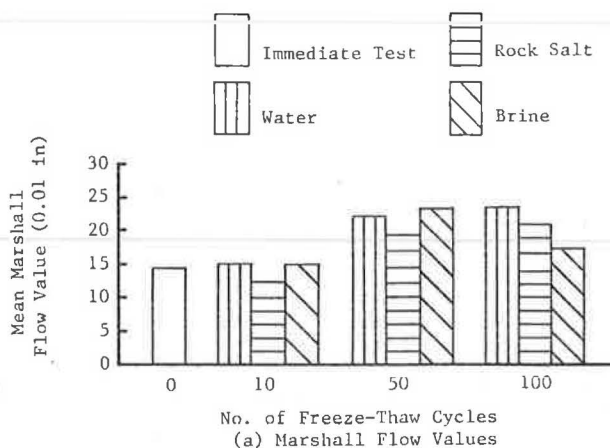


Figure 1. Marshall stability test results for bituminous concrete specimens subjected to freeze-thaw cycles of water, rock salt solution, and natural brine.

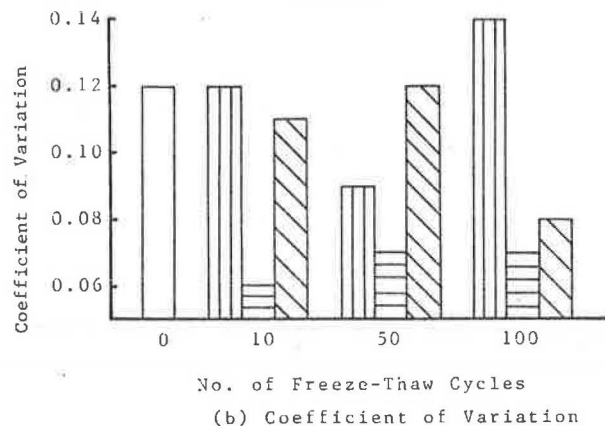
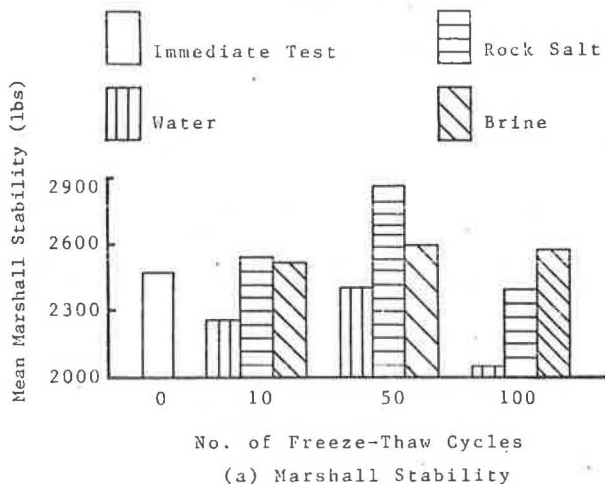


Figure 3. Water change test results for bituminous concrete specimens subjected to freeze-thaw cycles of water, rock salt solution, and natural brine.

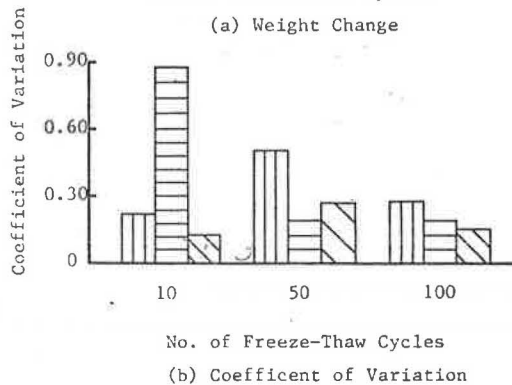
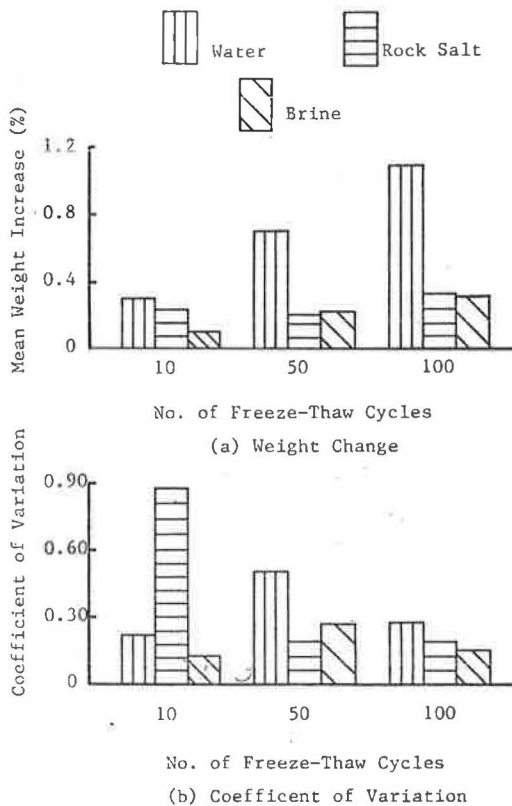
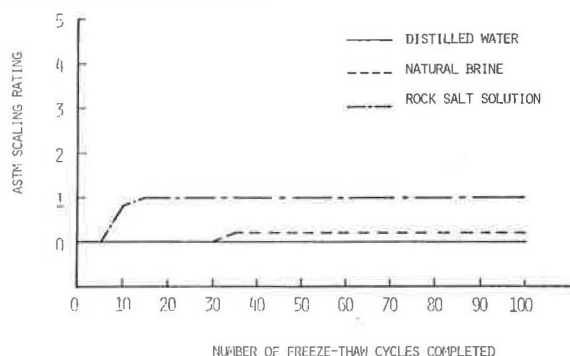


Figure 4. Effect of deicing-agent solution on surface scaling of specimens subjected to freeze-thaw cycles.



duced flows higher than the control group. Because the mixture had a high flow value as designed, this is not believed to be of great concern. It has been suggested in a previous study (5) that increases in Marshall flow values would be expected because of volume increases in specimens or because of severe deterioration. None of these causes was discernible in the specimens tested in this study. Furthermore, the ranges (difference between extreme measurements) and coefficients of variation of flow values were relatively high, which indicated possible testing variability.

Any significant loss of aggregate through scaling or raveling on exposure to any of the test solutions would be indicated by a specimen weight loss. Weight changes of surface-dry specimens, which are expressed as a percentage of original specimen weight, are shown in Figure 3. All specimens gained weight during the testing; there was no loss of aggregate because of specimen exposure to the test solutions. The small weight gains can be attributed to normal increase in moisture content of specimens exposed to the solutions and are not considered detrimental to performance.

Specimens subjected to the rock salt solution and to natural brine experienced a smaller weight increase than specimens subjected to distilled water. This is attributable to increased density and viscosity of the solutions because of the dissolved salts. There was essentially no difference in weight change between those specimens exposed to rock salt solution and those exposed to natural brine.

In addition to the quantitative tests just described, specimens were photographed and visual observations were made both before and after testing. No loose particles or losses of aggregate were noted when specimens were removed from the solutions. There was little, if any, difference in appearance between the original specimens and those subjected to 100 test cycles in the three solutions.

#### Portland Cement Concrete

##### Surface Degradation Tests

The effect of each of the three solutions on the scaling resistance of PCC subjected to freezing and thawing is shown in Figure 4. Specimens covered with distilled water showed no change in surface condition; the visual rating of the surface remained 0 (no scaling) during the entire 100-cycle study period for all five specimens.

Concrete specimens subjected to the sodium and calcium chloride solution showed the earliest scaling. After the 10th cycle, four of the five specimens were rated at a value of 1. The remaining

Table 2. Summary of results of concrete compressive strength and pulse velocity tests.

Test Condition	Mean Compressive Strength (psi)	Mean Final Pulse Velocity (ft/sec)
Control	3,902	13,962
Water	3,294	13,852
Sodium and calcium chloride	3,318	13,858
Natural brine	3,542	13,851

specimen received a rating of 1 at the 15th cycle. The visual rating remained at this value for all specimens for the duration of the test period.

Concrete specimens subjected to natural brine solution scaled later and showed less scaling than specimens subjected to the sodium and calcium chloride solution. Only one specimen was rated 1 after 35 cycles; the other four specimens did not display scaling during the 100 cycles of the test. Thus natural brine appears to be no worse than traditional deicers in terms of detrimental effects on PCC pavement surfaces.

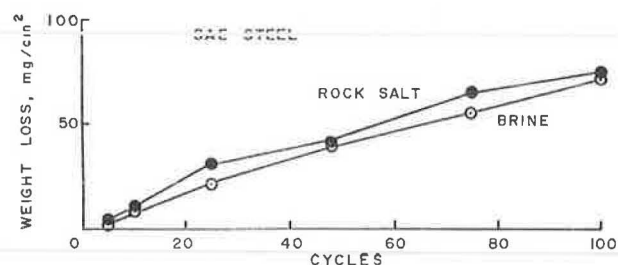
Specimen groups 4 and 5 underwent wet-dry cycles and were rated by using the same scheme as that for the freeze-thaw tests. Neither the specimens subjected to brine nor those exposed to the sodium and calcium chloride solution showed any scaling through the 100 cycles. Nevertheless, as the cycling continued the surfaces of the specimens subjected to brine took on an orange-brown rust color, apparently because of the iron in the brine. This discoloration became more conspicuous as the number of cycles increased. Scratching the surface with a metal spatula indicated that this was a surface phenomenon. Thus, although the color may be undesirable from an aesthetic standpoint, it does not appear to affect performance. It must be noted that the testing performed here was a severe test because fresh brine was applied to the concrete surface every 48 hr and allowed to stand for 24 hr. On an actual pavement brine would be removed from the surface by running water and by the sweeping action of vehicle tires; thus actual discoloration is expected to be insignificant. It is possible that the discoloration tendency of brine solutions may affect pavement markings after prolonged use. Application of brine, over a period of time, to an actual section of PCC pavement is recommended to determine whether discoloration will be a problem.

##### Compressive Strength and Pulse Velocity Tests

The mean compressive strength values for the control group and for cylinders subjected to 100 freeze-thaw cycles are given in Table 2. Based on the data in the table it appears that the effect of natural brine on concrete compressive strength is no worse than distilled water or sodium and calcium chloride solutions. Actually, the cylinders immersed in natural brine solution had the smallest reduction in compressive strength, compared with the control specimens, of any of the test solutions.

Mean final pulse velocities for the control group (tested immediately after curing) and for the cylinders subjected to distilled water, the sodium and calcium chloride solution, and natural brine are also given in Table 2. Final pulse velocity values for the three groups were nearly identical and only slightly less than those of the control group. Pulse velocity measurements for the groups did not indicate any significant difference when plotted versus time. Based on the results of the pulse

Figure 5. Relation between weight loss per surface area and number of cycles completed for SAE steel specimens.



velocity test given in Table 2, it can be concluded that, although the freeze-thaw cycles had a slightly detrimental effect on concrete performance, the natural brine solution was no more harmful than the sodium and calcium chloride solution. Furthermore, the salt solutions caused no more degradation than did the distilled water.

### Steel Corrosion

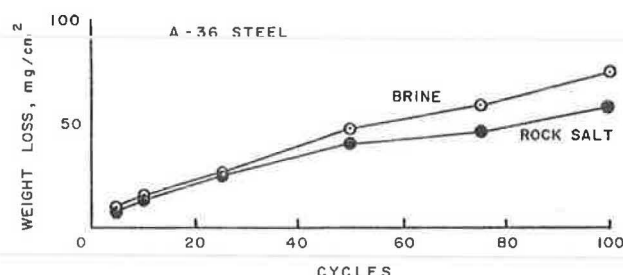
#### SAE Steel

Weight loss data for the automobile-body steel specimens are shown in Figure 5. As expected, the curves appear to be becoming asymptotic. Specimens immersed in the sodium and calcium chloride solution lost more weight than those immersed in natural brine (4 percent difference after 100 cycles).

During the cleaning process it was noted that corrosion products were easier to remove (with a razor blade) from the specimens immersed in brine than for those immersed in the sodium and calcium chloride solution. This was attributable to the smoother surface on the brine specimens. The coating of corrosion products was equally distributed over the surface of the specimens immersed in natural brine after 25 cycles. However, for the specimens immersed in the sodium and calcium chloride solution for the same period of time, the coating was thicker around the edges of the specimen than in the interior. Both of these characteristics persisted throughout the remainder of the test. Whiskers (or spikes) were noted on the surface of the specimens immersed in the sodium and calcium chloride solution after about 75 cycles. The whiskers were about 0.125 in. long and approximately 0.25 to 0.125 in. in diameter; density of the whiskers was about 0.3 whiskers per square centimeter.

As specimens were removed from the solution, a consistent pattern became apparent. Surfaces of specimens immersed in the sodium and calcium chloride solution were noticeably rougher; they had both high and low areas. After 75 and 100 cycles the bottom edges of specimens immersed in the sodium and calcium chloride solution were severely corroded and lost about 0.2 cm from their original length. Similarly, the other three edges had lost their original shape. In contrast, weight loss for specimens immersed in natural brine was uniformly distributed over the entire specimen. It is believed that one or more of the constituents of the brine inhibited corrosion and led to a more uniform weight loss. Careful examination of the specimens revealed no pitting in any of the groups, even after 100 wet-dry cycles. Because there are no large crystals to become trapped against the surface of the metal, liquid deicing agents would be expected to be less of a problem as far as pitting corrosion is concerned.

Figure 6. Relation between weight loss per surface area and number of cycles completed for A-36 steel specimens.



#### A-36 Steel

Weight loss results for the structural steel specimens are shown in Figure 6. The specimens immersed in both solutions had essentially identical weight losses through the 25th cycle. Beyond this point the specimens immersed in natural brine lost more weight than those in the sodium and calcium chloride solution, with a difference of 22 percent after 100 cycles.

The alternate immersion of the A-36 steel specimens had different results from the SAE steel. For specimens in both solutions, the coating was thicker around the edges than in the interior. However, the coating on the surface of the specimens immersed in the sodium and calcium chloride solution had high and low areas as opposed to the smoother surface of the specimens immersed in brine. As with the automobile-body steel, it was easier to remove the corrosion products from the surface of the specimens immersed in brine than from those in the sodium and calcium chloride solution. After 50 cycles whiskers appeared on the surfaces of specimens immersed in the sodium and calcium chloride solution; this phenomenon was not evident on the specimens immersed in natural brine. These whiskers were slightly longer than those described previously, but otherwise they had similar characteristics.

Surface characteristics of the A-36 steel were different from those that had been obtained with the SAE steel. Structural steel specimens in both solutions exhibited rough surfaces with high and low areas. There was no pitting in any of the A-36 specimens after 100 cycles. Some specimens displayed a tendency toward cratering. As defined in this study, a crater is a circular depression whose diameter is greater than its depth. It is possible that these characteristics are caused by different stresses in the surface from the rolling process. Stressed areas would be expected to corrode more readily than unstressed areas.

As has just been discussed, some of the results from the A-36 steel were different from those obtained with the SAE steel. The most likely explanation for this is the different chemical composition of the A-36 steel. The duration of the tests on the A-36 steel may have been too short. Some of the phenomena described would be more emphasized over time, and a longer test would provide a better explanation of the processes involved.

### CONCLUSIONS

Based on the results of 100 freeze-thaw cycles in the laboratory, the effects of natural brines on bituminous concrete pavements appear to be no different than the effects of traditional rock salt deicing agents. Thus, from a materials standpoint, there appears to be no reason why natural brines

could not be used as a deicing agent on bituminous concrete pavements.

In terms of PCC surface deterioration after exposure to 100 freeze-thaw cycles in the laboratory, natural brine performed somewhat better than traditional chloride deicing agents. Similarly, it can be concluded that the effect of natural brine on concrete compressive strength is no different from that of water or sodium and calcium chloride deicing agents. Although some discoloration of the concrete occurred because of iron in the brine, the problem is not expected to be significant under actual field conditions. Further study is warranted.

No general statement can be made about the effects of natural brine on the corrosion of steel. The effects will depend on the chemical composition of the steels and the constituents of the brine. In this study, which involved 100 wet-dry cycles, specimens of automobile-body steel demonstrated less corrosion in natural brine than in a sodium and calcium chloride solution. However, specimens of structural steel demonstrated opposite results.

#### RECOMMENDATIONS

Additional consideration should be given to the composition of natural brines. Although the sulfate levels in the brine used did not appear to present problems as far as concrete deterioration, it would be desirable to examine other brines with higher sulfate levels. In addition, the duration of the test should be longer than that used in this study. Trace metal levels in certain brines may be of environmental concern; therefore, there is a need for additional work in this area. Because brine use is expanding beyond deicing applications to the area of dust control, such additional study is important.

The results of the research described in this paper suggest several other areas for further study. It would be desirable to investigate the effects of natural brines on bituminous concrete, PCC, and various types of steels in the field. For PCC, field testing should focus on the potential discoloration caused by natural brines. For steel, major emphasis should be placed on evaluating the long-term corrosive effects of natural brines. It would also be desirable to test a reinforcing-type steel in concrete to provide an indication of corrosion behavior under these conditions. In all cases field studies should be supplemented by additional laboratory tests of longer duration than those performed in this study. The 100-cycle testing used may not have been sufficient to provide an indication of the long-term effects of some brine constituents.

The study presented here used phenomenological approaches in studying the three materials. The physical and chemical behavior responsible for the results observed was not examined. Additional examination of these phenomena at the microscopic level would be beneficial.

The natural brine evaluated in this study is typical of that found in the northern and central Appalachian region. As noted earlier, however, brine composition may vary significantly with depth of occurrence and the formation in which it is located. Additional experimentation is warranted by using other brines that contain different ratios of major and minor constituents.

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