

Effect of Salt Additives on Concrete Degradation (Phase II)



Research

FUNDING ACKNOWLEDGEMENT

This project was conducted with funding provided by the Minnesota Local Road Research Board (LRRB). The LRRB's purpose is to develop and manage a program of research for county and municipal state aid road improvements. Funding for LRRB research projects comes from a designated fund equivalent to 1/2 of one percent of the annual state aid for county and city roads.

Technical Report Documentation Page

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|--|--|--|-----------|
| 1. Report No. MN/RC - 96/10 | 2. | 3. Recipient's Accession No. | |
| 4. Title and Subtitle EFFECT OF SALT ADDITIVES ON CONCRETE DEGRADATION (PHASE II) | | 5. Report Date February 1995 | |
| | | 6. | |
| 7. Author(s) Ji-Won Jang, Iwao Iwasaki, Paul Weiblen | | 8. Performing Organization Report No. | |
| 9. Performing Organization Name and Address University of Minnesota Department of Geology and Geophysics 108 Pillsbury Hall 310 Pillsbury Drive SE Minneapolis, MN 55455 | | 10. Project/Task/Work Unit No. | |
| | | 11. Contract (C) or Grant (G) No. (C) 71262 TOC #120 | |
| 12. Sponsoring Organization Name and Address Minnesota Department of Transportation 395 John Ireland Boulevard Mail Stop 330 St. Paul Minnesota, 55155 | | 13. Type of Report and Period Covered Executive Summary 1994-95 | |
| | | 14. Sponsoring Agency Code | |
| 15. Supplementary Notes | | | |
| 16. Abstract (Limit: 200 words) <p>This research builds on a previous investigation, which found that corrosion-inhibitor-added deicing salts caused degradation of concrete by both anions and cations. The latest research phase looked at methods to detect the chemical reactions between concrete and corrosion-inhibitor-added deicing salts, and to determine the chemical compositions of the precipitates formed by chemical reactions between concrete and the corrosion-inhibitor-added deicing salts.</p> <p>The research led to the following conclusions:</p> <ul style="list-style-type: none"> ● a simple method was developed for the detection of chemical reactions between deicing chemicals and concrete; ● the results provided clear evidence of the chemical reactions between concrete and the corrosion-inhibitor-added deicing salts; ● the different amounts of precipitates (chemical reaction products) found in the test cells were dependent on the type and concentration of corrosion-inhibitor-added deicing salts; ● precipitates formed by chemical reactions between deicing chemicals and concrete were identified by using chemical analysis, scanning electron microscopy, and X-ray diffraction analysis; ● and precipitates were calcium and/or magnesium phosphates as a major component, and gypsum as a minor component. | | | |
| 17. Document Analysis/Descriptors Precipitates Corrosion-inhibitor-added Deicing Salts | | 18. Availability Statement No restrictions. Document available from: National Technical Information Services, Springfield, Virginia 22161 | |
| 19. Security Class (this report) Unclassified | 20. Security Class (this page) Unclassified | 21. No. of Pages 20 | 22. Price |

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Executive Summary

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February 1995

Published by

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This report represents the results of research conducted by the authors and does not necessarily reflect the official views or policies of the Minnesota Department of Transportation. This report does not contain a standard or specified technique.

Acknowledgment

The authors express appreciation to the Office of Maintenance and the Office of Materials, Research, and Engineering of the Minnesota Department of Transportation (Mn/DOT) for support of this report. We are indebted to Henry Gillis of Physical Research and personnel of the Concrete Section of the Office of Materials, Research, and Engineering of Mn/DOT for their help in fabricating the cone-shaped concrete samples.

Executive Summary

This research builds on a previous investigation (1-3), which found that corrosion-inhibitor-added deicing salts caused degradation of concrete by both anions and cations. The precipitates resulting from chemical reactions between concrete and corrosion-inhibitor-added deicing salts were analyzed, and dramatic pH changes were noted in the concrete-saturated solution mixed with the corrosion-inhibitor-added deicing salts.

The effects of the corrosion-inhibitor-added deicing salts on the concrete degradation are not well understood, and the methods for determining the effects of the corrosion-inhibitor-added deicing salts on concrete degradation were not available. This investigation looked at methods to detect the chemical reactions between concrete and corrosion-inhibitor-added deicing salts and to determine the chemical compositions of the precipitates formed by chemical reactions between concrete and the corrosion-inhibitor-added deicing salts.

In the previous investigation (1), cone-shaped concrete samples were fabricated to accelerate the deterioration of the concrete by providing a large exposed surface area to corrosion-inhibitor-added deicing salt solutions. The varying diameter enables quicker penetration in the top portion of sample. Six corrosion-inhibitor-added deicing salts and plain sodium chloride were mixed with deionized water to produce 3, 6, and 20 percent solutions. A sample cone and the test cells are shown in Figure 1.



Figure 1. A cone-shaped concrete sample (a) in the test cell (b) for concrete degradation by corrosion-inhibitor-added deicing salts.

After immersing the concrete samples in the 3, 6, and 20 percent corrosion-inhibitor-added deicing salt solutions for a day, varying amounts of precipitates were observed on the concrete surfaces and/or at the bottom of the test cells depending on the type and the concentration of corrosion-inhibitor-added deicing salts. However, no precipitates were observed in the test cells containing NaCl, either in tap water or in deionized water. The amount of precipitates did increase as a function of time.

As part of this research project, precipitates were collected from test cells for quantitative and qualitative analyses to identify the chemical elements involved in the reactions by using chemical analysis, scanning electron microscopy, and X-ray diffraction analysis. After collecting precipitates from the test cells, precipitates were rinsed three times with alcohol to remove the salt solution by displacement from the precipitates, then dried in an oven at 120 degree C. The chemistry of the precipitates formed by chemical reactions between concrete and deicing chemicals was determined by (i) a DIONEX 4000i ion chromatography for anions and a Perkin Elmer/Sciex Elan 5000 inductively coupled plasma-mass spectrometer for cations, and (ii) a Simens D-500 Diffractometer.

Chemical composition by weight percentages of the precipitates determined by chemical analysis is presented in Table I, and Figure 2 shows the X-ray diffraction patterns of precipitates formed by Deicing Salts B, C, and E. Table II shows the major and minor chemical components in precipitates determined by chemical analysis and X-ray diffraction.

| Deicing Salt | Ca | Na | K | Mg | SiO ₂ | P | SO ₄ | Cl |
|--------------|-------|------|------|-------|------------------|------|-----------------|-------|
| A | 4.22 | 6.20 | 0.01 | 8.65 | 0.63 | 4.91 | 1.68 | 10.12 |
| B | 13.60 | 0.12 | 0.01 | 10.58 | 0.61 | 7.79 | 1.50 | 0.03 |
| C | 13.71 | 2.54 | 0.17 | 0.85 | 0.72 | 0.03 | 1.08 | 1.40 |
| D | 12.63 | 3.26 | 0.01 | 0.48 | 0.60 | 8.17 | 0.06 | 0.49 |
| E | 22.56 | 2.60 | 0.01 | 0.41 | 1.00 | 7.40 | 3.33 | 0.89 |
| F | 18.61 | 1.10 | 0.03 | 7.10 | 3.90 | 8.26 | 6.00 | 0.41 |

Table I. Chemical composition by weight percentage of precipitates determined by chemical analysis.

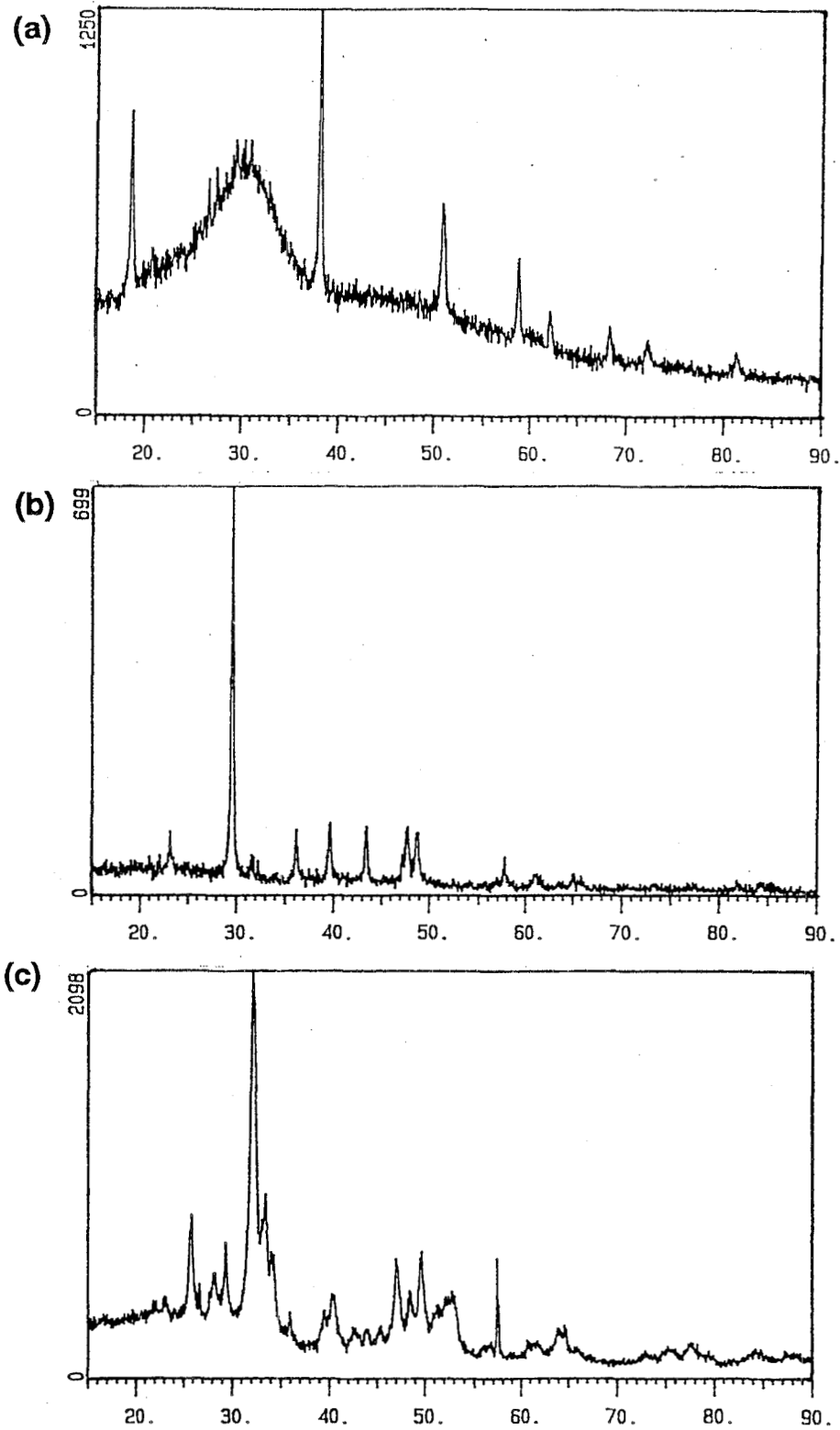


Figure 2. X-ray diffraction of precipitates formed by chemical reactions between concrete and (a) Deicing Salt B, (b) Deicing Salt C, and (C) Deicing Salt E.

| Deicing Salt | Major | Minor |
|--------------|--|--|
| A | Mg(OH) ₂ Mg ₃ (PO ₃) ₂ | Ca ₃ (PO ₄) ₂ ·xH ₂ O Ca ₂ Na ₃ (SO ₄) ₃ |
| B | Mg(OH) ₂ CaP ₆ O ₁₉ | Ca ₂ Na ₃ (SO ₄) ₃ |
| C | CaCO ₃ | Ca ₂ Na ₃ (SO ₄) ₃ Ca ₃ (PO ₄) ₂ · xH ₂ O |
| D | Ca ₃ (PO ₄) ₂ · xH ₂ O | Mg(OH) ₂ Ca ₂ Na ₃ (SO ₄) ₃ |
| E | Ca ₃ (PO ₄) ₂ · xH ₂ O | Ca ₂ Na ₃ (SO ₄) ₃ Mg(OH) ₂ CaCO ₃ SiO ₂ |
| F | CaCO ₃ | Ca ₂ Na ₃ (SO ₄) ₃ Ca ₃ (PO ₄) ₂ · xH ₂ O SiO ₂ Ca ₂ SiO ₄ |

Table II. Chemical compounds in precipitates formed by chemical reactions between corrosion-inhibitor-added deicing salts and concrete.

The precipitates of Deicing Salts D and E contained calcium phosphate as major components, while those of Deicing Salts C and F were calcite. The precipitates of Deicing Salts A and B contained magnesium hydroxide as a major component along with calcium or magnesium phosphate.

Ca₂Na₃(SO₄)₃ was found as a minor component in all deicing chemicals tested in this investigation. The precipitates of Deicing Salts E and F contained some forms of silica as a minor component. In general, the chemical reactions in concrete by the deicing chemicals produced calcium or magnesium phosphate, magnesium hydroxide, and calcite.

The chemical changes of the test solutions as well as the physical changes of the concrete samples were monitored as a function of time. The results collected so far provided clear evidence of chemical reactions between concrete and the corrosion-inhibitor-added deicing salts. The impact of the chemical reactions on the concrete degradation can be understood by determining the chemical and mineralogical changes of the concrete caused by the corrosion-inhibitor-added deicing salts. The chemical changes in the solutions provide a part of the necessary information on changes in the chemistry and bonding-strength of concrete, but the mineralogy of the precipitates also must be determined. The physical changes of the concrete samples after 550 days of reaction were not significant enough (minimum 15 percent weigh and dimension changes) to determine the extent of changes by the corrosion-inhibitor-added deicing salt solutions.

A number of alternative chemical deicers and salt-additive corrosion inhibitors have been developed in recent years. In tests conducted by the Iowa Department of Transportation (4) with steel coupons and reinforced concrete blocks, the only alternative deicer showing significant inhibition of corrosion of reinforcing steels in concrete was pure CMA (among CMA, CMA + NaCl, Quicksalt + PCI, and CG-90), though all deicers were less corrosive than NaCl. The steel coupons were placed in a 15 percent solution of a deicer in distilled water to determine which deicer caused the least amounts of weight loss from corrosion. The reinforced concrete blocks were ponded with a 15 percent solution of a deicer, and corrosion state of the steel was monitored by copper-copper sulfate half cell potential measurements.

The Washington Department of Transportation (5) evaluated a number of deicers such as CG-90, FREEZGARD + PCI, Urea, CMA, Quicksalt + PCI, and Ice Stop CI both in laboratory and field. The deicers were less corrosive than salt. Some deicers appeared to be effective in reducing rebar corrosion. Three percent deicer solutions were used in the laboratory coupon tests.

However, the studies performed by the University of Minnesota (2,3) indicated that the effectiveness of corrosion-inhibitor-added deicing salts on rebar corrosion was dependent on (i) concentration of corrosion-inhibitor-added deicing salts, and (ii) environmental conditions such as temperature and oxygen content, and that most deicing chemicals were inferior to NaCl for rebar corrosion protection.

Also, the corrosion-inhibitor-added deicing salts caused changes in the properties of concrete (6). The salt interacts with concrete by chemical reactions. Some of the reactions are ettringite formation, carbonation, and penetration of chloride ions into C-S-H gels. The salt actions in concrete also affect the freeze-thaw resistance (7). An increase in deicer impurities, such as calcium sulfate, increased damage to cement mortars (8).

In a previous investigation (1), numerous cracks and rough surfaces on concrete were found on the slabs tested with 3 percent Deicing Salt B and E solutions. The slabs tested with Deicing Salt B and with Sodium Formate solutions contained cracks but did not show any yellow rust stains on the surfaces. On the other hand, the slab surfaces tested with salt (NaCl)

solutions showed signs of rebar corrosion in concrete, but no cracks were observed. These observations indicate that the cracks in concrete slabs may be created by both rebar corrosion and chemical reactions between corrosion-inhibitor-added deicing salts and concrete. The results suggested the need to further investigation on the concrete degradation caused by chemical reactions between deicing media and concrete.

Tables III and IV suggest that the high phosphate contents in Deicing Salts A, D, and E formed calcium or magnesium phosphate precipitates by chemical reactions with concrete. In Figure 3, high concentrations of phosphates were observed in the top portion (0.5 cm) of the concrete when the corrosion-inhibitor-added deicing salts or salts substitutes contained phosphates as inhibitors. This is coincident with the phosphate components of the precipitates of Deicing Salts A, D, and E as shown in Table I. Thus, the phosphates added to deicing chemicals as corrosion-inhibitors could not penetrate into concrete to prevent rebar corrosion because of the chemical reactions.

| Element | Percentage |
|------------------------------|--------------|
| Ca ⁺⁺ | 0.35 ~ 20.00 |
| K ⁺ | 0.01 ~ 0.39 |
| Mg ⁺⁺ | 0.01 ~ 3.68 |
| Na ⁺ | 0.57 ~ 37.00 |
| Si ⁺⁺ | 0.00 ~ 2.13 |
| PO ₄ ⁼ | 0.05 ~ 9.52 |
| SO ₄ ⁼ | 1.79 ~ 33.00 |
| Cl ⁻ | 0.79 ~ 56.25 |

Table III. Chemistry of corrosion-inhibitor-added deicing salts used in the previous research (1,2).

| | | Type I | Type II | Type III |
|--|--|--|---|--|
| Definition | | Decomposition of concrete by action of liquid (or lime leaching) | Exchange reaction (or chemical reaction) between hardened cement constituents and a solution | Accumulation, crystallization and polymerization of reaction products |
| Phenomena | | ·Dissolve ingredients of hardened concrete ·pH value of concrete is reduced | Easily soluble reaction products are removed from concrete internal structure by diffusion, or may deposit as an amorphous mass which has no binding properties | Increase volume of crystallized phase with pore structure of concrete and increase internal stresses |
| Mechanism | | Leach out $\text{Ca}(\text{OH})_2$ formed by carbonation from mass of concrete | Precipitates of $\text{Mg}(\text{OH})_2$ and CaSO_4 | Precipitates and crystal growths of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$) |
| Factors influencing rates of deterioration | | ·Permeability of concrete ·Content of calcium oxide or hydroxide ·Mineral composition of cement clinker ·Temperature | ·Solubility of calcium salt ·Temperature | ·Wet-dry cycle ·Freeze-thaw cycle ·Temperature |
| Effect of chemical elements | Ca^{++} | Decreases solubility of $\text{Ca}(\text{OH})_2$ | Interact with MgSO_4 or MgCl_2 to form CaSO_4 or CaCl_2 | Decreases solubility of CaSO_4 , then invites $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ |
| | K^+ | Increases solubility of $\text{Ca}(\text{OH})_2$ | - | - |
| | Mg^{++} | Small quantities of Mg ions tend to retard dissolution by transforming $\text{Ca}(\text{OH})_2$ to $\text{Mg}(\text{OH})_2$. $\text{Mg}(\text{OH})_2$ deposits of surface layer and decreases the permeability of concrete. | ·Interact with $\text{Ca}(\text{OH})_2$ to form $\text{Mg}(\text{OH})_2$ precipitate · Ca^{++} as a binding agent of concrete may be replaced gradually by Mg^{++} | Increase MgO, then decrease sulfate resistance |
| | Na^+ | Increase solubility of $\text{Ca}(\text{OH})_2$ | Increase extraction of SiO_2 , CaO and Al_2O_3 | Na^+ in NaCl retards precipitates by increasing solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ |
| | SiO_3^- | - | - | - |
| | PO_4^- | - | - | - |
| | SO_4^- | Increase solubility of $\text{Ca}(\text{OH})_2$ | Increase reaction of MgSO_4 to form $\text{Mg}(\text{OH})_2$ precipitate | Promotes formation of gypsum and ettringite |
| | Cl^- | ·Increase solubility of $\text{Ca}(\text{OH})_2$ · Cl^- in MgCl_2 , not NaCl or KCl , reacts with lime and forms unstable and water-soluble compound | · Cl^- in MgCl_2 accelerates formation of $\text{Mg}(\text{OH})_2$ precipitate · Cl^- in NaCl increases solubility of $\text{Mg}(\text{OH})_2$ | Cl^- in NaCl and CaCl_2 increases solubility of ettringite |
| Remark | · CaCl_2 retards leaching because of common cation in $\text{Ca}(\text{OH})_2$ and CaCl_2 · $\text{Ca}(\text{OH})_2$ aggravates ASR | $\text{Mg}(\text{OH})_2$ precipitates are highly soluble, so may be an obstacle to the diffusion of SO_4 ions and retard sulfate reaction | - | |

Table IV. Types of deterioration of concrete.

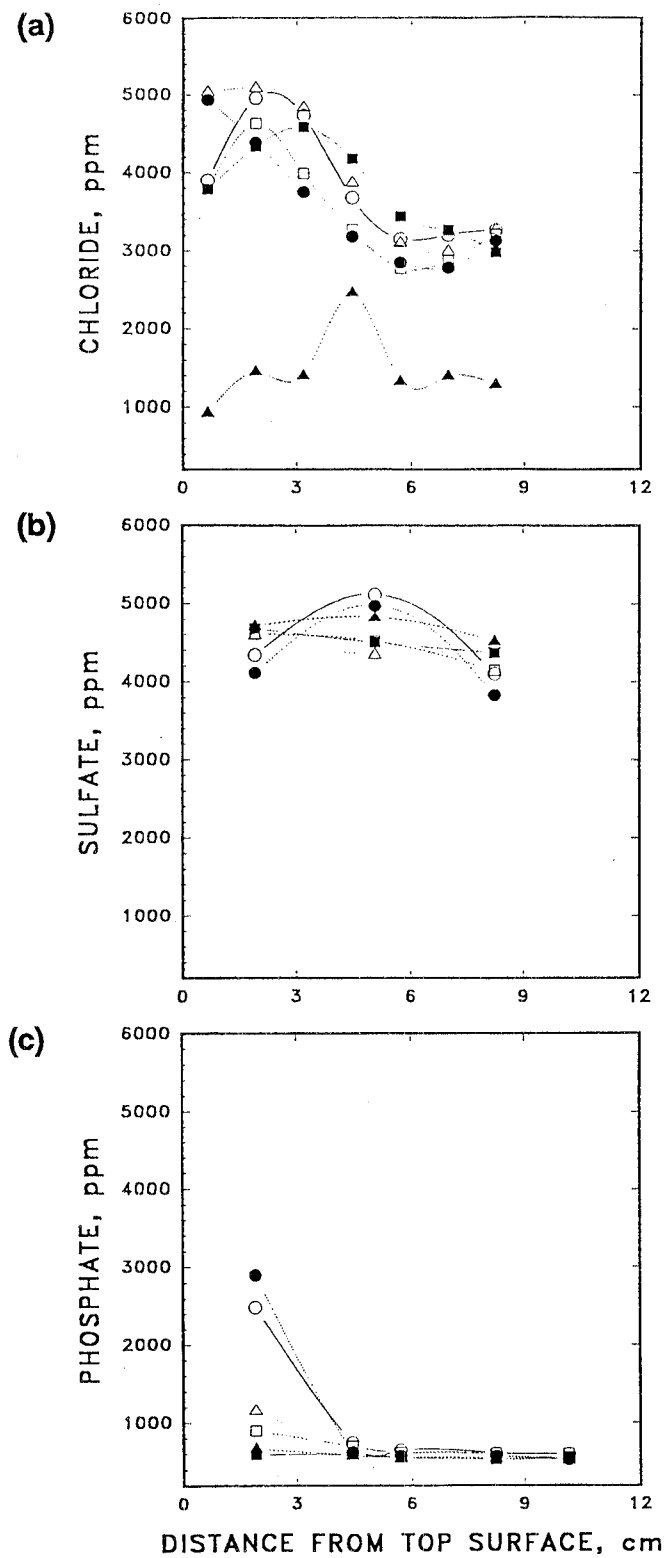


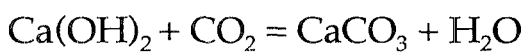
Figure 3. (a) Cl⁻, (b) SO₄²⁻ and (c) PO₃⁴⁻ distributions in concrete slabs ponded with 3% corrosion-inhibitor-added deicing salts solutions.

Sodium phosphate is an anodic inhibitor effective in the presence of oxygen, and its protective properties toward steel are a function of pH (9). Whether phosphate ion can act as an accelerator or as an inhibitor for steel corrosion depends on its concentration. At low concentrations, PO_4^{3-} will develop pits on the surface of the metal. Higher concentrations of 15 to 20 mg/L reverse this role, and the ion contributes to the stabilization of gamma- Fe_2O_3 (10, 11). Polyphosphates are widely used together with cathodic inhibitors that are relatively insensitive to concentration.

If PO_4^{3-} in the corrosion-inhibitor-added deicing salts are lost by precipitation, the effectiveness of the corrosion-inhibitor-added deicing salts on rebar corrosion could drop significantly. On the other hand, the formation of precipitates in cracks may act as a barrier to the penetration of the salt solutions, thereby acting as an inhibitor. Alternatively, some of the precipitates may form in micro-cracks or pores of concrete, and facilitate propagation of cracks. The solubility of $\text{Ca}_3(\text{PO}_4)_2$ decreases with increasing pH. Because of the low solubility of $\text{Ca}_3(\text{PO}_4)_2$ in concrete at pH 12 ~ 13, the precipitates remain in the air voids in concrete or microcracks (12).

The effect of sulfate ion on the potentiodynamic polarization behavior of 1020 steel (mild steel) in a saturated $\text{Ca}(\text{OH})_2$ solution at 22 degrees C was investigated, and the corrosion potential was found to become more negative with increasing sulfate concentrations. This implies that greater amounts of sulfate ions increase the corrosion rate of 1020 steel in a saturated $\text{Ca}(\text{OH})_2$ solution (13).

The calcite precipitates formed by Deicing Salts C and F may decrease the concrete pH. Lime is the dominant substance in cement. As a result, large quantities of Ca(OH)_2 are crystallized in pores. The impermeability of concrete, the reserve of hydroxide, and the low CO_2 concentration in air are the primary reasons why the carbonation process proceeds slowly in concrete (14). The carbonation entails:



The reaction gives rise to neutralization of the pore solutions to pH values under nine. The neutralization takes place in stages and several intermediate reactions occur. One of the final products is CaCO_3 .

However, the effect of pH changes on concrete is not well understood at this time. The effect of precipitates found in this investigation on concrete durability is yet to be determined by research in progress.

The research led to the following conclusions:

- A simple method was developed for the detection of chemical reactions between deicing chemicals and concrete.
- The results provided clear evidence of the chemical reactions between concrete and the corrosion-inhibitor-added deicing salts.
- The different amounts of precipitates (chemical reaction products) found in the test cells were dependent on the type and concentration of corrosion-inhibitor-added deicing salts.
- Precipitates formed by chemical reactions between deicing chemicals and

concrete were identified by using chemical analysis, scanning electron microscopy, and X-ray diffraction analysis.

- Precipitates were calcium and/or magnesium phosphates as a major component, and gypsum as a minor component.

The physical changes of the concrete sample were not significant enough to date to note any dimensional changes by the corrosion-inhibitor-added deicing salt solutions. Further investigation is recommended until significant physical changes of the concrete samples may be observed.

To obtain a copy of the original report, *Effect of Salt Additives on Concrete Degradation*, contact the Office of Research Administration, Minnesota Department of Transportation, 200 Ford Building; MS 330, 117 University Ave., St. Paul, MN 55155, 612/282-2274.

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