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ROAD MAP TRACK 1
Performance-Based Concrete
Pavement Mix Design Systems

PRIMARY SOURCE
Deleterious Chemical Effects of Concentrated Deicing Solutions on Portland Cement Concrete
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Moving Advancements into Practice (MAP) Briefs describe innovative research and promising technologies that can be used now to enhance concrete paving practices. MAP Brief 1-2 provides information relevant to Track 1 of the CP Road Map, Performance-Based Concrete Pavement Mix Design Systems.

The Long-Term Plan for Concrete Pavement Research and Technology (CP Road Map) is a national research plan developed and jointly implemented by the concrete pavement stakeholder community. Publications and other support services are provided by the Operations Support Group and funded by TPF-5(185).

MAP Brief 1-2 is available at:
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"Moving Advancements into Practice"

MAP Brief 1-2:

Describing promising technologies that can be used now to enhance concrete paving practices

Deleterious Chemical Effects of Deicing Solutions on Concrete Pavements

Introduction

Safety and mobility are key concerns for State Highway Agencies (SHAs), especially during the winter season, when ice and snow accumulation on roads and bridges can create hazardous or impassable driving conditions. Various chemicals, including magnesium, sodium, and calcium chloride; calcium magnesium acetate; and urea, are used by SHAs as anti-icing and deicing solutions on transportation infrastructure.

The effectiveness of these chemicals for deicing and anti-icing has been demonstrated. However, the possible detrimental effects to concrete in transportation structures have not been fully examined and documented. Although these chemicals offer possible cost savings advantages to SHAs, the true cost effectiveness cannot be determined without establishing the potential for chemical attack and premature deterioration, leading to costly rehabilitation or replacement.

Recent research at Michigan Technological University and the University of Toronto examined the chemical effects of deicing and anti-icing chemicals on portland cement concrete and recommended changes to concrete mixture designs, construction practices, and winter maintenance procedures that will not compromise concrete durability.

Research Description

The degradation of concrete used in pavements and bridges that may occur as a result of attack by deicing and anti-icing solutions is the result of an increased concentration of dissociated calcium, magnesium, and chloride ions in the concrete pore water. These ions are available to combine

with materials in the concrete to form expansive or weak reaction products, such as brucite or magnesium silicate hydrates.

The dissociated chloride ions in the pore water solution are well documented as a primary cause of reinforcing steel corrosion. In addition, the study identified the formation of destructive oxychlorides as a potentially significant cause of deterioration.

A series of field explorations and laboratory experiments were performed, including the characterization of concrete field specimens from both pavement sites and bridge decks, laboratory experiments on portland cement mortar, and laboratory experiments on portland cement concrete.

Characterization of field specimens

In general, the pavement sites examined lacked unambiguous evidence of distress associated with deicers. The research team also obtained cores from a number of bridge decks that were exhibiting distress. Although these bridge decks were, in recent years, maintained using various non-NaCl deicers, they had been in service for numerous years and, as a result, have been exposed to NaCl deicers for a significant portion of their service lives. Ultimately, because of this history, any distress identified would be difficult to associate with a specific deicing chemical.

Deicing and Anti-icing Chemical Acronyms

- CaCl₂ - Calcium chloride
- CMA - Calcium magnesium acetate
- MBAP - Magnesium chloride-based agricultural product
- MgCl₂ - Magnesium Chloride
- NaCl - Sodium Chloride

Observations of all field specimens include the following:

- Calcium hydroxide depletion along cracks and surfaces exposed to deicing solutions.
- Higher chloride ingress rates (diffusion rates) for concrete with deicer exposure at early ages.

Laboratory experiments on portland cement mortar

Three different mortar mixtures were prepared using 20-30 Ottawa sand (ASTM C778), ASTM C150 Type I/II cement, and variable water-cementitious (w/c) ratios of 0.40, 0.50, 0.60. Two-inch diameter by four-inch high [50 mm by 100 mm] mortar cylinders were prepared and then soaked in solutions of CaCl_2 (17 wt. %), MgCl_2 (15 wt. %), NaCl (17.8 wt. %), and saturated lime water at 40° F [4.4° C] for 84 days.

The specimens exposed to CaCl_2 and MgCl_2 (figures 1 and 2) exhibited severe deterioration, while those exposed to NaCl and lime water did not show any signs of deterioration (figures 3 and 4).

Other mortar specimens (cubes and length change bars) were prepared using a w/c of 0.485 and cement-sand ratio of 2.75, per the ASTM recommended mixture for mortar specimens (ASTM C1012- 04, “Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution”). However, these specimens were immersed in three molar concentration solutions of the respective deicers and subjected to tests at various time intervals. The specimens exhibited significant loss in strength and expansion, as shown in figures 5 and 6, as well as mass gain.

In all cases, petrographic analysis found that the observed deterioration was caused by the formation of expansive calcium oxychloride and magnesium oxychloride. The oxychloride phases form through a chemical reaction between calcium hydroxide in the hardened cement paste and chloride ions from the deicer.

Laboratory experiments on portland cement concrete

Concrete mixtures used in this experiment were made with a high quality, partially crushed gravel coarse aggregate (maximum aggregate size of 1 inch [25 mm]), natural sand, 564 lb/ yd³ [335 kg/m³] ASTM C150 Type I/II cement, vinsol resin air entraining agent (air content of 6 ± 1%), and a w/c of 0.45 and 0.55. Two additional mixtures were prepared—one made with 15% replacement of cement with Class F fly ash and another made with 35% replacement of cement with ground blast furnace slag (GBFS).

Specimens were moist cured at 100% humidity for one day, de-molded and then wet cured in lime saturated baths for 27 days. Specimens cast were standard four-inch diameter by eight-inch high [100 mm by 200 mm] cylinders, which in



Figure 1. Cylinders exposed to CaCl_2 solution after 84 days of constant low temperature test. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.



Figure 2. Cylinders exposed to MgCl_2 solution after 84 days of constant low temperature test. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.



Figure 3. Cylinders exposed to NaCl solution after 84 days of constant low temperature test. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.



Figure 4. Control cylinders exposed to lime water solution after 84 days of constant low temperature test. From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.

turn were sectioned to produce three four-inch diameter by two-inch high [100 mm by 50 mm] specimens per cylinder.

The specimens were immersed in the same deicers used in the mortar experiments, as well as calcium magnesium acetate and a magnesium chloride-based agricultural product. The concrete specimens were exposed under the same conditions used in the mortar experiments (i.e. for both solution strength and temperature) but for longer times, up to 500 days. Deterioration of the concrete specimens resembled that seen for the mortar specimens (figures 7-8). In all cases, the observed distress was associated with the formation of the oxychloride phases seen in the mortar specimens.

Effects of fly ash and slag

In all cases, concrete mixtures prepared using Class F fly ash or GBFS performed significantly better than those made with portland cement alone, with no distress observed in specimens after 500 days of exposure (figure 9). Quantitatively, the reduction in chloride ingress observed was shown by a dramatic reduction in diffusivity for all deicers, a reduction in sorptivity, and microstructurally by reduced calcium hydroxide depletion and oxychloride formation.

Conclusions

- Exposure of concrete and mortar to NaCl results in little to no chemical interaction or related distress. NaCl appears to be safe for use as a deicing and anti-icing chemical with respect to possible chemical interaction with concrete. NaCl should still be considered harmful to concrete in terms of its potential to induce corrosion in embedded steel, given its demonstrated ability to diffuse into concrete more readily than the other deicers tested.
- Exposure of concrete and mortar to MgCl₂ and CaCl₂-based deicing chemicals results in significant chemical interaction and related distress. Both appear to not be safe for use as a deicing or anti-icing chemical with respect to possible damage to concrete.
- In all cases, the observed distress is less as the concentration of deicer is reduced. Therefore, if MgCl₂ and CaCl₂-based deicing chemicals are to be used, they should be used at the lowest possible concentration.
- Results were mixed regarding the effect of w/c on performance of concrete and mortars exposed to deicing chemicals. Although the general parameters (i.e. sorptivity, bulk diffusion, rapid chloride permeability) improved with decreasing w/c as expected, the performance in low temperature immersion was, in many cases, opposite of expected. That is, the low w/c mixtures often performed worse.
- In general, concrete mixtures containing 35% GBFS showed the lowest susceptibility to chemical degradation

by deicing chemicals, concrete mixtures containing 15% Class F fly ash were next best, and straight portland cement mixtures were the worst performing. One exception is that with the tests performed, concrete mixtures containing fly ash had a diffusion coefficient higher than that measured for straight portland cement mixtures. However, in other experiments such as the low temperature immersion test, concrete mixtures containing fly ash performed better.

- In general, sealants were very effective at reducing chloride ingress at 60 days. The siloxane appeared to perform better than the silane. After 500 days exposure, both sealants showed reduced effectiveness.

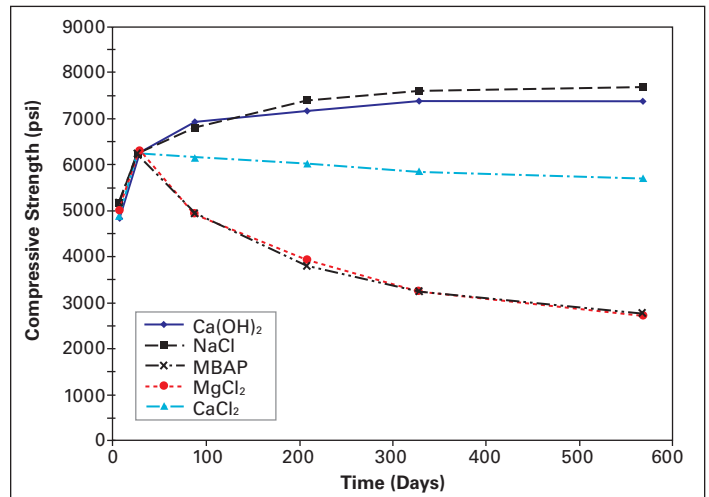


Figure 5. Compressive strength evolution with time of mortar cubes exposed to different deicers.

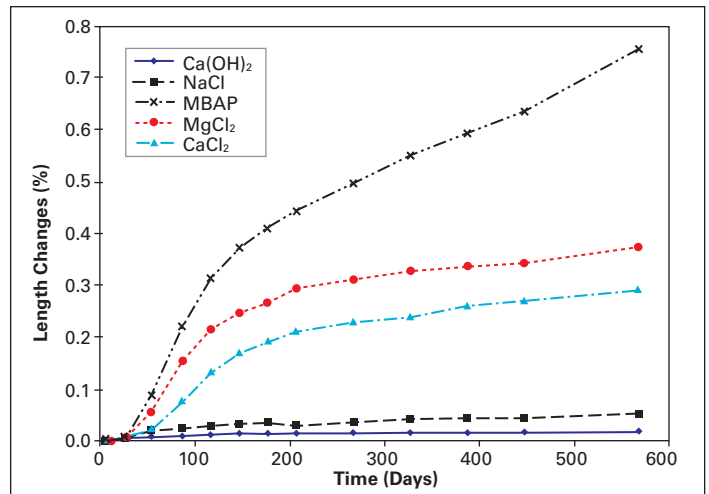


Figure 6. Length change of mortar bars with time for mortar bars exposed to different deicers.



Figure 7. Four-inch [100 mm] diameter 0.45 w/c portland cement concrete specimens after 500 days in high concentration brines. L to r: Samples exposed to CaCl₂, MgCl₂, and MBAP brines.

Recommendations for Future Work

As a result of this research, clear evidence was presented that $MgCl_2$ and $CaCl_2$ both chemically attack concrete causing increased permeability, loss of strength, expansion and cracking. Also, this research project identified viable maintenance and mitigation strategies, recognizing that these deicing chemicals are a key part of modern winter maintenance strategies and that SHAs need to continue their use for that purpose.

However a number of questions were not answered as part of this research and it is important that SHAs continue research in this area. One unanswered question pertains to how these deicing chemicals impact the life-cycle of concrete pavements and bridges. This question has become more important in light of recent reports from a number of states regarding premature distress along longitudinal and transverse joints.

In a number of upper-Midwestern states, for example, several concrete pavements constructed since 1999 have developed unexpected scaling/spalling with associated dark-

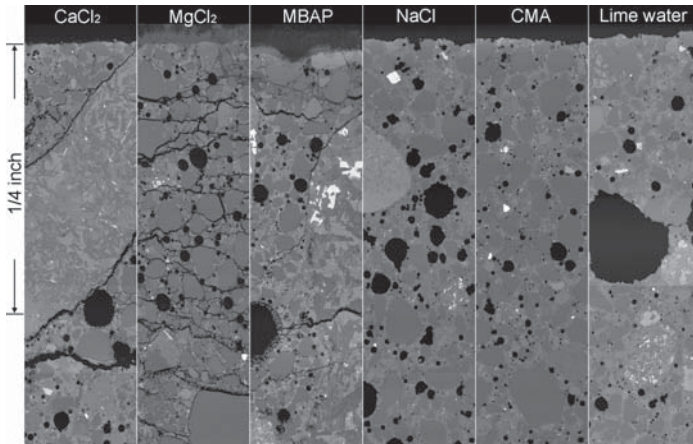


Figure 8. Cross-section at concrete surface after long-term exposure to various solutions at 40° F, back-scattered electron images

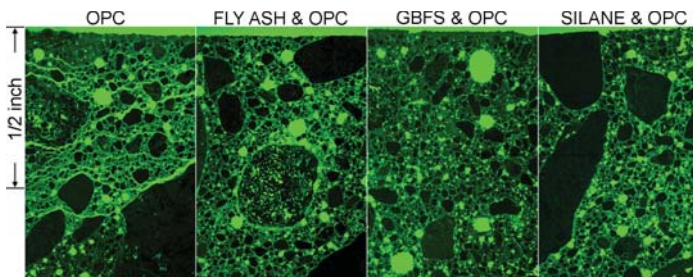


Figure 9. Cross-section at concrete surface after long-term exposure to magnesium chloride brine at 40° F, epifluorescent optical microscope images

staining along joints (figure 10), particularly the longitudinal, centerline joint. Initial studies have identified a number of possible causes, including chemical attack from deicers. Understanding the cause of this reported premature deterioration is integral to understanding the life-cycle impact of deicers on concrete.

Other suggested areas for additional research

- Further testing to determine the effect of different replacement levels of supplementary cementitious materials on the resistance of concrete to deicers and anti-icing chemicals
- A detailed experiment to determine the effects of w/c on deicer related distress
- A study of highway deicer chemical contributions to alkali-silica reaction (ASR)
- Further testing to better understand field reports of scaling/spalling and joint-related distress related to use of $MgCl_2$ and $CaCl_2$.

For More Information

The executive summary, final report, and guidelines are available for viewing at the South Dakota Department of Transportation website:

<http://www.state.sd.us/Applications/HR19ResearchProjects/oneproject_search.asp?projectnbr=SD2002-01>

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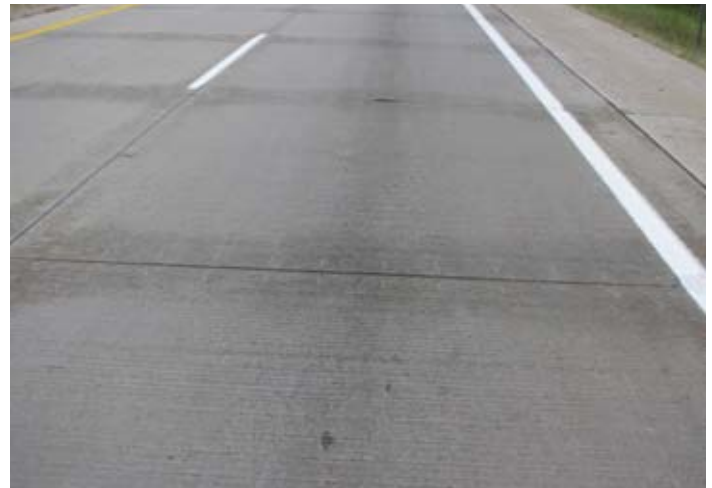


Figure 10. Several concrete freeway pavement projects constructed since 1999 have developed unexpected spalling with associated dark staining along joints.

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