

## Additives to Lessen the Damage Caused by Road Salt

Peter P. Hudec

*Geology Department, University of Windsor, Windsor, Ont., Canada*

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### ABSTRACT

Road salt NaCl is the common deicing agent used in the northern latitudes of North America. However, the price of keeping the road safer in winter is the deterioration of pavements, bridges, and parking garages, and the despoiling of the environment. The deterioration is in the form of scaling of concrete surfaces and oxidation of reinforcing steel bars.

Alternatives to NaCl have been suggested; some are as harmful (KCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, urea), while one definitely harmless deicer, calcium magnesium acetate or CMA, is about 10 times as expensive. The research carried out by the author suggests that it is possible to add certain chemicals to the NaCl salt to reduce its undesirable effects while still maintaining the deicing action. Of these, the phosphate group of chemicals has proven to be the most attractive. Experiments have shown that certain Na, K, and Ca phosphates can reduce the freeze-thaw damage significantly when mixed in 5-10% concentration with salt.

The paper discusses the benefits obtained by mixing of various types of phosphates with salt in varying proportion. To reduce the freeze-thaw damage by one half, it is estimated that using the Ca phosphate additive will approximately double the cost of the NaCl deicer. Phosphates, of course, are anti-corrosion agents; experiments have shown that addition of phosphate also significantly reduces or eliminates corrosion to any exposed steel.

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### INTRODUCTION

The use of deicing salts (largely NaCl) in the northern latitudes of North America has resulted in progressive deterioration of the concrete road infrastructure, especially the bridges. The infrastructure replacement costs are estimated at several hundred million dollar annually. The use of the chloride-based salts for deicing is increasingly questioned, and non-damaging deicing alternatives are being actively promoted. One such alternative, calcium magnesium acetate (CMA), is finding increasing favour, mainly because it is non-corrosive and environmentally benign. Although CMA costs 10 to 20 times as much as NaCl, when the cost of repair and environmental damage is factored in, it is increasingly a more attractive alternative.

If the chloride salts are to continue as deicers, either the aggregate, concrete, and steel which they degrade must be made more resistant to them, or the chloride salts must be made less aggressive. Physical separation of less resistant particles to improve the quality of the aggregate has been used successfully for years. It is based on the observation that most deleterious aggregate fragments are generally of

lower specific gravity than the bulk of the 'good' aggregate. Heavy liquid suspension is the most common method of 'floating' and separating the deleterious fraction. The method works on such materials as chert, shale, and weathered rock fragments. It is ineffective against the more subtly deleterious particles, such as very fine grained and argillaceous fragments of many rock types, but especially carbonates. Surface coating of aggregate by polymers and oils (Cady et al., 1978; Ohama et al., 1987) has been suggested means of beneficiation. The surface coating, to be effective, should not affect the bonding properties of aggregate, and should, preferably, be permeable to water but not to salt — a molecular sieve. Similar techniques have been tried on concrete, with varying degrees of success.

A better approach to minimize the aggressiveness of sodium chloride deicing salt is to interfere chemically with the aggressive process. Before this can be attempted, an understanding of the aggressive process is required. The following section describes the causes of *physical* breakdown of porous materials — aggregate, brick, concrete, etc. — under the influence of NaCl deicing salt.

## GENERAL THEORY OF DEICER DAMAGE

A classical paper on the relationship of the physical properties on the frost resistance of aggregates was written by Verbeck and Landgren (1960). Since then it was found that the grain size, pore size, and total internal surface area of rock aggregates has a major influence not only on freeze-thaw durability, but also on wetting-drying resistance and overall durability of the aggregate. As the grain size decreases, the total surface area of the same mass of solid increases. Internal surface area of a rock composed of fine particles plays a major role in aggregate and concrete deterioration (Hudec, 1989a).

The physical breakdown observed in diverse materials is strikingly similar, starting with the development of microfractures and cracks. These may lead to complete disintegration of the material. Deterioration occurs only in the presence of water. Pure water was shown to be innocuous; it is the nature and the concentration of dissolved ions in the water that dictate the severity of deterioration. The general scenario of deterioration involving dissolved ions was summarized by Hudec (1989b) and can be outlined as follows:

The pore surfaces possess residual charges, usually negative, the strength of which is the function of the degree of disorder in the crystal lattice of the minerals making up the surface. The surfaces attract the ions dissolved in pore water, concentrating them in layers along the surface. The small pores thus contain a higher concentration of ions relative to a larger pore; an osmotic differential may develop with attendant expansive and contractive forces. The expansive forces, acting against the tensile strength of the solid, may microfracture the solid, creating more fine pores. Changes in the conditions of exposure such as wetting, drying, freezing, and thawing affect the pore water ion concentration, and thus the magnitude of the osmotic force. These changes are reflected in the volume change of the solid. The solid particle itself may be disrupted, or, by virtue of expansion, exert disruptive forces on the enclosing matrix, fracturing it (as in the case of an aggregate particle in concrete).

Not all ions are equally disruptive. The cation with high charge/ionic size ratio, such as Na, behave more aggressively than a larger K ion. The aggressive behaviour of the ions is not restricted to creating destructive osmotic forces. Na and K cations are involved in an alkali-silica and alkali-carbonate reaction that has proven destructive to concrete.

The cation in the deicing salt is thought to be preferentially attracted to the pore surface, and in turn attract the polar water molecules to itself. One

way to decrease or eliminate the deleterious effects of salt cations is to either not allow them access to the pores (semi-permeable or impermeable membrane), displace them by other ions, or satisfy their charge, and thus minimize their attraction for water molecule. It is this latter approach that was chosen for the research described in the following sections.

General durability and response of aggregates to freezing and thawing can be determined by a variety of direct and indirect tests. Freezing and thawing of aggregates is perhaps the most direct way of determining their resistance to this climatic factor. Several tests exist for this purpose. The freeze-thaw test that gives the most consistent results, is relatively fast, and best approximates the conditions of freezing and thawing in service. It has been developed by the author, and is now used as a specifying test by the Ontario Ministry of Transportation (MTO, 1989, No. LS-614). The test is performed by first saturating the aggregate in 3% by weight of NaCl solution for 24 h. The aggregate is then placed in a mason jar of sufficient size with 2-3 ml of solution remaining in the jar. The jar is sealed, placed on a side, and frozen for 16 h at  $-18^{\circ}\text{C}$ , and thawed at room temperature for 8 h. The freeze and thaw cycle is repeated five times, the jar rotated 1/4 turn with each cycle. Loss is determined by back-sieving on the same size sieve. A more severe variation of the test is to place the aggregate on a saturated mat or sponge in a flat container rather than the jar.

Corrosion of steel by chlorides, both the steel embedded in the concrete (reinforcing bars) and the exposed steel (girders, railings, cars, etc.) is well known. Corrosion of rebars is a chemical process, aided by the physical deterioration of the concrete by the freezing and thawing cycles. The physical deterioration theories will be discussed briefly. The understanding of the physical deterioration process, and the role of the deicing salt (NaCl) in it, is essential before an alternate deicer can be found. The main variables in the frost damage of porous materials are the nature of the pore surface, pore and capillary size, pore and capillary size distribution, and the total internal surface area per unit volume.

## OSMOTIC THEORY OF FREEZE-THAW DETERIORATION

### Nature of pore surface

All surfaces, including mineral surfaces, possess a surface charge; the amount of charge is a function of the nature of the surface. In minerals that make up the rock used as natural aggregate, the surfaces can be mineral faces (rarely), cleavage faces, and frac-

ture faces. The latter are the most active, since fracture surface breaks randomly across chemical bonds of the mineral; cleavage face represents a direction of minimum bonding between elements of the crystal and are less active. Furthermore, if the crystal is 'imperfect', i.e., has an incomplete lattice, or a lattice in which under- or over-size elements substitute, or has a lattice that has been tectonically strained, the surfaces of that mineral will possess a greater charge. The charge on the surfaces is generally negative. The negative surfaces attract polar water molecules. The action is similar to that of sorption of cations onto clay particles — the "double layer" theory.

### Effect of grain size

The grain size was visually categorized as 1 = small (fine), 2 = medium, and 3 = coarse. The results of the freeze-thaw test were plotted against these categories, and are shown in Fig. 1. The coarse grain sized aggregate showed a uniform low loss; as the grain size decreased, the loss increased. The fine grained aggregate showed a wide range of losses, indicating that the grain size alone is not a good indicator of freeze-thaw resistance. It does, however, suggest that the fine-grained rocks are more prone to freeze-thaw damage.

The grain size by itself has no effect on durability. It is the pore size related to grain size that does. Fine grain size produces fine pore size, which in turn produces large internal surface area for water and ion sorption. The relationship between water adsorbed at 98% relative humidity and at 23°C, and the freeze-thaw loss is illustrated in Fig. 2. A good correlation is seen, as expected from previous work by the author and others (Hudec, 1987). Water is adsorbed on the surfaces of the pore wall; if the pore is small enough, the adsorbed water can completely fill the pore. The pore thus contains water of lower vapour pressure than the water in the surrounding, larger pores, and becomes a centre of osmotic in-flow. Water adsorbed at the humidity of the experiment fills pores less than 1  $\mu\text{m}$  in diameter. The correlation suggests that more small pores the rock contains, the more prone it is to freeze-thaw damage. These pores can be termed "force pores", in that they are probably responsible for the expansive forces that expand and deteriorate the rock.

If the rock is saturated in the deicing solution, dried, and then exposed to the same humidity conditions, the amount of water adsorbed increases. Figure 3 shows the relationship between water adsorbed on the same sample before and after treatment with 3% NaCl salt solution. It is seen that the salted specimens adsorb approximately 10%

### FREEZE-THAW LOSS vs GRAIN SIZE

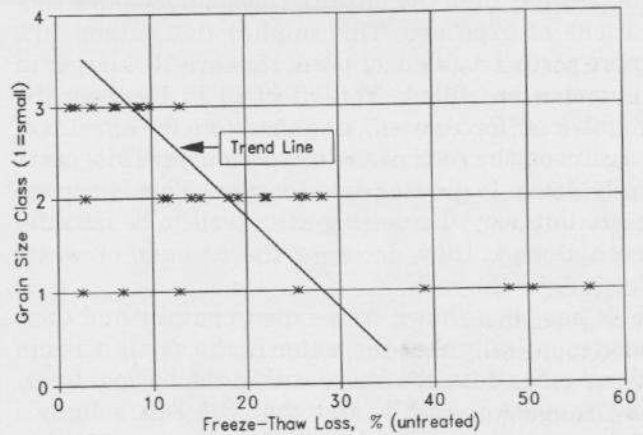


Fig. 1. Relationship of grain size to freeze-thaw loss.

### FREEZE-THAW LOSS vs ADSORPTION

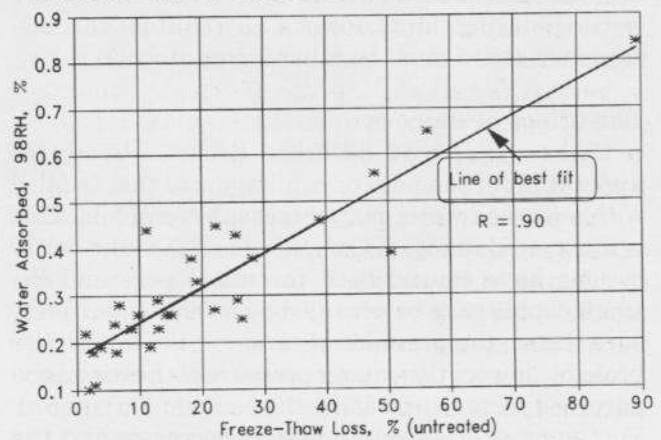


Fig. 2. Freeze-thaw loss as function of water adsorption at 98% relative humidity, 22°C.

### ADSORPTION Untreated vs NaCl Treated

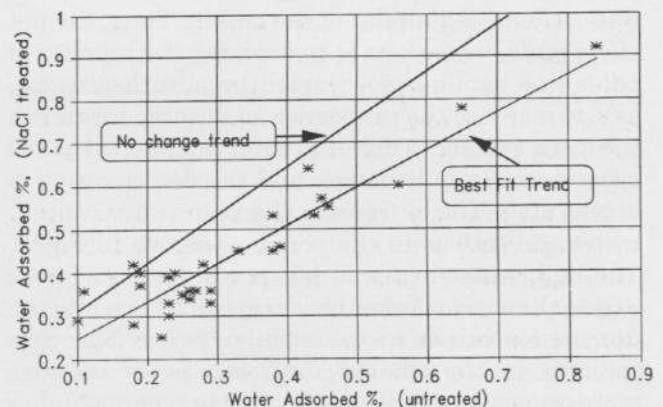


Fig. 3. Relationship between water adsorbed before and after treatment with 3% NaCl salt solution.

more water than the unsalted ones under same conditions of exposure. This implies that either 10% more pores are filled, or pores that are 10% larger in diameter are filled. The effect is to increase the number of "force pores", and therefore the amount of expansion the rock particle experiences. This, naturally, leads to greater deterioration. This is one explanation why the deicing salts tend to be harmful even though they decrease the amount of water freezing in the rock.

It has been shown both experimentally and thermodynamically that the water in the small pores in these rocks does not freeze within the normal freezing range (to  $-20^{\circ}\text{C}$ ), and that the salt solutions decrease the amount of water freezing in all porous materials. If there is no freezing, or the amount of water freezing is reduced, then obviously there must be a decrease in the hydraulic stress caused by freezing. Yet salt solutions increase the freeze-thaw (and wetting-drying) breakdown. To account for this discrepancy, there must be other forces at work.

#### The effect of deicers

If the pores hold adsorbed deicer cations, the upper limit of the pore or capillary size that is filled with adsorbed water may increase several fold. This is illustrated in Fig. 5. Compared to Fig. 4, the deicer cations have caused both the micro pore and the small capillary to be occupied by lower vapour pressure water; the presence of cation in the micro pore probably lowers the vapour pressure of the contained adsorbed water, increasing the osmotic differential. The amount of vapour pressure decrease, and the number of additional capillaries occupied by low vapour pressure water is a function of the concentration of the cations in the pore, the ionic size to charge ratio, and the clustering geometry of the water-ion system. Generally, the smaller the ionic radius and smaller the ionic size to charge ratio, the greater the water clustering ability of the cation. Thus, the net effect of deicer cations is to increase the number of pores and capillaries occupied by adsorbed water, and to increase the proportion of adsorbed water in the pore system. Thus a greater number of pores become osmotically active, and the deterioration is accelerated. The of freezing the pore water concentrates the cations in the pores, as shown in Fig. 6. The bulk water in the larger pores that can freeze expels the cations from the ice crystal lattice into the unfrozen solution in the smaller pores. The pore solution in the smaller, unfrozen pores becomes more concentrated. Thawing of ice provides a higher vapour pressure water which resides in the larger pores. The osmotic pressure difference between the concentrated solution and the 'outside' world of

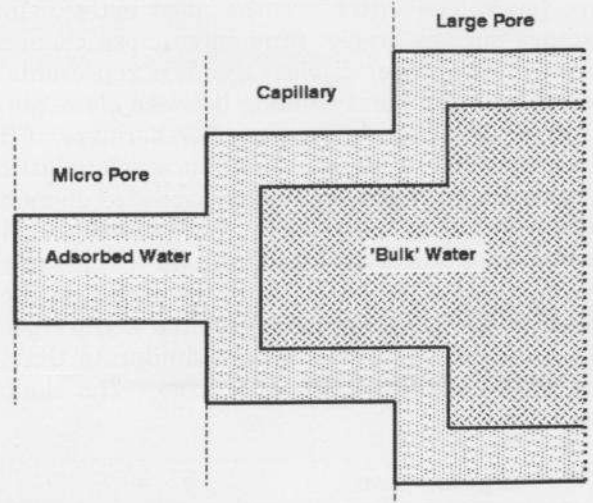


Fig. 4. Schematic diagram illustrating adsorbed and bulk water content in rock pores.

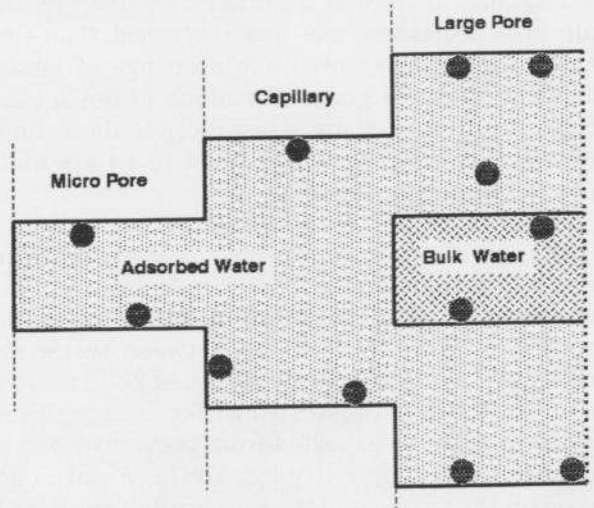


Fig. 5. Schematic diagram illustrating the effect of cations on the thickness of adsorbed water later in rock pores.

larger voids and capillaries increases. This in turns increases the severity of the deterioration.

#### Most damaging deicer concentration

Tests have shown that the most damaging NaCl deicer solution concentration is between 3 and 5% by weight. This is shown in Fig. 7, in which the results of the scaling tests on mortar cubes are given in NaCl solution of 3, 10, and 20% concentration. It is seen that the 20% concentration resulted in no scaling; freeze-thaw tests in 20% solution give similar results to freeze-thaw tests in water. Similar concentrations have been found for glycol, alcohol, and other chloride salts. This 'pessimum' concentration

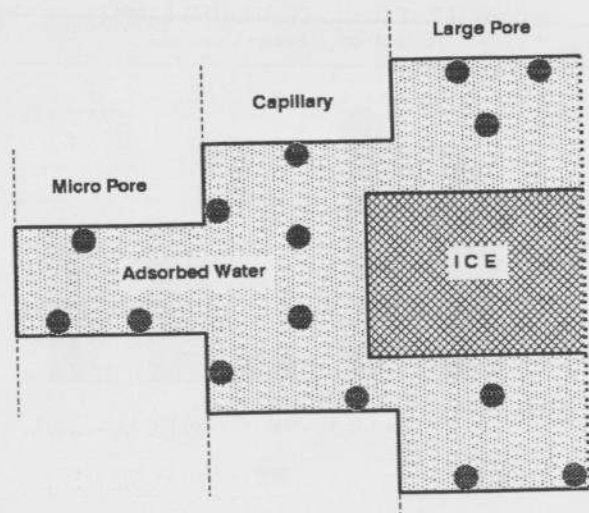


Fig. 6. Schematic diagram illustrating the freezing of water in larger pores, expelling and concentration contained cations.

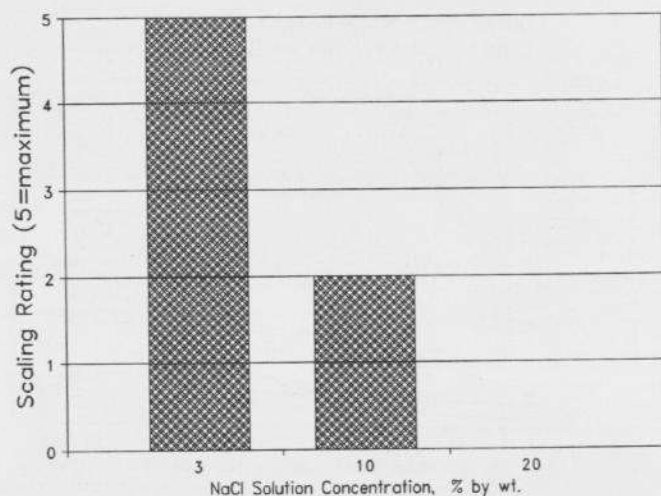


Fig. 7. Scaling test in NaCl solutions of 3, 10, and 20% concentration by weight.

is difficult to explain by the hydraulic theory of freeze-thaw failure. However, the osmotic theory gives an acceptable explanation of the pessimum effect.

All surfaces have a potential to adsorb ions. However, the sorption potential is finite. When the surface reaches its saturation potential, it can no longer adsorb; it will in fact repel additional ions of the same type. However, different, more aggressive ions or different ions in greater concentrations will replace the first sorbed ions — the well known concept of ionic exchange in soil science and clay mineralogy. The finer pores and capillaries, because of surface effect, can contain only a finite number of ions; how-

ever, the larger pores, away from the surface, can be filled with highly concentrated solution. An osmotic flow from the finer to coarser pores can result in shrinking or desiccation of the fine pores. The effect can be readily seen in desiccation shrinkage of fresh water clays placed in a brine solution. The shrinkage, however, is compressive, and acts against the compressive strength of the rock; it is therefore well resisted, and does not, in itself, cause problems. This explains why mortar shows almost no scaling in 20% as shown in Fig. 7.

## REDUCING THE DEICER SALT DAMAGE

Assuming the above scenario of deicer salt damage is correct, then to reduce the physical deterioration due to the fine pore system requires that the osmotic differential among the pores be reduced. The osmotic difference will be reduced if the proportion of adsorbed, low vapour pressure water is reduced.

Two potential remedies are suggested: (1) Satisfy the cations of the current deicer salts (NaCl) by substituting a strong anion that will preferentially bind to the cation at the expense of the water molecule, thus reducing the amount of adsorbed water; or (2) Develop a deicer that does not cluster water molecules and does not increase the adsorbed water content. The first suggestion can be accomplished by admixing a large ionic size, strongly electronegative anion salt to NaCl or CaCl deicer. The second remedy requires testing a variety of salts for their effectiveness in melting ice without causing scaling damage to the porous materials.

## Preventive treatments with existing deicer (NaCl)

Numerous chemical compounds were tested for their effectiveness as NaCl additives. The compounds were chosen mainly on the basis of their active anion, with the theory that the anion would bond with the adsorbed Na cation and interfere with water adsorption. Some of the major anion groups tested were nitrates, borates, other chlorides, and phosphates. The latter were found to be most effective, especially the mono cation phosphates: mono sodium, potassium, and calcium phosphates. Ammonium phosphates were also effective.

## Salt treatment

Figures 8 and 9 show the effect of mixing 5% of NaCl with 5% of the mono sodium and mono calcium phosphates respectively. The salts were dissolved in water, aggregates saturated, and the freeze-thaw test was carried out as described above. The results are compared to the 'untreated' solution, i.e., one

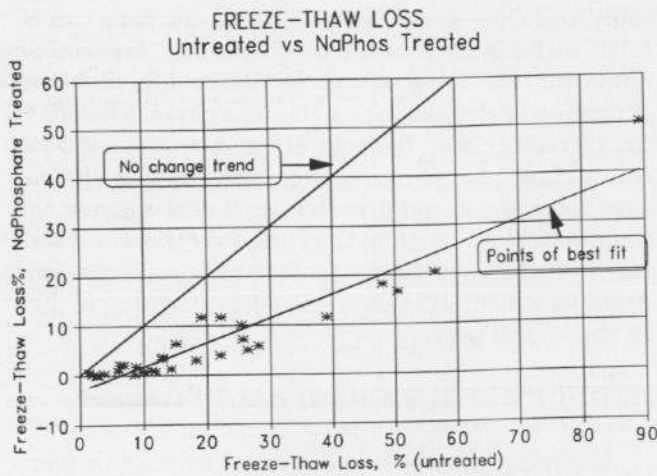


Fig. 8. Reduction of freeze-thaw damage by 1:1 admixture of Na phosphate to NaCl.

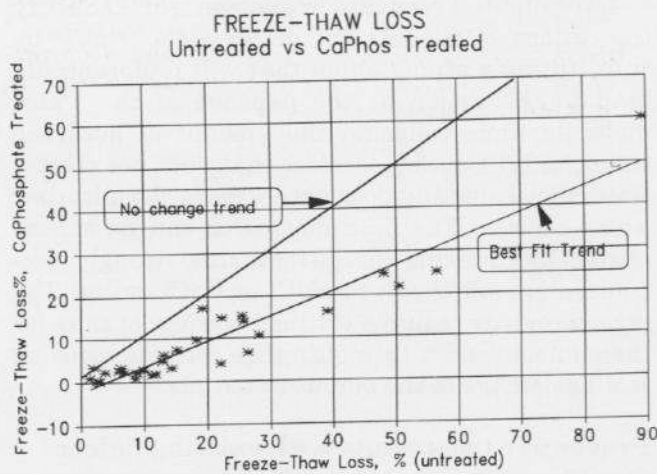


Fig. 9. Reduction of freeze-thaw damage by 1:1 admixture of acidified mono calcium phosphate to 5% NaCl.

containing only 5% NaCl. The figures show that the Na phosphate-salt mixture significantly reduced the freeze-thaw breakdown; Ca phosphate was somewhat less effective. The difference in effectiveness may be due to the almost infinite solubility of Na phosphate, whereas Ca phosphate is insoluble under normal pH conditions, and can only be dissolved in an environment of pH of less than 3. Upon contact with reducing conditions (such as carbonate aggregate), the phosphate precipitates as a film in the pores.

Precipitation of ammonium phosphate in the pores of concrete may confer a longer-lasting protection, as evidenced by samples treated with ammonium phosphate, and then subjected to leaching, followed by freeze-thaw test (Fig. 10). Ammonium phosphate (either administered with salt or directly to the

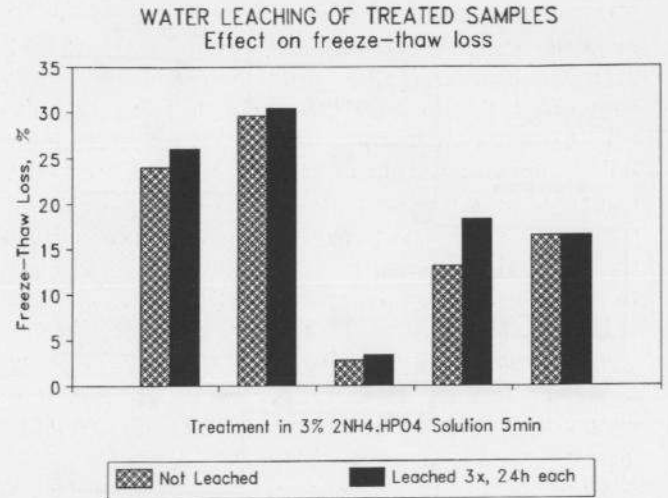


Fig. 10. Effect of leaching of treated aggregate on the freeze-thaw durability.

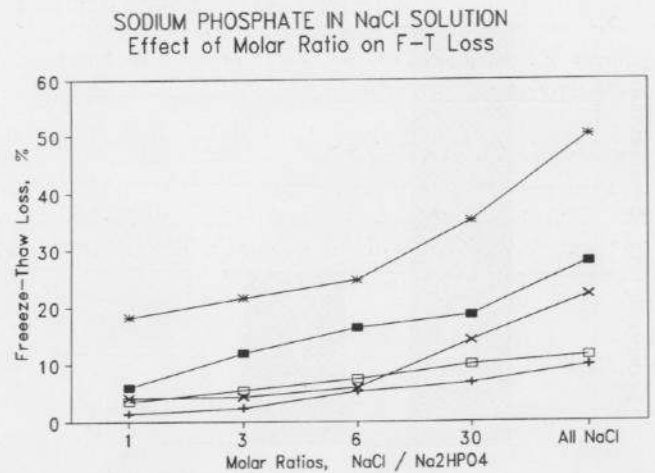


Fig. 11. Reduction of freeze-thaw damage by admixtures of Na<sub>2</sub>HPO<sub>4</sub> in NaCl.

aggregate) conferred residual protection against NaCl induced freeze-thaw breakdown as shown by lower losses of leached, treated samples as opposed to non-treated samples.

The effect of different proportions of Na phosphate to NaCl salt (expressed as molar ratios) on freeze-thaw loss is shown in Fig. 11. The figure shows results obtained for five different aggregate types. Significant reductions in freeze-thaw damage are achieved at molar ratios as high as 30 moles of Na chloride to 1 mole of Na phosphate.

### CONCLUSIONS

The immediate and residual protection of calcium phosphate admixture in rock salt, and the relatively

low molar ratios of phosphate required to confer protection to concrete and aggregate make the rock salt-calcium phosphate mixture a viable deicing compound. The cost of the first Ca phosphate admixture to rock salt to reduce freeze-thaw damage by half is approximately twice that of untreated salt. Subsequent applications of deicer-phosphate mixture can contain less phosphate (and cost less) due to the residual protection effect. Ca phosphate is thought to be relatively harmless to the environment because of its low solubility under ambient pH conditions.

More research is needed in the laboratory to determine the most viable and economic mixtures of rock salt and phosphate. Field exposure tests need to be conducted to test the mixtures in practice.

Phosphates are well known as rust and corrosion inhibitors in metals; laboratory experiments have shown that small amounts of phosphate in NaCl solution will protect ferrous metals from rust — an added bonus.

U.S. and Canadian patents have been granted to the author on the use of calcium phosphate as a beneficiating agent for aggregate, concrete, and deicing salts.

#### ACKNOWLEDGEMENT

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