

NATIONAL COOPERATIVE HIGHWAY RESEARCH PROGRAM  
REPORT **19**

**ECONOMICAL AND EFFECTIVE  
DEICING AGENTS FOR USE ON  
HIGHWAY STRUCTURES**

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## NATIONAL COOPERATIVE HIGHWAY RESEARCH PROGRAM

Systematic, well-designed research provides the most effective approach to the solution of many problems facing highway administrators and engineers. Often, highway problems are of local interest and can best be studied by highway departments individually or in cooperation with their state universities and others. However, the accelerating growth of highway transportation develops increasingly complex problems of wide interest to highway authorities. These problems are best studied through a coordinated program of cooperative research.

In recognition of these needs, the highway administrators of the American Association of State Highway Officials initiated in 1962 an objective national highway research program employing modern scientific techniques. This program is supported on a continuing basis by funds from participating member states of the Association and it receives the full cooperation and support of the Bureau of Public Roads, United States Department of Commerce.

The Highway Research Board of the National Academy of Sciences-National Research Council was requested by the Association to administer the research program because of the Board's recognized objectivity and understanding of modern research practices. The Board is uniquely suited for this purpose as: it maintains an extensive committee structure from which authorities on any highway transportation subject may be drawn; it possesses avenues of communications and cooperation with federal, state, and local governmental agencies, universities, and industry; its relationship to its parent organization, the National Academy of Sciences, a private, nonprofit institution, is an insurance of objectivity; it maintains a full-time research correlation staff of specialists in highway transportation matters to bring the findings of research directly to those who are in a position to use them.

The program is developed on the basis of research needs identified by chief administrators of the highway departments and by committees of AASHO. Each year, specific areas of research needs to be included in the program are proposed to the Academy and the Board by the American Association of State Highway Officials. Research projects to fulfill these needs are defined by the Board, and qualified research agencies are selected from those that have submitted proposals. Administration and surveillance of research contracts are responsibilities of the Academy and its Highway Research Board.

The needs for highway research are many, and the National Cooperative Highway Research Program can make significant contributions to the solution of highway transportation problems of mutual concern to many responsible groups. The program, however, is intended to complement rather than to substitute for or duplicate other highway research programs.

This report is one of a series of reports issued from a continuing research program conducted under a three-way agreement entered into in June 1962 by and among the National Academy of Sciences-National Research Council, the American Association of State Highway Officials, and the U. S. Bureau of Public Roads. Individual fiscal agreements are executed annually by the Academy-Research Council, the Bureau of Public Roads, and participating state highway departments, members of the American Association of State Highway Officials.

This report was prepared by the contracting research agency. It has been reviewed by the appropriate Advisory Panel for clarity, documentation, and fulfillment of the research plan. It has been accepted by the Highway Research Board and published in the interest of an effectual dissemination of findings and their application in the formulation of policies, procedures, and practices in the subject problem area.

The opinions and conclusions expressed or implied in these reports are those of the research agencies that performed the research. They are not necessarily those of the Highway Research Board, the National Academy of Sciences, the Bureau of Public Roads, the American Association of State Highway Officials, nor of the individual states participating in the Program.

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## FOREWORD

*By Staff*

*Highway Research Board*

This report will be of interest to a number of disciplines within the field of highway transportation. It describes the results of an 18-month experimental program directed to the development of deicing materials to minimize, or eliminate, various detrimental effects caused by the agents now in common use. Promising materials have been indicated in some respects, and recommendations have been made for field testing to confirm the research results. The knowledge gained from this study should broaden the perspective concerning the problems inherent in developing new or modified deicing agents and thus serve to provide guidance for an ultimate solution to the problem.

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Many states have instituted the so-called "bare pavement" policy in attempting to provide safer driving conditions in the presence of snow and ice. Larger or more frequent applications of deicing materials are therefore used. Not only do the present materials contribute to the corrosion of vehicles, bridge reinforcement, and bridge hardware, but they are highly suspect as to the extent of contributing to concrete deterioration through chemical or physical processes. The resulting economic impact has accentuated the need for materials less harmful to vehicles and structures.

The Illinois Institute of Technology Research Institute has attempted to meet this need with the development of new deicing agents which are both economical and effective. Laboratory experiments were first conducted to determine the effectiveness of several chemicals and combinations of compounds as freezing-point depressants, and the most promising were compared with those existing for practicability and economy.

Corrosion experiments employing sodium chloride and calcium chloride were conducted under environments approximating critical field conditions for both vehicles and structures, and corrosion rates for test specimens were observed. Subsequent studies were then made to determine the potential of various materials as corrosion inhibitors, and conclusions were drawn concerning the most promising.

The study of concrete deterioration by deicing chemicals was approached in a manner similar to that used for corrosion studies. Initial studies concerned the effects of common chloride deicers, and some investigations were then made of the mechanism of damage. Finally, studies were made of the alleviation of damage, either by the use of additives to the chlorides or by the use of alternate deicers.

This document constitutes a final report on the research. Inasmuch as this has been an experimental program conducted in the laboratory, the results cannot be interpreted as conclusively meeting the project objectives. Nonetheless, the results will provide valuable guidance for planning future investigations for the technical

findings are supported by pertinent cost data and factors indicating the logistical problems associated with use of the various materials. The effectiveness of the specific chemical formulations should be evaluated in the field in the presence of the many variables encountered in actual use. A related effort should consist of a systematic study to determine the deterioration mechanism of concrete subjected to deicing agents when in a freeze-thaw environment.

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# ECONOMICAL AND EFFECTIVE DEICING AGENTS FOR USE ON HIGHWAY STRUCTURES

## SUMMARY

Research has been conducted to develop economical and effective deicing agents which would minimize the corrosion of structural steel elements and vehicles, and the freeze-thaw deterioration of concrete. The use of additives to the common chloride deicing materials and the use of alternative deicing materials have been investigated. The major results of this program are summarized as follows:

1. Steel embedded in cracked concrete and in areas where dirt was present suffered increased corrosion during cyclic exposure if chloride deicer was present in the solution.

2. A composite deicing agent of urea and calcium formate having a eutectic point of  $-3F$  is suggested. Formamide can be added if lower temperature performance is needed. With this mixture the increased corrosion rate was not found; in fact, the rate was appreciably below that found with plain water exposure.

3. The increase in corrosion rate encountered with chloride solutions may be eliminated by the addition of a polyphosphate-based material or a long-chain amine to the sodium chloride solution.

4. Surface spalling of cement mortar increased markedly in the presence of chloride solutions during freeze-thaw cycling.

5. Use of the composite organic deicing materials afforded only little improvement in the cement mortar deterioration rates when used instead of chlorides.

6. Various materials when added to chloride deicer solutions reduced the rate of this freeze-thaw deterioration. Typical additives were sequestering agents such as the sodium salt of ethylenediamine tetraacetic acid, and polyhydroxy sugar-type compounds such as dextrose.

7. Other factors affected the rate of cement mortar deterioration during freeze-thaw testing. The rate was increased by contact of the specimen with plain water during freeze-thaw cycling in chloride solutions. More damage was found with low concentrations of the chloride solutions than with high concentration, and when low freeze temperatures were used. Longer curing periods reduced the rate of deterioration and reduced the amount of additive needed in the chloride solution to afford protection.

8. In addition to the surface spalling attack, there appeared to be a different type of attack which resulted in general softening and deep cracking. This type of deterioration was greater with increased concentrations of the solution and did not appear to be improved as much by additives to the chloride solution.

9. The deicing methods found to be less reactive with steel and concrete all result in materially increasing the cost of deicing, and would therefore be of primary value when applied to sensitive areas such as bridge decks.

10. Specific recommendations have been made for deicing agents and additives for field testing to confirm the results of this program.

## INTRODUCTION AND RESEARCH APPROACH

The purpose of the research project reported herein was the development of economical and effective deicing agents to minimize injury to highway structures and vehicles. To accomplish this objective, new deicing chemicals, as well as additives for use with conventional chloride-type deicing agents, were investigated.

The accumulation of dirt and dampness at the surface of metallic parts of vehicles and structures leads to corrosion, and freezing and thawing accelerate the degradation of portland cement concrete. A large amount of field and laboratory evidence shows that the presence of deicing salts, such as sodium or calcium chloride, will accelerate both of these undesirable actions, although the extent of this acceleration is still the subject of some controversy. The purpose of this project was not to assess the contribution of deicing materials to highway and vehicle repair costs, but rather, on the basis that the use of deicing chemicals is necessary for modern traffic conditions, to attempt to find materials which would perform this function with a minimum amount of damage.

### RESEARCH APPROACH

#### *Selection of Chemicals*

*New Deicing Chemicals.*—The freezing point of an aqueous solution is determined by the temperature at which the vapor pressure of the liquid is equal to the vapor pressure of the equilibrium solid phase (ice). The presence of a dissolved material lowers the vapor pressure of the solution so that it is in equilibrium with ice at a lower temperature; thus, the freezing point is lowered. In effect, when ice is in contact with a solution with a lower vapor pressure, the ice melts, diluting the solution. For ideal solutions, in which Raoult's law of vapor-pressure lowering holds, the freezing-point lowering of the aqueous solutions is only a function of the concentration of solute expressed in molality, with appropriate correction for the ionization of electrolytes. For water the freezing-point lowering is

$$\Delta T = 3.3 C \quad (1)$$

in which  $C$  is the concentration in moles (or equivalents for electrolytes) per 1,000 grams of solution and  $T$  is temperature in °C. Inasmuch as the number of moles is equal to the weight in grams divided by the molecular weight, the lighter the molecular weight the more effective a compound is for lowering the freezing point. Although Eq. 1 is accurate only for dilute solutions, it provides a useful guide for the selection of deicing agents.

In addition to low molecular weight, various other properties are important. One of these is solubility—the material must be soluble at low temperatures to produce

useful freezing-point lowering. This limitation, which affects many materials, often can be overcome by using mixtures of materials, because the total solubility often approaches the sum of the individual materials, if there is no appreciable interaction. Also, materials which are flammable, very volatile, very acid, or poisonous cannot be used. Sulfates cannot be used because of their damaging effect on concrete.

*Additives for Chloride Deicers.*—The mechanism of corrosion by brines has been studied extensively, and a variety of inorganic and organic materials are obvious candidates for the inhibition of corrosion. The mechanism of concrete deterioration by these materials in the freeze-thaw cycle is less well understood. Possible candidates for additives to reduce the damage caused by salt solutions are surface-active agents, which might modify the crystallization of the ice, and materials which would react with the concrete components to give a protective action.

The use of an additive to reduce the destructive effects of ice-melting chemicals has several advantages. Salt is very inexpensive; other chemicals which might be useful for ice-melting purposes cost several times as much. Thus, an additive of moderate cost could be used with salt at a considerable saving, compared with the use of some entirely different material. Another advantage is the treatment of sensitive areas such as bridge decks. If, as is sometimes proposed, salt is used to treat the roadway and some more expensive but less damaging material is used on the bridge decks and approaches, it is still probable that the salt will be carried onto the sensitive areas by traffic and cause trouble. However, this problem might not arise if an adequate salt-plus-additive treatment is used on the bridge decks and salt on the roadway. Thus, the use of an effective additive offers a potentially beneficial solution to the problem.

#### *Selection of Test Methods*

*Corrosion Tests.*—Past efforts involved the development of inhibitors to reduce the corrosion rate in the strong salt solutions formed by deicing chemicals. In usual laboratory corrosion tests metal panels are exposed to strong salt solutions, with alternate wetting and drying cycles. Phosphate-based corrosion inhibitors that have been developed substantially reduce the corrosion in such tests, and these materials have been used commercially in cities such as Rochester, N.Y., and Akron, Ohio. The results in these cities were not as good as the laboratory tests predicted. One of the primary reasons for this lack of agreement between field and laboratory was probably the type of corrosion caused by the presence of dirt in the field.

Corrosion involves the following electrochemical proc-

esses: (1) an area on the metal where an anodic reaction or oxidation can take place, such as iron going into solution as ferrous ions; (2) a cathodic area where a corresponding reduction can take place, such as the reduction of oxygen from the air; (3) a metallic path between the sites to transfer the electrons between the reactions; and (4) an electrolyte path between the sites so that the ions produced can be transferred and neutralize charges. A thin film of salt solution, such as is produced when a specimen is immersed and then removed from the solution, provides a corrosive situation. The thin film offers little resistance to the diffusion of oxygen to the surface to provide the cathode reaction. In addition, ionic conduction is excellent in the film of salt solution. The oxygen present at the anodic areas reacts with the ferrous ions to form the familiar red rust, ferric oxide. The buildup of this insoluble oxide reduces the rate of the diffusion of ions and of corrosion. Because insoluble ferric phosphates may be formed at the surface as a result of reactions involving ferrous ions and oxygen, the foregoing system is susceptible to inhibition by phosphates. These insoluble films greatly inhibit the reaction rates. Phosphates are relatively ineffective in the absence of oxygen.

Corrosion is accelerated by the presence of layers of dirt of uneven composition or thickness. In areas where the dirt is thinner or more porous due to the presence of sand, oxygen can diffuse readily into the surface and provide the cathodic reaction of the corrosion cell. In areas where the dirt is thicker or more compact, oxygen is prevented from reaching the surface, and the anodic reaction will proceed with the corrosion of the iron to form ferrous ions. The dirt also retains the salt solution and thus provides a good ionic path between these areas. Due to the low oxygen content at the anodic areas, oxidation to the ferric state and formation of the insoluble oxide or phosphate compounds take place farther from the metal surface, so that corrosion can proceed at a more rapid rate. The cells formed in this manner, due to areas of low and high oxygen concentration, are called differential oxygen concentration cells and can result in very high local corrosion rates. The corrosion takes place in areas such as joints, braces, and horizontal places where dirt can accumulate.

In addition, the presence of dirt presents another problem when inhibition is attempted. The corrosion inhibitors are reactive or surface-active substances and can be adsorbed by the dirt before they can get to the surface.

The test method used in this project to investigate the inhibition of corrosion, as well as the effects of various parameters (such as dirt) on corrosion, is based on the use of the corrosion probe technique. In this method, corrosion is detected by measuring the electrical resistance of a thin strip of the test metal, in this case steel. This technique of following changes in resistance allows the corrosion rate to be determined without disturbing the specimen. By compensating for temperature, either by incorporating a protected strip as a bridge element or by using tables of temperature coefficient of resistance, the corrosion can be detected to as low as 1  $\mu$ in.

The specimens are made of 1-mil shim stock, 0.25 x 1.50 in. exposed area, immersed in a porous-bottom container containing about 40 ml of soil. Ten ml of the desired test solution are poured over this soil daily and allowed to drain. The test containers are placed in a constant-humidity cabinet at 73 F and 33 percent relative humidity to control the rate of drying. The resistance of the specimen is determined before each cycle, and the total corrosion is plotted as a function of time.

Another type of corrosion test was used to determine the corrosion rate of steel embedded in cracked concrete. A 30-mil iron-wire corrosion probe was cast into a 1 x 1 x 6-in. cement mortar bar. The length of the wire area which was measured by the electrical resistance test was  $\frac{1}{4}$  in. A notch was cast in the bar at this point, and the bar was cracked after curing and drying. Four milliliters of the desired test solution were poured over the cracked area once each day, and then the bar was allowed to dry. Corrosion was measured as a function of time by measuring the electrical resistance of the wire specimen. All tests reported here were run at one time, at room conditions.

*Concrete Deterioration Tests.*—The mechanism of the deterioration of portland cement concrete caused by deicing chemicals is somewhat less understood than the corrosion reactions, but sufficient factors are known to allow the choice of a test method. In the selection of test methods for this project the following factors, which influenced the choice of the test methods, became apparent from a survey of the literature:

1. Some damage to the surface occurs when water without deicing chemicals is used in the freeze-thaw cycle. The damage, however, is greatly increased if the water contains a deicing chemical. Damage has been found with sodium chloride, calcium chloride, alcohol, and urea, with generally more damage in medium-strength solutions than in high-strength solutions. These factors indicated that the damage did not depend primarily on the formation of ice crystals, inasmuch as the damage with plain water is low. Furthermore, the damage experienced with various types of chemicals is less severe in more concentrated solutions.

2. Properly cured air-entrained concrete has increased resistance to the action of deicing chemicals. However, the use of an absorbent aggregate or variations in the surface air entrainment of the concrete can result in scaling even when the concrete is prepared properly. The amount of air entrained in the surface mortar layer is often considerably below that in the bulk mortar. This results in increasing the aggressiveness of deicing chemicals in the area most susceptible to damage.

3. Continuous immersion of concrete in salt solutions without freezing results in some damage, indicating that there may be some chemical deterioration in addition to the physical damage.

4. Damage appears to be greatest when water or deicer solution is in contact with the surface during the freezing portion of the cycle.

5. There are also some indications that damage may

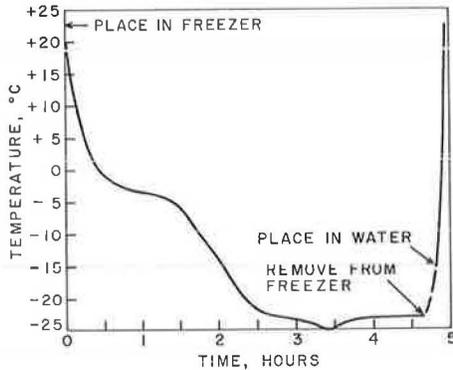


Figure 1. Thermal curve of freeze-thaw-wash cycle.

occur during drying by the recrystallization of the deicing agent.

In addition to the foregoing factors, a large number of solutions had to be tested in this program for their effects on concrete. It therefore was decided to carry out the initial concrete deterioration tests on a mortar bar with no coarse aggregate, using both a freeze-thaw cycle and a wet-dry cycle. Sonic modulus and weight loss were used to measure the deterioration.

The initial tests were run on 1 x 1 x 11¼-in. bars. Preparation of the mortar bars followed the procedures and mortar mix described in ASTM C109-58. The proportion consisted of 2.75 parts of graded sand by weight to one part of Type 1 portland cement, with a water-cement ratio of 0.46. The sand was an Ottawa sand with a grading such that none was retained on a No. 16 screen, 33.7 percent was retained on a No. 30 screen, and 99.1 percent was retained on a No. 50 screen. Mixing was in accordance with ASTM 305-58T for mechanical mixing of cement mortars.

After mixing, the plastic mortar was cast into 1 x 1 x 11¼-in. molds. The mix was allowed to set 4 hr and then was cured in a moist room for 28 days. After this period, the bars were removed from the moist room and allowed to stabilize in the laboratory environment for a week or longer before being subjected to the testing environments.

These specimens had no air-entraining agent and thus were more sensitive to treatment than normal concrete; degradation would occur at a much faster rate. Mechanical property changes in the bars were observed by using the nondestructive sonic method of measuring Young's elastic modulus. Two bars were used for each solution in the wet-dry cycle tests, and three bars were used for each solution in the freeze-thaw tests.

In the wet-dry tests the specimens were soaked in the deicing solution for 8 hr, and then dried at 110 C for 16 hr. In the freeze-thaw tests, the cycle was freeze at -25 C for 16 hr then thaw in the solution for 8 hr at 73 F. In both tests, the deicing solution was changed after each 5 cycles.

To allow more rapid evaluation of the effects of a number of materials on the deterioration of concrete during the freeze-thaw exposure, a simple screening test was run with 1-in. cubes cut from mortar bars prepared as described. The cured and stabilized specimens were dried at 110 C for 24 hr, and the initial weight recorded. They were then placed in a plastic ice-cube tray and covered with 15 ml of the test solution. The specimens were then subjected to 12 to 18 freeze-thaw cycles (5-16 hr at -20 F and 4 hr at 75 F). Some of the series were run with a wash cycle after each freeze-thaw cycle, with a drying cycle and reweighing after each 6 cycles. Series of tests were also run with a wash cycle after each 5 freeze-thaw cycles, with drying and reweighing after 15 cycles. Both types of test gave similar results, and standards were run with each series to permit comparison to be made between the tests. The wash cycle consisted of immersion of the specimen in Chicago tap water for 2-4 hr, with fresh test solution being used for subsequent cycles.

The rate of cooling and warming of a 1-in. cube specimen in this type of exposure is shown in Figure 1. In this experiment, the temperature was determined by placing a thermocouple in the center of a specimen. The solution used for this test was 6 percent NaCl. The temperature of the wash water was 25 C. It can be seen that equilibrium was reached during the test periods chosen.

*Freezing-Point Determinations.*—For the purpose of determining freezing points a method was developed based on American Oil Chemists' Society Method Cc 12-41, a method for determining the solidification point of fats and oils. In this method a test tube of the solution is immersed in a cold bath, with a thermistor temperature indicator and a mechanically-driven ring stirrer in the tube. The bath used was acetone-dry ice. The freezing was recorded as the first appearance of ice crystals.

## RESULTS

### FREEZING-POINT LOWERING

The effectiveness of several chemicals and combinations of compounds as freezing-point depressants is shown in Figure 2. Several other materials also were checked in the laboratory and in the literature for their effectiveness as freezing-point depressants, but were eliminated because of their corrosivity, volatility, etc. Table 1 lists the "effective molecular weight," which is the molecular weight of the material divided by the number of ions formed by dissociation, for several materials. Although this concept is only accurate at very low concentrations, it provides an indication of the effectiveness of a material as a freezing-point depressant. In addition, the value for the "effective molecular weight" determined from the measured freezing-point lowering of 15 percent solutions is given.

It can be seen that the measured effectiveness of the materials as deicing agents is similar to the calculated rate, except for calcium chloride and calcium formate. These departures from the theoretical value result from some molecular phenomenon such as association with water or failure to completely ionize. It is probable that the greatest molecular weight of a material which would prove feasible would be near 60, because at this point the materials already require more than twice as great a weight to produce the same melting action as chloride salts and most of them are considerably more expensive than sodium chloride.

In considering the list of materials which may be useful, the alcohols can be eliminated because they are too flammable and too easily evaporated; ammonium nitrate is very corrosive towards steel; and sodium sulfate promotes the deterioration of concrete. Therefore, the useful materials are urea, calcium formate, formamide, and acetamide. Urea and calcium formate are interesting materials because they are solids and could be applied easily, but they both suffer from limited solubility; thus, they have a lower temperature limitation near 20 F. However, a mixture could be used at temperatures down to 0 F, and if formamide is used, ice can be melted at even lower temperatures.

Thus, a system to be used for melting ice could be based on these three materials, instead of chloride salts. Urea could be the primary material and would be used when the temperature was down to 25 F. At lower temperatures, a mixture of urea and calcium formate would be used, or as an alternative plan, a mixture of urea and calcium formate could be used at all but extremely low temperatures. When the temperature is very low, it would be necessary to add formamide, which would complicate spreading inasmuch as it is a liquid. However, a spray device that would add the required amount

of the liquid material when needed could be added to an ordinary salt spreader.

Such a system would be considerably more expensive than calcium or sodium chloride. The following are approximate prices per ton of chemical, and will vary depending on location and other factors:

<i>Material</i>	<i>Price (\$/ton)</i>
Sodium chloride	10—20
Calcium chloride	30—35
Urea	90
Calcium formate	70—90
Formamide	200

Thus, the basic urea-calcium formate mixture might cost about \$85 per ton, or up to \$115 per ton if formamide was required by very low temperatures. In addition, a larger amount of material would have to be used because these materials are only about one-half as effective as the chloride salts as ice melters. Thus, the increase in cost as compared to the chloride salts would be considerable, although the ratio of costs as applied to the highway would probably be less than indicated by the foregoing figures, as the chemical cost is only a part of the total cost of the highway deicing operation. The actual economics of the use of these materials in place of the chlorides would have to take into account any potential savings in reduced maintenance which might be effected. At the minimum, the addition of calcium formate will increase the temperature range over which urea is effective by lowering the eutectic point to -3 F, and the cost of the mixture should be the same or lower than for urea alone. Thus,

TABLE 1  
EFFECTIVE MOLECULAR WEIGHTS OF  
FREEZING-POINT DEPRESSANTS

MATERIAL	EFFECTIVE MOLECULAR WEIGHT	
	CALC.	MEAS.
Sodium chloride	29	30
Methanol	32	31
Calcium chloride	37	26
Ammonium nitrate	40	
Calcium formate	44	58
Formamide	45	
Ethyl alcohol	46	47
Sodium sulfate	47	
Acetamide	59	
Urea	60	60
Ethylene glycol	62	58
Glycerine	92	83

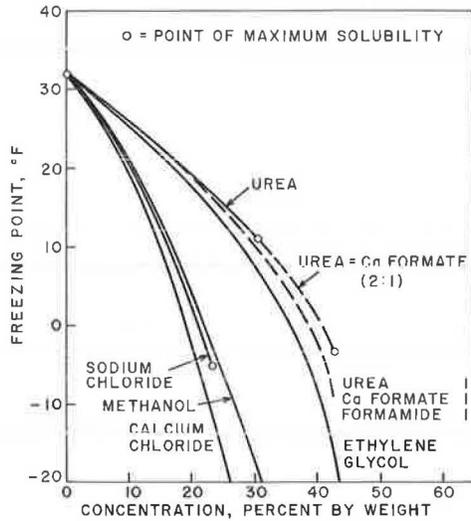


Figure 2. Effect of concentration of solution on freezing point.

this mixture should offer an advantage where urea has been used in the past.

The toxicity of these materials has not been investigated in this project, but a brief examination of the literature indicates that no special problem would be expected with urea or calcium formate. Formamide is known to be an irritant, however, and the toxicity of its solutions under deicing use conditions would have to be studied before extensive use.

#### CORROSION BY DEICING CHEMICALS

The corrosion tests used for the investigation of various deicing chemicals and additives to chlorides were based on measurement of the corrosion of thin steel specimens partially embedded in dirt which was periodically wet with

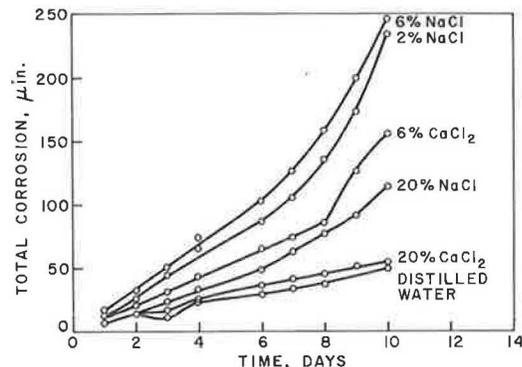


Figure 3. Results of corrosion tests with chloride solutions.

the solution under test. The results with this test were expected to correlate with auto body corrosion and the corrosion of exposed metallic structural parts. In addition, several chemicals which had shown promise on this test were studied for inhibition of the corrosion of reinforcing steel in cracked concrete. The results obtained in these investigations are considered in this section.

#### Steel-Dirt-Deicing Chemical System

**Corrosion Rates with Various Deicing Chemicals.**—The results of corrosion rate studies with solutions of sodium and calcium chloride are shown in Figure 3. It can be seen that corrosion is more rapid with sodium chloride. The rate reached a maximum with concentration; the 2 and 6 percent solutions corroded more rapidly than the 20 percent solution. Corrosion under dirt layers is caused by differential aeration, with the metal under the deeper layers being the corroding anode and the metal nearer the surface forming the cathode, depolarized by oxygen diffusing through from the air. Because the anode and cathode are separated by quite a distance, the increased conductivity caused by adding an electrolyte such as chloride results in a greatly increased rate. However, as the solution becomes more nearly saturated the oxygen solubility is reduced and the rate again drops.

The corrosion rates with a series of different compounds at 6 percent concentration are given in Figure 4. Ammonium nitrate was extremely corrosive, but the rest of the materials were less corrosive than sodium chloride. The sudden upward inflection of the curves near the end of the test indicates pitting. The corrosion rates of these materials as derived from the slopes of the curves in Figure 4 are given in Table 2.

**Additives for Chloride Deicing Chemicals.**—A series of tests was run by using the steel-dirt-sodium chloride solution system to evaluate the effectiveness of various additives in reducing the corrosivity of sodium chloride deicing solutions. These results are reported in Table 3. In

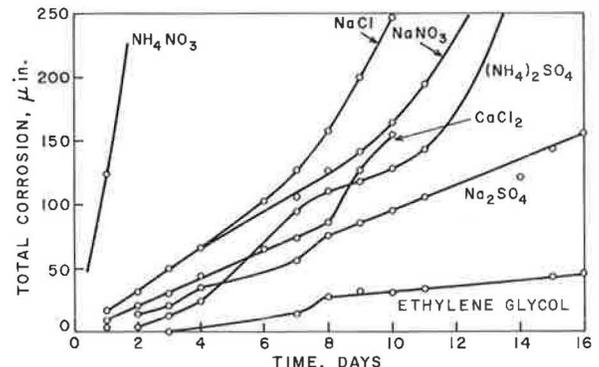


Figure 4. Results of corrosion tests at 6 percent concentration.

these tests the salt solution was at 6 percent concentration. The effectiveness of the additives is given in terms of percent protection; that is, the percent reduction in the corrosion rate as compared with the salt solution without additive. The corrosion rate of the uninhibited salt solution ranged from 6 to 10 mils per year. Proprietary compounds are identified in Appendix A.

In addition to the materials listed, the following materials were tested but were not sufficiently dispersible to be useful: di-coco amine, the dioleic amide of diethylenetriamine, and three high molecular weight sulfonates.

Several of the organic amines tested gave up to two-thirds reduction in the corrosion rate (Table 3a). Several different types of long-chain amines were tested, and representatives of most classes gave protection in this range. The protection provided by the tertiary amine, the ethoxylated amine, the quaternaries, and the sulfonate material were on a somewhat lower level.

Table 3b indicates that polyphosphates are not effective inhibitors unless a metallic cation such as zinc, calcium, or magnesium is present. This is not surprising, inasmuch as polyphosphates are known to be relatively ineffective as corrosion inhibitors in many applications with pure water. The most generally accepted mechanism for the inhibitive action of polyphosphates involves the formation of a positively charged colloidal complex iron-calcium-phosphate, which is attracted to the cathodic area where the charge is neutralized. The precipitated material forms a barrier that interferes with the cathodic corrosion mechanism. If the calcium present in the water is not sufficient it is necessary to add some cation of this class with the inhibitor.

Another series of tests with polyphosphate-cation inhibitors was run by using 3 percent sodium chloride brine. Under these conditions, a concentration of 0.06 percent polyphosphate was necessary to give good protection with either calcium or zinc present. This corresponds to 2 percent, based on the weight of salt present. This series also indicated that the amount of zinc present was somewhat critical; if too much zinc was present pitting resulted. Because this condition was not found in the series reported in Table 3 when silicate was present, this material

TABLE 2  
CORROSION RATES OF VARIOUS COMPOUNDS <sup>a</sup>

COMPOUND	CORROSION RATE (MILS/YR)
Ammonium nitrate	50.0
Sodium chloride	6.4
Sodium nitrate	5.6
Ammonium sulfate	2.3 <sup>b</sup>
Calcium chloride	3.9
Sodium sulfate	3.6
Ethylene glycol	0.9
Distilled water	1.5

<sup>a</sup> Six percent solutions.

<sup>b</sup> Calculated on basis of first four days; remainder of curve assumed to be due to pitting.

was incorporated when zinc was used as the metallic cation.

The results of tests with other inorganic inhibitors (Table 3c) show good protection only with large amounts of sodium silicate. Several high-pH materials such as sodium carbonate, calcium hydroxide, trisodium phosphate, and borax were tested, but only calcium hydroxide gave useful protection. In the case of calcium hydroxide, in which the corrosion rate was cut in half, it is probable that the mechanism is not based on high pH but rather on the formation of insoluble calcium carbonate by reaction with carbon dioxide from the air. A similar reduc-

TABLE 3  
EFFECT OF ADDITIVES ON CORROSION OF STEEL <sup>a</sup>

ADDITIVE	CONCENTRATION (%)	PROTECTION (%)
<b>(a) ORGANIC MATERIALS</b>		
Dimethyl coco amine	0.12	44
Coco amine	0.12	64
Coco propylenediamine	0.12	38
Soya propylenediamine	0.12	64
Ethoxylated coco amine	0.12	37
C <sub>12</sub> hydroxyethyl imidazoline	0.12	68
C <sub>18</sub> hydroxyethyl imidazoline	0.12	57
Fatty aminoethyl imidazoline	0.12	50
C <sub>18</sub> amidoethanol amine	0.12	53
C <sub>12</sub> amidoethylene diamine	0.12	64
C <sub>12</sub> benzyl imidazoline quaternary	0.12	45
C <sub>18</sub> benzyl imidazoline quaternary	0.12	45
Sodium petroleum sulfonate	0.12	34
<b>(b) POLYPHOSPHATE-CONTAINING MATERIALS</b>		
Sodium pyrophosphate	0.12	0
Sodium polyphosphate	0.12	0
Sodium polyphosphate + zinc acetate, 7:3	0.17	82
Sodium polyphosphate + calcium hydroxide, 3:5	0.16	88
Sodium polyphosphate + zinc acetate + sodium metasilicate, 5:1:5	0.15	76
Sodium polyphosphate + sodium metasilicate + magnesium chloride, 5:5:1	0.15	59
Sodium polyphosphate + sodium metasilicate, 1:1	0.12	0
<b>(c) OTHER INORGANIC MATERIALS</b>		
Calcium hydroxide	0.10	52
Calcium hydroxide + borax, 1:5	0.62	24
Borax	0.52	0
Borax + sodium carbonate, 1:2	0.80	28
Sodium carbonate	0.30	1
Sodium metasilicate	1.0	88
Sodium metasilicate	0.12	25
Trisodium phosphate	0.45	0
Sodium nitrite	1.0	— <sup>b</sup>
Sodium nitrite + borax, 2:1	1.5	— <sup>b</sup>

<sup>a</sup> System of steel-dirt-6 percent sodium chloride.

<sup>b</sup> Accelerated.

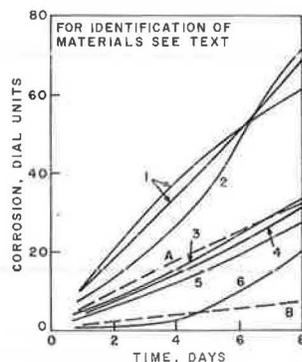


Figure 5. Corrosion of steel in cracked mortar bars wet daily with 3 percent sodium chloride solution.

tion in corrosion rate was seen earlier when calcium chloride was compared with sodium chloride solutions. The addition of sodium nitrite resulted in a corrosion rate more than twice as high as the blank. This was evidently due to depolarization of the cathodic areas of the cell by the oxidizing nature of the nitrite at a rate faster than can be accomplished by the normal diffusion of air to these areas.

From these results it appears that a substantial reduction in the corrosivity of sodium chloride brines could result from the incorporation of either a long-chain amine compound or a polyphosphate with calcium or zinc and silicate added. These additives were included in the tests of the corrosion of reinforcing steel in cracked concrete.

#### Steel-Cracked Concrete-Deicing Chemical System

The results of the tests with steel embedded in cracked concrete are shown in Figure 5. Because the particular specimens could not be calibrated, the corrosion is reported in terms of dial units rather than  $\mu\text{in}$ . Thus, absolute rates cannot be determined, but the following comparative information can be drawn. The numerical rates reported are the average rates between the 1st and 8th days unless otherwise noted.

Curve 1—These are the observed corrosion rates for two tests with 3 percent sodium chloride solution. The observed rates are 7.3 and 8.3 units per day.

Curve 2—The test solution was 3 percent sodium chloride plus 0.06 percent sodium polyphosphate. The rate for days 1 to 4 was 6.0, rising to 11.5 for days 4 to 8. The solutions were not renewed, and this increase could have been caused by reversion of the polyphosphate.

Curve 3—This curve was obtained by using a solution of 3 percent sodium chloride with 0.06 percent of a commercial corrosion inhibitor with a polyphosphate base. The observed rate was 4.0, which is similar to that found for distilled water, and one-half that found for uninhibited sodium chloride solution.

Curve A—This curve was obtained with distilled water. The corrosion rate was 3.7, which is about one-half that obtained with the 3 percent chloride solution.

Curve 4—The test solution was 3 percent chloride, 0.06 percent polyphosphate, 0.006 percent zinc chloride, and 0.03 percent sodium silicate. The observed rate was 3.9, similar to that found for distilled water and the commercial polyphosphate treatment.

Curve 5—This test was run with 3 percent sodium chloride and 0.06 percent of a  $C_{12}$  hydroxyethyl imidazole. The observed rate was 3.4, again similar to the distilled water and the polyphosphate-inhibited salt solutions.

Curve 6—The test solution was 3 percent chloride, 0.06 percent sodium polyphosphate, and 0.10 percent calcium hydroxide. For the first 4 days the rate was very low (0.3), rising to 4.5 for days 4 to 8. The results of this test are somewhat inconclusive, because it is difficult to decide which of these rates would correspond to the rates expected in field use.

Curve B—This curve represents three separate tests run with non-chloride deicing agents. In each case 6 percent agent was used in order to give approximately equal ice-melting properties when compared with the chloride. The rates of corrosion were very low, as follows:

Agent	Conc. (%)	Corrosion Rate
Urea	6	1.2
Calcium formate	6	0.8
Formamide	6	0.8

This would indicate that the use of these chemicals or mixtures, as suggested earlier, could result in less damage to sensitive areas than when using either plain or inhibited chloride solutions.

#### CONCRETE DETERIORATION BY DEICING CHEMICALS

The study of concrete deterioration by deicing chemicals was approached in a manner similar to that used for corrosion studies. Initially, the effect of the common chloride deicers on cement mortar bars was studied; some investigation of mechanism of damage was made; and, finally, the alleviation of the damage by the use of additives to the chlorides, or by the use of alternate deicers, was studied.

#### Effect of Chloride Deicers

The results of sonic modulus and damping factor tests on the mortar bars subjected to a wet-dry cycle are shown in Figures 6 and 7. Only the specimens subjected to the calcium chloride solutions showed any deterioration. Those subjected to sodium chloride solutions, the glycol solution, and plain water did not deteriorate, even after 35 cycles.

Freeze-thaw tests with the same solutions are shown in Figures 8 and 9. In the first 20 cycles the 29 percent calcium chloride solution was quite aggressive and there

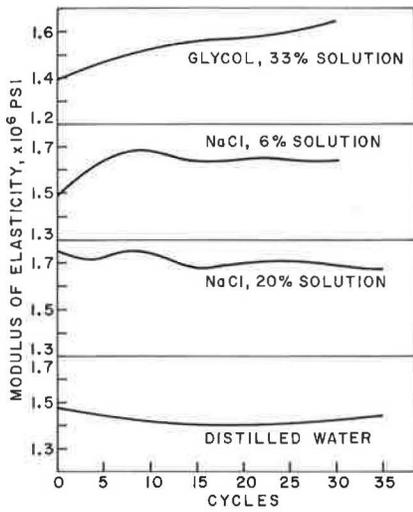


Figure 6. Results of wet-dry tests using glycol, sodium chloride, and distilled water.

was some decrease in the modulus of the specimen subjected to the 6 percent calcium chloride, but no effect was noted in the others. At the end of 20 cycles the specimens were washed in water, dried, and the freeze-thaw cycle was continued. After this washing rapid deterioration was noted in all specimens except that in the glycol solution. This effect of the incorporation of a wash period into the freeze-thaw cycle was noted on several occasions, and the possible reasons for the increased deterioration rate are considered in the section on deterioration mechanisms.

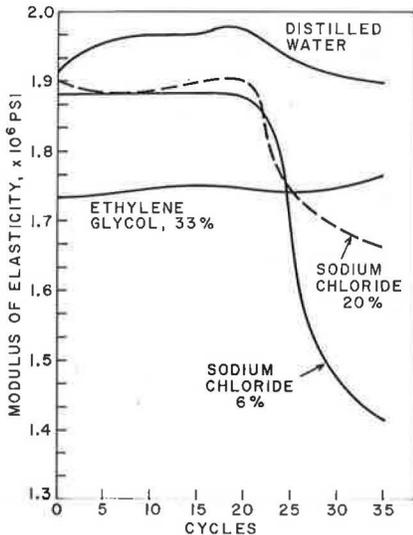


Figure 8. Results of freeze-thaw tests using glycol, sodium chloride, and distilled water.

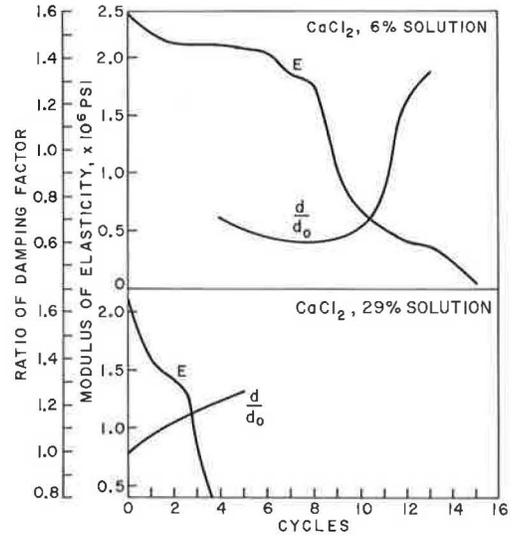


Figure 7. Results of wet-dry tests using calcium chloride.

One of the interesting characteristics of the chloride deicers was the type of attack. Figures 10 and 11 show the bars after 20 freeze-thaw cycles, and 15 wet-dry cycles. Only the bars in calcium chloride showed any change in modulus, and the attack on these bars was primarily by deep cracks through the specimens, running either across the bars or along their length. This can be seen in both wet-dry tests and in the center bar of the strong freeze-thaw test. With sodium chloride (Fig. 11) the bars suffered only surface damage of the spalling type, with little

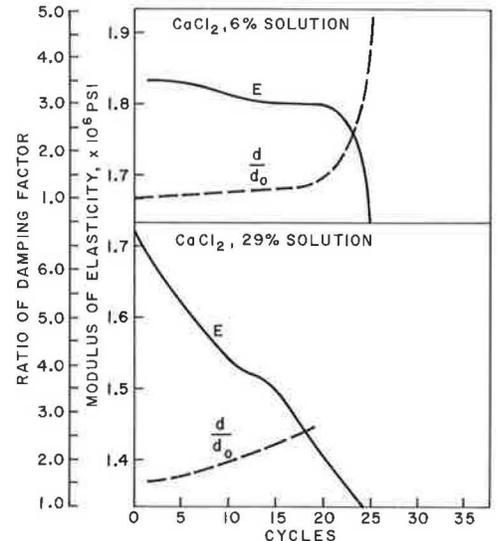


Figure 9. Results of freeze-thaw tests using calcium chloride.

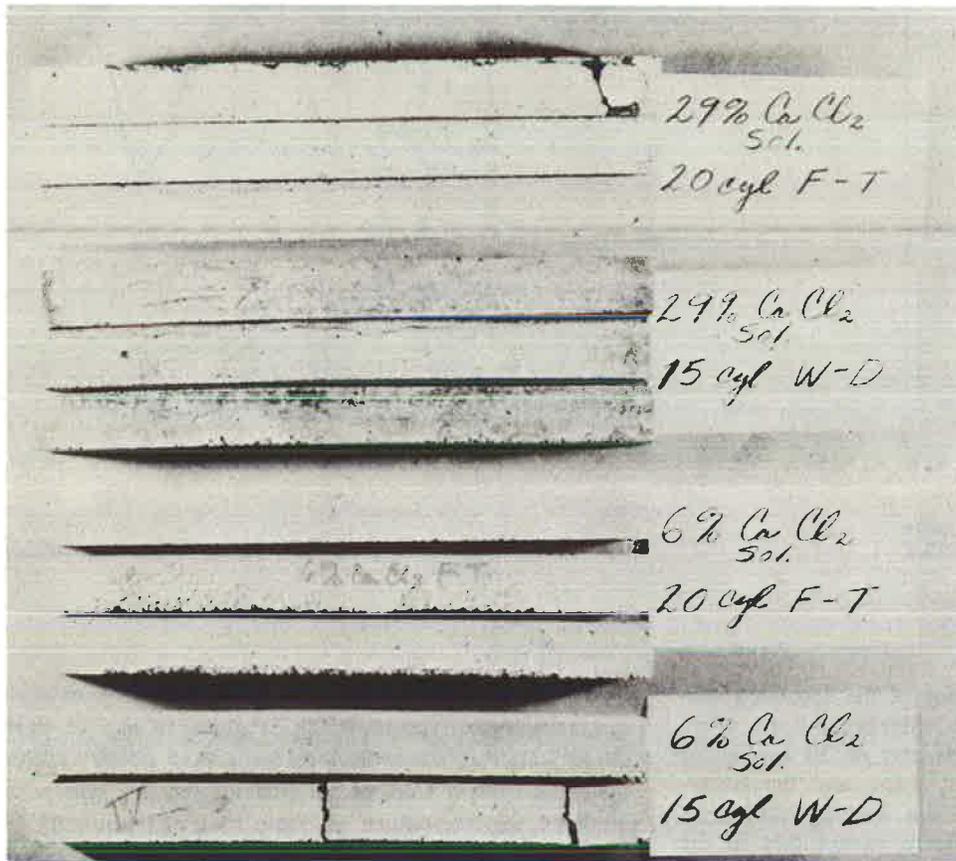


Figure 10. Mortar bars after 20 freeze-thaw cycles and 15 wet-dry cycles using calcium chloride.

TABLE 4  
EFFECT OF CONCENTRATION OF  
DEICING CHEMICAL

CHEMICAL	CONC. (%)	WEIGHT LOSS(MG/SQ CM)		
		6 CYCLES	12 CYCLES	18 CYCLES
Distilled water	—	3	3	8
		2	2	13
Tapwater	—	2	2	—
		4	9	—
Sodium chloride	1	47	137	—
		49	142	—
	6	29	51	87
		32	53	86
20	7 <sup>a</sup>	17 <sup>a</sup>	26 <sup>a</sup>	
	8 <sup>a</sup>	17 <sup>a</sup>	—	
Calcium chloride	1	43	224	—
		41	241	—
	6	18	47	87
		15	42	79
	20	14 <sup>a</sup>	18 <sup>a</sup>	—
		16 <sup>a</sup>	17 <sup>a</sup>	—

<sup>a</sup> Weight gain.

effect on the modulus before the wash cycle (Figs. 6 and 8).

The weight-loss screening test was used to evaluate the effect of concentration on freeze-thaw disintegration of the mortar-bar specimens. These results are given in Table 4. At the 1 percent level both specimens had more rapid deterioration than at the 6 percent level; with 20 percent deicer no deterioration was found. Also, the marked increase in deterioration rate with calcium chloride as compared with that with sodium chloride, which was found in the sonic modulus tests, was not noted here. In both—the effect of concentration and the comparison of the two chlorides—these screening test results correlate with the visual spalling attack noted in the previous tests (Fig. 11), rather than the cracking type of attack which showed up in the drop in modulus.

#### *Effect of Test Conditions on Deterioration by Chlorides*

The effect of the age of the cement mortar was shown by a series of tests with specimens used immediately after completion of the 28-day moist-cure period. These results were compared with those of the foregoing tests, in

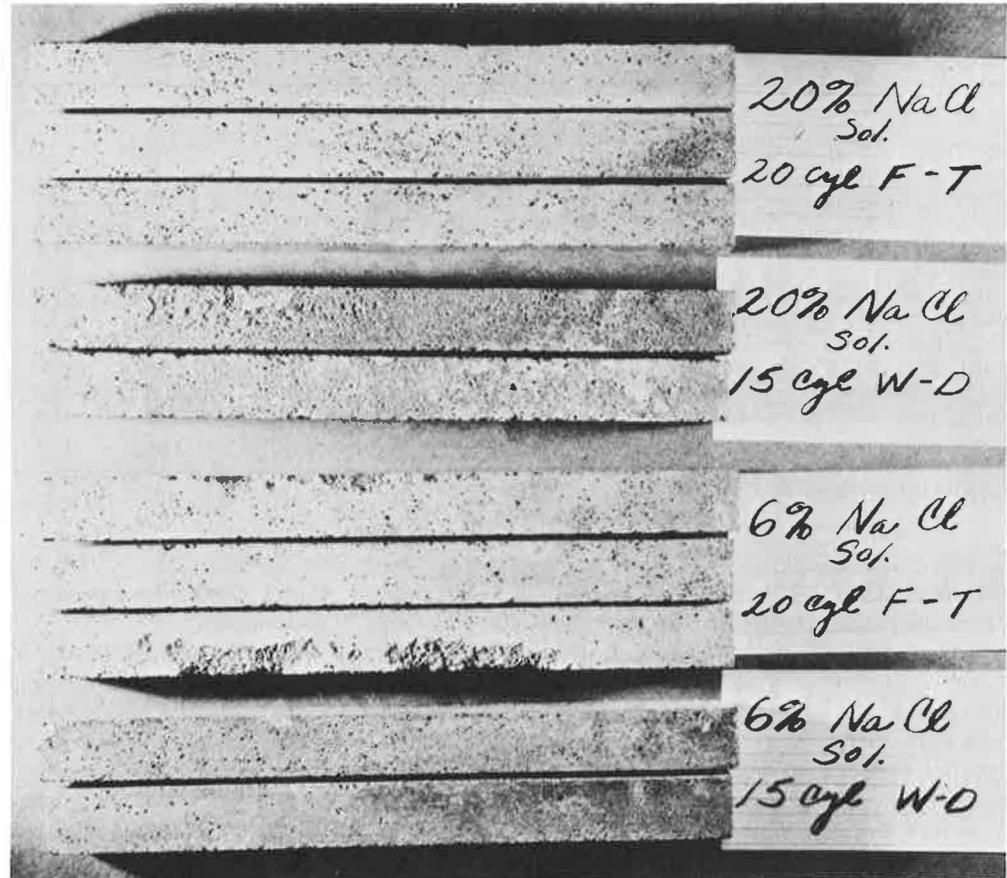


Figure 11. Mortar bars after 20 freeze-thaw cycles and 15 wet-dry cycles using sodium chloride.

which the specimens were several months old. Results of several tests are given in Table 5 for the green and aged specimens. The aged specimens were affected to a much lesser extent than those exposed shortly after curing. This agrees with field experience on new concrete subjected to deicing chemicals.

The effect of the temperature of the freeze portion of the cycle was investigated at  $-20$  F in these tests, and for the 1 percent sodium chloride at  $+20$  F also. At the higher temperature no deterioration was noted, even though the  $+20$  F temperature was well below the freezing point

of a 1 percent solution. This result would tend to throw some doubt on the damage caused by light freezing.

#### Mechanism of Cement Mortar Damage by Chlorides

During this program, which was designed to find methods to reduce concrete damage during freeze-thaw cycling, a number of factors were found which may throw some light on the mechanism by which this damage takes place. Although the information is not sufficient to determine the mechanism, these results are discussed with the hope

TABLE 5  
EFFECT OF SPECIMEN AGING ON DETERIORATION  
OF CEMENT MORTAR SPECIMENS BY CHLORIDES

FREEZE-THAW EXPOSURE	WEIGHT LOSS AFTER 12 CYCLES (MG/SQ CM)			
	SOLUTION	CONC. (%)	AGED SPEC.	GREEN SPEC.
Sodium chloride	1	140	234	
Calcium chloride	6	44	158	

TABLE 6  
CHEMICAL ANALYSES OF CEMENT MORTAR SPECIMENS

TEST SOLUTION	CYCLE		COMPOSITION (%)						
	TYPE <sup>a</sup>	NUMBER	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O
Water	F-T	35	75.0	0.77	1.09	12.3	4.25	0.03	0.01
NaCl, 6%	F-T	35	73.2	0.76	1.13	13.6	4.27	0.14	0.01
NaCl, 20%	F-T	35	73.8	0.80	1.30	13.8	3.89	0.22	0.02
CaCl <sub>2</sub> , 6%	F-T	25	72.2	0.75	1.07	14.3	4.53	0.04	0.01
CaCl <sub>2</sub> , 29%	F-T	25	72.7	0.75	0.85	13.0	4.10	0.03	0.02
Water	W-D	35	74.8	0.88	1.07	13.2	5.20	0.04	0.01
NaCl, 6%	W-D	35	74.3	0.76	1.17	13.2	3.38	0.18	0.01
NaCl, 20%	W-D	35	75.1	0.69	1.15	13.0	3.43	0.21	0.01
CaCl <sub>2</sub> , 6%	W-D	15	71.9	0.70	1.09	14.2	3.31	0.04	0.01
CaCl <sub>2</sub> , 29%	W-D	5	71.7	0.61	1.02	11.8	4.07	0.03	0.02
Unexposed	—	—	74.7	0.80	1.08	13.5	4.86	0.05	0.02

<sup>a</sup> F-T = freeze-thaw; W-D = wet-dry.

that they may prove useful to others working in the field. Three additional groups of data are given, then various significant data are summarized.

Table 6 gives analyses of the bars subjected to the freeze-thaw and wet-dry cycles. In addition, four of the bars were analyzed by thermogravimetric techniques; the results are given in Figure 12. Table 7 gives the analysis of solutions (distilled water and 6 percent sodium chloride) from tests in which subjected to a freeze-thaw cycle.

From these and previous results, the following points can be summarized:

1. There appear to be two types of attack, one of which results in surface spalling and disintegration. This attack is more severe with dilute solutions than with concentrated solutions. The other type of attack results in deep cracking and appears to be more severe in the more concentrated solutions.

2. Contacting the specimens with plain water (a wash

cycle) during the freeze-thaw cycles increased the deterioration rate.

3. The amount of damage is not directly related to the degree to which the solution totally freezes. For example, in water the solution would be expected to completely freeze, and with 1 percent sodium chloride at 20 F the equilibrium solution would be about 90 percent ice and 10 percent of a 1:9 sodium chloride solution. Neither of these gave significant deterioration. With 6 percent sodium chloride at -10 F the solution would be completely solid, and with 6 percent calcium chloride at +10 F the equilibrium would consist of 80 percent ice and 20 percent of a 1:3 calcium chloride solution. Both of these tests resulted in severe deterioration. These results indicate that the lower temperatures are more damaging not because the solutions freeze solid, but because more concentrated solutions are formed, or lower temperatures are reached.

Another result, discussed later, also indicates that this is true. For one test series, at -20 F during the freezing cycle, the deterioration with 3 percent sodium chloride was 120 mg per sq cm (the sodium chloride eutectic is at -6 F). The deterioration with 3 percent urea (eutectic at about 11 F) was 30 mg per sq cm, and with a 3 percent solution of a 2:1 urea-formamide mixture (eutectic below -2 F) the deterioration increased to 72 mg per sq cm.

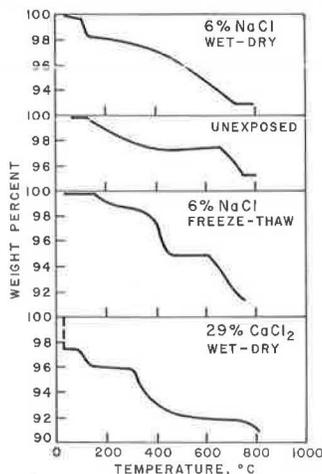


Figure 12. Thermogravimetric analysis of cement mortar test specimens.

TABLE 7  
ANALYSIS OF SOLUTIONS FROM  
FREEZE-THAW TESTS

DETERMINATION	ANALYSIS (PPM)	
	DIST. WATER	6% NaCl
Sodium	20.5	—
Calcium	72.	137.
Aluminum	1.7	1.7
Magnesium	0.0	24.8

Thus, when formamide was added to urea so that the eutectic point was lowered from 11 to below 0 F, the deterioration more than doubled.

4. The analytical results do not indicate any obvious pattern to help elucidate a deterioration mechanism, except for the general lowering of the magnesium content. This might well indicate a chemical attack, as confirmed to a degree by the analysis of the sodium chloride solution exposed to concrete during a freeze-thaw cycle. An appreciable amount of magnesium was found in that solution after the test, but none was found in a comparable test run with distilled water.

5. The results of the thermogravimetric analyses indicate that changes have taken place after exposure. For instance, the specimen from the 6 percent sodium chloride freeze-thaw test showed a 3 percent loss in weight at about 400 F; this loss did not appear in the unexposed specimen. Unfortunately, there was not sufficient time to pursue this line of attack, but these results indicate that further thermogravimetric and differential thermal analyses would probably be most useful to more carefully elucidate the deterioration mechanism.

6. One of the important factors in the deterioration of concrete would be the solubility of various cement components as a function of temperature and the presence of chloride and other deicing agents. Time limitations prevented investigation of this aspect. Figure 13 shows the effect of sodium chloride on the solubility of calcium sulfate and indicates the type of data that could be obtained from such an investigation.

These results do not give a clear picture of the mechanism of the deterioration, but they do give indications of the processes which occur. Two of the results—the increased deterioration which took place when a wash cycle was introduced, and increased deterioration suffered when less concentrated solutions were used—indicate that concentration gradients may play an important role. When the deicer solution freezes in concrete, the first thing which takes place is the formation of ice crystals; thus, the remaining solution is more concentrated. This would result in the formation of ice near the surface, and the concentrated salt solution would be deeper in the concrete. The analytical and thermogravimetric results indicate that chemical changes participate during the cycle.

One possible explanation of the deterioration is that the more concentrated solutions penetrate into the concrete by the freezing mechanism and that the solubility of certain concrete components in the more concentrated solutions increases because of the increased ionic strength and/or the lower temperatures. As the temperature begins to rise in the melting cycle, these concrete components are precipitated out by the increased temperature and the dilution of the salt as ice crystals begin to melt with a consequent plugging of the fine pores in the concrete. The concrete could then act as a semipermeable membrane and allow the passage of water but restrict the passage of large or charged ions, as has been observed with crystalline materials such as the aluminosilicates and zirconium phosphates. This would then set up conditions for the development of large osmotic pressures due to the con-

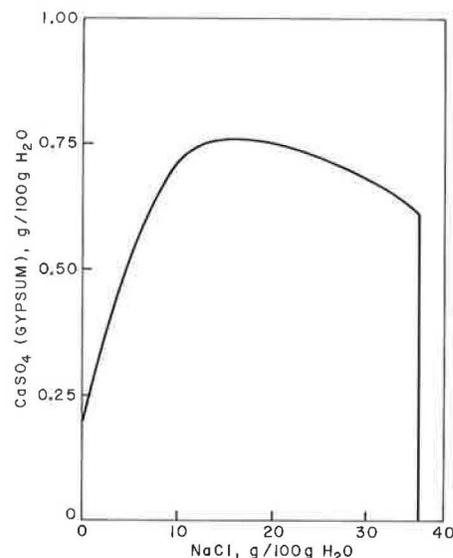


Figure 13. Effect of chlorides on solubility of calcium sulfate.

centration gradient between the surface, where the salt concentration is low, and the areas of trapped, highly concentrated, salt solutions. In such a system the water from the more dilute side tends to flow into the area where the more concentrated solution is present; consequently, large internal pressures develop. This phenomenon is known as osmotic pressure, and pressures of hundreds of pounds per square inch can be developed, which result in cracking of the concrete.

Such a mechanism is consistent with the analytical data obtained and with most of the factors which were found to be important in determining the deterioration rate. It has been previously suggested by several investigators that osmotic pressure contributes to cement deterioration through sulfate and freeze-thaw attack. The incorporation of the solubility behavior of cement components as a function of temperature and solution ionic strength into the theory helps to explain the increased rates with chloride salts as compared with those with organic materials. If this mechanism does operate, various ways would be proposed to reduce the deterioration, including modification of the concrete structure and incorporation of additives into the salt solution to interfere with the reprecipitation of the cement components. Modification of the concrete structure was not within the scope of this project, but the incorporation of additives was investigated. The results of these investigations are discussed in detail in the next section.

A second type of attack would seem to be operative in the deep cracking and general weakening found in some of the earlier tests. This type of attack increased with increasing solution strength and was manifested by reduced strength, as shown by the lowering of Young's modulus, and the appearance of deep cracks rather than surface spalling. The dependence on concentration might well indicate a primarily chemical attack.

TABLE 8  
EFFECT OF ADDITIVES ON DETERIORATION OF  
AGED CEMENT MORTAR SPECIMENS<sup>a</sup>  
SUBJECTED TO 6 PERCENT SODIUM CHLORIDE

ADDITIVE	CONC. (%)	RED. IN DETERI- ORATION (%)
Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	1.5	100
	0.5	79
	0.15	71
	0.05	14
EDTA-Na	1.5	100
	0.5	92
	0.15	71
	0.05	16
Borax	1.5	73
	0.5	73
	0.15	0
	0.05	8
Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O/EDTA-Na, 1:1	0.3	88
Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O/borax, 1:1	0.3	17
Borax/EDTA-Na, 1:1	0.3	67
Sodium phosphate	0.15	0
Citric acid	0.5	69
Sucrose	0.5	96
Gluconic acid	0.5	87
MgCl <sub>2</sub>	0.5	29
Sodium silicate, 40%	0.38	87

<sup>a</sup> Untreated loss 52 mg per sq cm, 12 cycles.

#### *Effect of Additives on Freeze-Thaw Deterioration in Chloride Solutions*

The results of the tests to determine the effect of additives on freeze-thaw behavior are given in Table 8 through 12. Table 8 shows appreciable protection with sodium silicate, borax, the sodium salt of ethylenediamine tetraacetic acid (EDTA), citric acid, sucrose, and gluconic acid. All of these materials might be expected to have some effect on the solubility or reprecipitation of cement paste components. The silicate and borax are alkaline and form insoluble calcium and magnesium salts; EDTA, citric acid, and gluconic acid are well-known complexing agents; and the polyhydroxy compounds, such as sucrose and gluconic acid, have been used as precipitation modifiers in scale-preventing compounds.

The series reported in Table 9 was run on the "green" mortar samples mentioned earlier. It was found that these samples not only deteriorated at a faster rate but also required a greater concentration of additive to give protection. Figure 14 shows this in a comparison of the results obtained with EDTA-Na as an additive on the aged and "green" specimens. The results obtained with these specimens (Table 9) show that dextrose, mannitol, and EDTA-Na gave protection of more than 60 percent and maltose, dextrine, and sucrose showed fair protection. The results with borax, silicate, and gluconic acid did not show the promise which had been observed on the aged specimens.

In the series with 3 percent NaCl solution (Table 10),

TABLE 9  
EFFECT OF ADDITIVES ON DETERIORATION OF  
"GREEN" CEMENT MORTAR SPECIMENS<sup>a</sup>  
SUBJECTED TO 6 PERCENT SODIUM CHLORIDE

ADDITIVE	CONC. (%)	RED. IN DETERI- ORATION (%)
Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	0.5	11
	1.0	0
Borax	0.5	7
	1.0	0
Sucrose	0.15	0
	0.3	42
	0.5	45
Dextrose	0.15	39
	0.5	77
Lactose	0.15	0
	0.5	0
Maltose	0.15	0
	0.5	53
Dextrine	0.15	2
	0.5	49
Mannitol	0.15	37
	0.5	80
Gluconic acid	0.5	17
	0.3	23
	0.15	37
Benax 2Al	0.5	6
	0.5	61
EDTA-Na	0.3	51
	0.15	26
	0.5	14
Starch	0.5	14
	0.15	5

<sup>a</sup> Untreated loss 175 mg per sq cm, 12 cycles.

the best results were obtained with dextrose, a modified starch, and with the two complexing agents, EDTA-Na, and NTA-Na (sodium salt of nitrilotriacetic acid). Dextrose gave the highest degree of protection, and the others showed better protection at lower dosages.

Two series of tests were run by using 1 percent sodium chloride solutions (Table 11). The specimens were subjected to the same freezing temperatures (-20 F) as the other tests in this report. Silicate, sucrose, and EDTA-Na showed appreciable protection under these conditions, again with the "green" specimens. Another series of duplicate tests was run with the temperature of the freeze portion of the cycle at 20 F. In this series no deterioration was noted in either the treated or the untreated tests.

Table 12 gives the results of tests in which the additives with 6 percent calcium chloride were used on the "green" specimens. Silicate and borax could not be used with the calcium chloride solutions because insoluble precipitates formed. Best results were again obtained with the EDTA-Na, sucrose, and citric acid. The amount of protection obtained was only on the order of 50 percent, but this is encouraging because this series was also run on the "green" specimens, which were much more susceptible to deterioration and required greater concentrations of additives in the deicing solution.

From the results of these tests it appears that the most promising additives to deicing solutions for the prevention of cement mortar deterioration are the complexing agents and the polyhydroxy carbohydrate materials. Representative materials of these two classes are the sodium salt of ethylenediamine tetraacetic acid and dextrose. The rate of deterioration was substantially reduced when these materials were incorporated at 5 to 30 percent by weight in the salt. The exact mechanisms by which these materials work were not determined, but it seems quite possible that they affect the permeability characteristics of the cement paste.

The action of the complexing materials, when used in calcium chloride solutions, is especially puzzling, inasmuch as these materials would already be present in a calcium complex form under these conditions and probably could not have much effect on the calcium salt precipitation. The fact that they do reduce the deterioration suggests that some ion other than calcium, possibly magnesium or iron, is the critical component in the formation

TABLE 10  
EFFECT OF ADDITIVES ON DETERIORATION OF  
AGED CEMENT MORTAR SPECIMENS<sup>a</sup>  
SUBJECTED TO 3 PERCENT SODIUM CHLORIDE

ADDITIVE	CONC. (%)	RED. IN DETERI- ORATION (%)
Dextrose, commercial	0.01	28
	0.025	0
	0.05	0
	0.05	6
	0.1	22
	0.15	56
	0.3	34
Sucrose	0.5	91
	0.05	0
	0.15	3
	0.5	75
Mannitol	0.05	8
	0.15	3
	0.5	56
Glycerine	0.05	0
	0.15	3
	0.5	47
Pentaerythritol	0.05	8
	0.5	0
Modified starch A	0.05	0
Modified starch B	0.5	12
	0.05	47
	0.5	72
EDTA-Na	0.05	47
	0.15	16
	0.5	56
NTA-Na	0.05	22
	0.15	44
	0.5	66
Glucoheptonate-Na	0.05	10
	0.15	7
	0.5	12
Methyl glucoside	0.05	9
	0.5	72

<sup>a</sup> Untreated loss 120 mg per sq cm, 15 cycles.

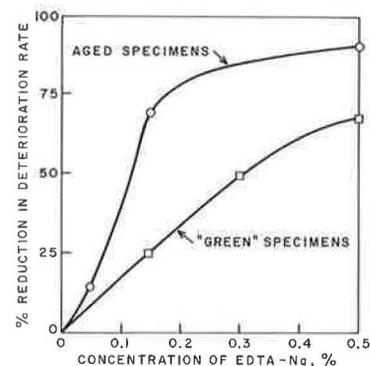


Figure 14. Effect of specimen age on amount of additive needed for protection of cement mortar specimens in freeze-thaw-wash tests.

of the semipermeable characteristic of the cement paste during the freeze-thaw cycle. The ability of sugar solutions to solubilize certain cement components, as indicated by the sugar solubility test, may well play a role in preventing the buildup of a semipermeable membrane by the additives based on the carbohydrate structure.

TABLE 11  
EFFECT OF ADDITIVES ON DETERIORATION OF  
"GREEN" CEMENT MORTAR SPECIMENS<sup>a</sup>  
SUBJECTED TO 1 PERCENT SODIUM CHLORIDE

ADDITIVE	CONC. (%)	RED. IN DETERI- ORATION (%)
Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	1.0	67
	0.15	4
Sucrose	0.5	54
	0.15	28
Borax	0.5	0
	0.15	0
EDTA-Na	0.5	68
	0.15	44

<sup>a</sup> Untreated loss 304 mg per sq cm, 12 cycles.

TABLE 12  
EFFECT OF ADDITIVES ON DETERIORATION OF  
"GREEN" CEMENT MORTAR SPECIMENS<sup>a</sup>  
SUBJECTED TO 6 PERCENT CALCIUM CHLORIDE

ADDITIVE	CONC. (%)	RED. IN DETERI- ORATION (%)
EDTA-Na	0.5	49
Sucrose	0.5	42
Citric acid	0.5	44
Gluconic acid	0.5	30
Sulfonate wetting agent	0.5	22

<sup>a</sup> Untreated loss 158 mg per sq cm, 12 cycles.

### *Freeze-Thaw Tests with Large Concrete Specimens*

The tests reported in the foregoing were all run on mortar bars. In an effort to obtain results which might be more directly applicable to the field, a series of tests was run on large concrete specimens. The series included both the non-chloride deicing chemical composition and the two representative additives with sodium chloride. The specimens were evaluated by visual inspection and by determination of the sonic modulus.

Unfortunately, these tests with portland cement concrete specimens did not yield any useful results. The sonic modulus determined on these test specimens before starting the test gave values of from 1.2 to  $3.4 \times 10^6$  psi. This indicates an unfortunate lack of reproducibility in

the specimens themselves. The type of attack found in these tests seemed to be a general weakening and softening of the specimens rather than a surface spalling, which had been expected (based on previous results). The results of the visual inspection and the sonic modulus determinations were not reproducible enough to draw any firm conclusions except that the test using distilled water showed considerably less deterioration than those using either sodium chloride, sodium chloride with EDTA-Na added, sodium chloride with dextrose added, or tests with the organic deicer mixture discussed earlier. These tests were made in the final weeks of the program; there was not sufficient time to re-run them because of the long cure period needed for the specimens and the long test periods involved.

## CHAPTER THREE

# APPRAISAL OF RESULTS

### CORROSION

Both the corrosion of automobiles in areas of accumulated dirt and debris and the corrosion of reinforcing steel in cracked concrete involve similar mechanisms—steel corrodes in areas of reduced oxygen supply. This differential aeration type of corrosion behaved similarly in both systems when the deicing solution was modified. The corrosion rates were two or more times faster in the presence of dilute chloride solutions than in the presence of plain water. Two general approaches reduced the corrosion caused by the presence of deicing solutions: (1) the use of non-chloride deicers and (2) the addition of chemicals to the salt to reduce the corrosivity.

Many of the alternate deicers which were in a practical economic range suffered from insufficient solubility (high eutectic point) or were unsatisfactory for reasons of corrosivity, volatility, etc. The most practical solution along these lines appears to be a mixture of organic materials, urea, calcium formate, and formamide. For moderately low temperatures a mixture of the solid urea and calcium formate could be spread, and for very low temperatures the liquid formamide would be added by a spray device or other means. These materials were the least corrosive of any material or formulation tested for reinforcing steel in cracked concrete. The main disadvantages of these materials are their increased cost and the complexity of operation in their use. This overall increase in cost would probably restrict their use to areas such as bridge decks where reduction in the corrosion of metallic structural components could justify the added expense.

The second type of solution involves the use of chemical additives to the salt to reduce the corrosivity of the deicing solutions. This type of solution has some advantages:

the cost will be lower, the chlorides are very effective deicing agents, and application to bridge decks and other sensitive areas will not be harmed by tracking of material to the area from the roadway. If a non-chloride chemical is used on sensitive areas, the tracking of chlorides to the area may cause accelerated corrosion even though the deicer used is itself noncorrosive. With the additive approach this will not be a problem if the additive is used in sufficient concentration.

Polyphosphate-based formulations were found to give significant reductions in the corrosion rate of salt solutions. In the test for corrosivity of reinforcing steel in cracked concrete, for example, a typical commercial polyphosphate treatment and a polyphosphate treatment containing small amounts of a zinc salt and sodium silicate reduced the corrosivity of a 3 percent salt solution by about 50 percent. Thus, the corrosivity was about equal to that of plain water.

On some of the tests designed to simulate corrosion of automobile bodies in areas of dirt accumulation, the polyphosphates gave an even greater percentage reduction. The addition of small amounts of lime with the polyphosphates increased the corrosion protection, probably because of the alkaline nature of the lime and the fact that polyphosphates are more effective in the presence of calcium. The alkaline nature of the lime might cause some problems, however, so its use would have to be restricted to small amounts. One problem which might arise in the field use of polyphosphates is their tendency to revert to the less active orthophosphate. Although replenishment of the inhibitor by repeated application of deicing chemicals or the dilution of the salt by melting snow and ice on warm days may make this problem insignificant, this aspect should be carefully observed in any field testing.

Another class of additives which resulted in significant reductions in corrosion were the long-chain amine materials. Several of these amine materials resulted in appreciably reduced corrosion rates in the automobile dirt-steel test, but were somewhat less effective than the polyphosphates in reducing rates of corrosion. The amine included in the concrete-reinforcing steel test was at least as effective in reducing corrosion rates as the polyphosphates on this test. These amine materials have the advantage that they would not suffer from reversion as might be the case with polyphosphates. They are, however, somewhat more expensive and may be more difficult to apply.

From the point of view of corrosion, none of the salt-plus-additive solutions gave test results which were as satisfactory as with the organic deicing materials.

### CONCRETE DETERIORATION

The results of the concrete deterioration phase of the project are not as clear-cut as the results of the corrosion phase. Two types of attack occurred on cement mortar bars when a freeze-thaw cycle was used in the presence of deicing chemical solutions—surface spalling and a general softening and cracking. Most of the tests were run by a method which seemed to be sensitive to the spalling type of attack. In this type of test the rate of deterioration was highest for lower concentrations of salt and for lower freezing temperatures. In fact, no deterioration was found when the tests were run on dilute solutions at 20 F, but severe attack was experienced at -20 F. It appeared that this type of attack of chloride solutions could be reduced substantially by adding chelating agents or sugar-derived compounds to the chloride. The amount of additive required was relatively high and increased in ratio to the salt as the concentration of salt was reduced. For example, when a 3 percent salt solution was used, the amount of additive required ranged from 10 to 15 percent, based on the weight of the salt. Also, the amount of additive required and the rate of deterioration increased if the cement mortar was not aged long enough before exposure. The use of additives with deicing salts to prevent concrete deterioration might prove useful in those areas which are especially sensitive to spalling, such as bridge decks and concrete that has not had time to age before the freezing season.

The use of non-chloride deicers was not as effective in reducing the attack on cement mortar as in reducing corrosion. The rates of deterioration were somewhat lowered as compared with sodium chloride, but not sufficiently to justify their added expense.

In the tests in which the attack appeared to be primarily of a cracking and softening nature, the more concentrated solutions of chloride deicers were the most aggressive, and the use of additives did not appear to be as successful. However, results from this test do not appear to be too reliable, inasmuch as interpretation was complicated by poor reproducibility and the apparently different type of attack found in the test series as compared with the spalling attack more commonly found in the field.

### CHEMICAL FORMULATION RECOMMENDATIONS

The following are the specific chemical formulations recommended for field testing to confirm the results of this program.

#### *Alternative Organic Deicing Chemicals*

The basic mixture consisting of from 1 to 2 parts of urea with 1 part of calcium formate is recommended as an alternative deicing chemical to be used instead of chlorides. It should be tested initially at a rate of application twice that used for chlorides. This solid mixture should be used to moderately low temperatures, probably in the range of 5-10 F. When the temperature drops too low for this mixture, it would be necessary to add 1 part of formamide by spraying. Formamide, however, is known to be an irritant under some conditions and possible hazards should be investigated before it is used generally.

#### *Materials to Reduce the Corrosivity of Chlorides*

Polyphosphate treatments can be used in several ways to reduce the corrosivity of sodium chloride deicing solutions. A commercial polyphosphate formulation was found to be effective in the laboratory tests, and it is probable that other commercial polyphosphate formulations can be obtained which will also be useful.

In addition, formulations consisting of 62 percent of a long-chain polyphosphate, 6 percent zinc chloride, and 32 percent sodium metasilicate, or of 63 percent slaked lime and 37 percent sodium polyphosphate, were found effective. It is recommended that the polyphosphate formulations be tested at 2 percent based on the weight of the salt, except for the lime-polyphosphate material, which should be used at 5 percent.

Although not tested in the program, it appears quite possible that if a deicing mixture containing calcium chloride is used, additives to the polyphosphate would not be necessary. Thus, a sodium polyphosphate material alone could be used with a saving in cost.

Long-chain amines were also found to give substantial corrosion inhibition. Examples of the types which were found effective are Armeen C, Duomeen S, and the Nalcamine G and A series, especially G-11 and A-31. It is recommended that these materials also be used in concentrations of 2 percent by weight of the salt. These materials may be somewhat more difficult to apply and more expensive, but their use might be justified if the effective life of the polyphosphate materials proves to be too short in the field tests.

#### *Materials to Reduce Concrete Spalling*

Various materials were found to be effective additives to sodium and calcium chloride deicing chemicals to reduce concrete spalling. Representative of the types of materials found to be effective are dextrose and the sodium salt of ethylenediamine tetraacetic acid. These are recommended as the materials for the field tests. The concentration needed appears to be at least 5 percent by weight of the salt.

### Future Work

There are two areas of work which appear to be highly desirable extensions of the present program. The first involves field testing of the results of this program. The second would be a basic laboratory study of the mechanisms of concrete deterioration. The following are descriptions of some of the areas which should be covered in these investigations and the possible benefits which might be realized.

*Deicing Agent Field Test.*—This project has involved a laboratory investigation of deicing agents which might be less aggressive toward steel and concrete than are presently used chloride deicing agents. The program has resulted in development of new deicing materials, and additives for use with present chloride deicers. These materials have been tested in the laboratory using methods designed to give results indicative of their performance in the field. However, there are a number of variables and factors in field use which cannot be satisfactorily incorporated into a laboratory investigation. Thus a field testing program is desirable. The following points should be covered in such an investigation:

1. The proposed organic deicing mixture should be evaluated for speed of melting at various temperatures and conditions and its spreading and storage characteristics determined.
2. The corrosivity of the present chloride deicers should be compared with that of the organic deicing mixture and with that of chlorides inhibited with polyphosphate-based materials or the long-chain amine type of inhibitor. The evaluation of automobile corrosion is subject to so many variables that a useful program is prohibitively expensive. However, useful information on this problem and on the corrosion of exposed structural steel elements could be

obtained by the placement of properly designed corrosion specimens in the splash zone alongside the roadway being deiced. In addition, corrosion specimens should be embedded in the concrete to determine the effect of the deicing composition on the corrosion of reinforcing steel. In both of these types of exposure the use of corrosion probe specimens would be desirable to determine the corrosion rate as a function of time. This will permit correlations between the corrosion rates and such factors as weather and length of exposure.

3. The value of the addition of chelating and sugar-type compounds to chloride deicers to control the deterioration of concrete should be investigated. This investigation should include both new and aged concrete in bridge areas where spalling is considered possible.

### Investigation of Mechanisms of Concrete Deterioration

A major area in which further laboratory investigation is needed is the elucidation of the mechanisms responsible for the deterioration of concrete in freeze-thaw exposure. Some of the results obtained in the present program gave clues on possible mechanisms, and there is some work reported in the literature in this area. A systematic study is needed, however, to determine the processes which take place. This should include chemical analysis, thermogravimetry, differential thermal analysis, and X-ray analysis of the structure changes which take place. The effect of temperature and deicing chemicals on the solubility and permeability of the various cement phases should be determined. A better understanding of these processes would materially contribute to any future efforts to control deterioration, and should aid in the development of more resistant concretes through the use of admixtures or the control of composition.

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## APPENDIX

### IDENTIFICATION OF PROPRIETARY COMPOUNDS

- A. Olin Mathieson Chemical Co., Joliet, Ill.  
Sodium Polyphos.
- B. Nalco Chemical Company, Chicago, Ill.  
Nalcamine G-11 and G-12—C<sub>12</sub> and C<sub>18</sub> hydroxyethyl imidazolines.  
Nalcamine G-39M—fatty aminoethyl imidazoline.  
Nalcamine A-12—C<sub>18</sub> amidoethanolamine.  
Nalcamine A-31—C<sub>12</sub> amidoethylenediamine.  
Nalquat G-8-11 and G-8-12—C<sub>12</sub> and C<sub>18</sub> benzyl imidazoline quaternarys.
- C. Armour Chemical Company  
Armeen C—coco amine\*.  
Duomeen C—coco propylenediamine\*.  
Duomeen S—soya propylenediamine\*.  
Armeen 2C—di-coco amine\*.  
Armeen DMCD—dimethyl coco amine\*.  
Ethomeen C/25—ethoxylated coco amine.
- D. Wyandotte Chemical Company  
Benax 2A1—a sulfonate wetting agent.
- E. Bryton Chemical Company, Marcus Hook, Pa.  
43L, T, HY—sodium sulfates.
- F. Shell Oil Co.  
Shell OS—an oil-soluble sodium petroleum sulfonate.
- G. Dow Chemical Co.  
Versene 100—solution of sodium salt of ethylenediamine tetracetic acid.
- H. Corn Products Co.  
Cerelese 2001—commercial dextrose.  
Starch 7001, 7071—modified starches.  
Glucoheptonate-Na—commercial sodium glucoheptonate.
- I. Geigy Chemical Co.  
Chel NTA—solution of sodium salt of nitrilotriacetic acid.
- J. Calgon Corp.  
Banox—a commercial corrosion inhibitor for use with deicing salt; contains polyphosphates.

\* Tested as the acetate salt.