The Deleterious Chemical Effects of Concentrated Deicing Solutions on Portland Cement Concrete

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Michigan Tech and the U.P.

► Largest undergraduate Civil and Environmental Engineering program in Michigan
  - 650 undergraduate students and 100 graduate students

► State-of-the-art concrete laboratory facilities
  - 15,000 ft² for concrete production and testing
  - World-class materials characterization facilities

► Located in the U.P. 200 miles from the nearest Interstate and 100 miles from the nearest Menards, Lowes, or Home Depot!
The Keweenaw Peninsula Is Also Home To Some Good Performing Concrete Pavements

- Oldest concrete pavement in Michigan
  - Blome Granitoid pavement constructed in Calumet in 1906

- Original sections of US 41
  - Paved in the 1930’s

- Good performing sections of US 41 still carrying heavy traffic
  - Paved in 1959
Granitoid pavement
- Placed in two layers
- A relatively porous 5¼” thick layer of concrete with abundant gaps and air voids
- Topped by an extremely dense 1¼” thick layer of mortar

Tailings from local copper mines, primarily basalt, were used as aggregate

Alpha brand portland cement was used

After placement, a machine which traversed on rails was used to stamp a brick-like pattern into the surface of the pavement
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Concrete pavements are inherently durable, having a history of exceptional long-term performance. In some instances, pavement service life has been adversely affected by the concrete’s inability to maintain its integrity in the environment in which it was placed. These distress manifestations are categorized as materials-related distress (MRD).
What is Materials-Related Distress?

► MRD is commonly associated with the “durability” of the concrete

► Durability is not an intrinsic material property
  ▪ “Durability” cannot be measured
  ▪ Concrete that is durable in one application may rapidly deteriorate if placed in another

► Deicing chemicals can be an important part of the concrete’s environment

Other Considerations for MRD

► Strength does not equal durability

► The concrete constituents, proportions, and construction all influence MRD

► Water is needed for deleterious expansion to occur

► Severe environments (e.g. high sulfate soils, freezing and thawing, deicer exposure, etc.) are major contributors
Deicer Basics

- Highway agencies objective - keep roads safe & passable year round
- Always looking for easier, safe, cost effective means for highway deicing/anti-icing
- Brines have become the main tool for winter maintenance
  - Sodium Chloride (NaCl)
  - Magnesium Chloride (MgCl₂)
  - Calcium Chloride (CaCl₂)
  - Calcium Magnesium Acetate (CMA)

How do salt brines work?

- **Freezing point depression**
- Some substances when combined freeze at a temperature lower than either ingredient
  - Eutectic mixtures
  - Solder (combination of lead and tin)
  - Auto anti freeze (ethylene glycol and water)
- Salts and water form a “binary eutectic”
- Graphically represented with a “phase diagram”
How do salt brines work?

X axis is the amount of salt dissolved in water. 0% is pure water and 100% is pure salt.
How do salt brines work?

Y axis is the temperature the solution is exposed to.
How do salt brines work?

[Diagram showing temperature vs. concentration with a point labeled Brine Solution (Liquid).]

How do salt brines work?

[Diagram showing temperature vs. concentration with a point labeled Eutectic Point.]
How do salt brines work?

Concentration that produces a brine with the lowest possible freezing point

How do salt brines work?
How do salt brines work?

**Diagram 1:**
- Ice + Solid Salt (Solid)

**Diagram 2:**
- Brine + Solid Salt
How do salt brines work?

Concentration that produces a brine with the lowest possible freezing point

[Graph showing the relationship between temperature and concentration, highlighting the eutectic point.]
How do salt brines work?
Types of Common Pavement MRD

► Physical mechanisms
  - Freeze-thaw deterioration of hardened cement paste
  - Deicer scaling/deterioration
  - Freeze-thaw deterioration of aggregate

► Chemical mechanisms
  - Alkali-aggregate reactivity
  - Sulfate attack
  - Corrosion of embedded steel
  - Chemical Deicer Attack
Physical Protection Against Freeze-Thaw Damage

- The hydrated cement paste is physically protected against F-T damage by being relatively impermeable and having an acceptable air-void system
  - The size and spacing of the air voids is critical to preventing the build-up of stress as ice forms, acting as pressure relief valves
  - Total air is irrelevant but is related to air-void size and spacing
  - The air-void system is created through the use of air entraining admixtures

Big Bubbles, Few of Them
Small Bubbles, More of Them

Small Bubbles, Lots of Them
Impact of Poor Finishing

0.5 to 1 inch

Air-Void System Analysis
Deicer Scaling/Deterioration

- Deicer chemicals can amplify paste freeze-thaw deterioration
  - Finishing may play a role
- Chemical mechanisms have also been identified
- Manifest as scaling, spalling, or map cracking with possible staining near joints
- Typically appears within 1 to 5 years after construction
Traditional Deicing Practices

- Solid deicing salts mixed with sand
  - Normally NaCl
  - Slow dissolution leads to low concentration solutions - solid may be blown off road
- Applied after precipitation event to melt snow and ice
- Relatively low concentration of deicer in melt water
Why Do Deicers Make F-T Damage Worse?

- Primarily physical effects
  - Increase level of saturation
  - Can lead to “thermal shock”
  - Increase osmotic pressure
  - Can produce salt recrystallization pressures

- Potential chemical effects
  - Corrosion
  - Dissolution of calcium hydroxide
  - Formation of expansive/weak phases in hardened cement paste

More Recent Practices

- Use of liquid anti-icing and deicing agents
  - Magnesium chloride, calcium chloride, and calcium magnesium acetate, among others
  - Blended with food processing wastes

- Very effective
  - Some are more environmentally friendly
  - Applied in high concentrations (>25%)

- Liquid presentation can amplify both positive and negative effects
Disadvantages of New Practices

► Greater potential for physical damage due to higher concentration
  ▪ Liquid presentation contributes to a higher degree of interaction
  ▪ If storm event doesn’t materialize, long-term exposure to concentrated anti-icing agent results

► Greater potential for chemical deterioration from MgCl₂ and CaCl₂
  ▪ Formation of hydrated calcium oxychloride
  ▪ With MgCl₂, Mg(OH)₂ and M-S-H formation
Research Objectives

- Determine the long term effects on concrete from exposure to concentrated solutions of MgCl₂, NaCl, CaCl₂, and CMA
- Identify protective or design strategies that minimize material damage from chemical exposure

Approach

► Characterization of Field Specimens
  - Determine distress mechanisms present in the field

► Phase I Laboratory Experiments
  - Performed on mortar specimens (cement, sand, and water)
  - Identify distress mechanisms
  - Assess the role of mixture properties and deicer types

► Phase II Laboratory Experiments
  - Performed on concrete (cement, sand, aggregate, and water)
  - Confirm distress mechanisms active in concrete
  - Determine the role of deicer concentration, concrete mixture design, and the effectiveness of sealants
Phase I - Details

► Expose mortars to deicer solutions at fixed concentrations (less than typical application conc.)

► Monitor Physical Effects
  ▪ Strength Loss
  ▪ Expansion
  ▪ Freeze-Thaw Performance

► Monitor Chemical Effects
  ▪ Petrographic analysis to identify alterations to the mortar

Phase I - Details

► Five different deicer solutions
  ▪ MgCl₂ - Magnesium Chloride (15 wt%)
  ▪ CaCl₂ - Calcium Chloride (17 wt%)
  ▪ NaCl - Sodium Chloride (23 wt%)
  ▪ Proprietary - Magnesium Based Agricultural Products
  ▪ CMA - Calcium Magnesium Acetate
  ▪ Saturated limewater (control)

► Exposed for various times
► Exposed at different temperatures (40, 72, 135°F)
Phase II - Details

- Concrete mixtures were made using:
  - high quality, partially crushed gravel coarse aggregate
  - natural sand
  - 564 lb/yd³ Type I/II cement
  - vinsol resin and synthetic AEA
  - w/c of 0.45 and 0.55

- Two additional mixtures were prepared,
  - 15 percent replacement of cement with Class F fly ash
  - 35 percent replacement of cement with ground blast furnace slag (GBFS)

- Exposed to same deicers as Phase I

Phase I Laboratory Results
Cylinders exposed to \( \text{MgCl}_2 \) solution after 84 days of exposure @ 40 °F. From left to right: 0.40, 0.50, and 0.60 w/ c mortar cylinders.

Cylinders exposed to \( \text{CaCl}_2 \) solution after 84 days of exposure @ 40 °F. From left to right: 0.40, 0.50, and 0.60 w/ c mortar cylinders.
Cylinders exposed to NaCl solution after 84 days of exposure @ 40 °F. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.

Cylinders exposed to lime water solution after 84 days of exposure @ 40 °F. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.
Mechanism

► Specimens were held at a constant 40 °F so no freezing occurred that could result in the damage observed

► Expansion was caused by the formation of calcium oxychloride

► Results from the reaction of calcium hydroxide (present in the hardened cement paste) with chloride ions (provided by the deicer)

Scanning electron microscope images of thin sections prepared from cylinders immersed in, from left to right, MgCl₂, CaCl₂, NaCl, and saturated lime solutions.

► SEM Analysis
► Backscattered electron images
  - Parallel cracks
  - Ca(OH)₂ and oxychloride deposition in the voids of the MgCl₂ and CaCl₂ specimens
From top to bottom: plane polarized light, cross polarized light, and epifluorescent mode.

► Petrographic Analysis
  ▪ Cracks and air voids filled with remnant calcium oxychloride crystals in thin section prepared from MgCl$_2$ solution immersed sample

From top to bottom: plane polarized light, cross polarized light, and epifluorescent mode.

► Petrographic Analysis
  ▪ Cracks and air voids filled with remnant calcium oxychloride crystals in thin section prepared from CaCl$_2$ solution immersed sample
Compressive strength evolution with time of mortar cubes

![Compressive strength evolution with time of mortar cubes](image)

Length change of mortar bars

![Length change of mortar bars](image)

- Ca(OH)₂: ~0.8% expansion
- NaCl: ~0.4% expansion
- MBAP: ~0.3% expansion
- MgCl₂: ~0.3% expansion
- CaCl₂: ~0.4% expansion
Mass change of mortar bars

Laboratory Results - Phase II
17% CaCl₂ – 500 days – 40 deg F

15% MgCl₂ – 500 days – 40 deg F
15% MgCl₂ MBAP – 500 days – 40 deg F
Typical Diffusion Profiles for 0.45 w/c Concrete Exposed to 15% MgCl$_2$ - PCC, 15% Fly Ash, 35% GGBFS Mixtures
Silane Sealer Profiles

17% CaCl₂
15% MgCl₂
Surface concentration 0.3%

Sorptivity of 15% MgCl₂ into 0.45 w/c Concrete Mixture

Absorption [mm] vs Time [s/²]
**Sorptivity of 15% MgCl₂ into 0.45 w/c Concrete Mixtures**

![Graph showing sorptivity](image)

**Freeze Thaw Testing - Length change of concrete prisms**

![Graph showing freeze thaw testing](image)
Conclusions

► MgCl₂, CaCl₂, and proprietary deicers containing MgCl₂ cause expansion, cracking, and loss of strength for concrete and mortars exposed at 40 °F.

► NaCl caused no observed distress to concrete, however it is known to be detrimental to reinforcing steel in concrete.

Cyclic freeze-thaw exposure exacerbates the damage caused by these deicers.

► In all cases, the mechanism of failure is the formation of oxychloride phases by the interaction of the deicer with calcium hydroxide in the hardened cement paste.
Conclusions

► Concrete mixtures prepared with ground blast furnace slag or fly ash as a portland cement replacement performed significantly better in tests as compared to concrete prepared with portland cement only

► Silane and siloxane sealants both improved the performance of concrete exposed to deicing chemicals

► Sealants are a good maintenance strategy but need to be reapplied every 3-5 years in order to remain effective

Questions

► How quickly will distress occur in “real-world” applications?
  - Exact concentration of deicers, as applied, varies
    - Concentration varies
    - Application rates
  - Deicers are diluted by weather events (positive)
  - When deicers are applied in an anti-icing strategy, high concentration solutions are presented to the concrete and if the weather doesn’t occur no dilution results (negative)
Summary

- The greatest threat is to lower quality concrete
  - Residential/commercial/municipal
  - Paving concrete not meeting specs
- Evidence suggests that liquid based MgCl₂ and CaCl₂ pose the greatest risk of negatively affecting concrete

And if you are ever up in our way, stop in for a cold one, eh!