

Detrimental Effects of Anti-Icing Brines on Concrete Durability

A comparative study based on continuous immersion over a 5-year period

by Colin B. Van Niejenhuis and Carolyn M. Hansson

On average, 5 million tonnes (5.5 million tons) of road salts are used as deicers on Canadian roadways each year.¹ Over 24.5 million tonnes (27.0 million tons) of rock salt were applied to U.S. roads in 2014 alone.²

The application of rock salt to roads and highways as an ice preventative, or anti-icing agent, is highly inefficient because it can be blown off the pavement by passing traffic before any precipitation allows it to adhere to the pavement. It is thus scattered in adjacent areas, damaging foliage and contaminating lakes and streams.³ Consequently, in recent years, many municipalities have been using salt brines, as either a sprayed anti-icing agent or as a wetting agent for rock salt, to improve the adhesion to the pavement. The brines used in Ontario are calcium chloride (CaCl_2), magnesium chloride (MgCl_2), sodium chloride (NaCl), or natural multichloride brines taken from local aquifers and which vary in composition over time and by geographic location.

In addition to the wetting of the pavement and allowing the retention of the brine where it is needed, the CaCl_2 and MgCl_2 solutions have other benefits for the safety of traffic and pedestrians. The eutectic temperature (the lowest possible temperature at which the salt solution is liquid) for NaCl brine occurs at -21°C (-6°F) and a concentration of 23.3 wt.%, with a maximum useful temperature for melting ice in the range of -10 to -15°C (14 to 5°F). At the other extreme, the eutectic temperature for CaCl_2 brine is -51°C (-60°F) at a concentration of 29.8 wt.%. Calcium chloride is, therefore, much more useful for melting ice at very low temperatures. Magnesium chloride brine is intermediate, with a eutectic temperature of -33°C (-27°F) at a concentration of 21.6 wt.%.

Studies of the impact of exposure to CaCl_2 and MgCl_2 on cement paste, mortar, and concrete have shown these salts to be more detrimental than NaCl to both cementitious materials⁴⁻⁶ and reinforcing bars.⁷⁻⁹ While it is recognized that the salts can affect scaling¹⁰ and joint deterioration,¹¹ the

research described in this article is focused on the potential negative effects on concrete structures under load, such as bridge support structures, decks, and barrier walls.

The interaction between CaCl_2 and $\text{Ca}(\text{OH})_2$ in cement paste to form calcium hydroxychloride ($3\text{CaO}\cdot\text{CaCl}_2\cdot 15\text{H}_2\text{O}$) was reported 40 years ago.¹² Since then, a number of investigations have shown the calcium hydroxychloride to be an expansive product¹³⁻¹⁵ that can crack the paste (Fig. 1). This, in turn, can lead to more rapid chloride ingress, which is detrimental to the reinforcing bars.

For MgCl_2 brines, the reaction $\text{MgCl}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCl}_2$ also results in the formation of calcium hydroxychloride.⁴ Moreover, $\text{Mg}(\text{OH})_2$ is far less soluble than



Fig. 1: The bottom of a mortar bar exposed, at the top, to a 35% calcium chloride brine for 2 months at 23°C (73°F) (photo courtesy of A. Poursaee and C.M. Hansson)

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Ca(OH)₂ and precipitates in the pores of the paste, reducing the pH of the pore solution to about 9.2, at which level carbon steel will actively corrode.⁷

For reinforcing bar corrosion, any chloride ions will break down the passive film formed on the steel in the high-pH environment of concrete. However, the chloride threshold for this breakdown is lower for CaCl₂ and MgCl₂ than it is for NaCl,^{8,9,15,16} and the corrosion rates are somewhat higher. These effects are attributed primarily to a reduction in the pH of the cement paste pore solution by both salts but particularly by MgCl₂.

Most of the previously noted studies have been performed on cement paste and mortar because the abundance of the paste phase allows for a more rapid reaction. Work on concrete has been more limited. The internal strains produced in concrete blocks, exposed outdoors to CaCl₂, MgCl₂, and multichloride brines contained in a 50.8 mm (2 in.) deep ponding well on top of the specimens, were found to be significantly higher than the same concrete exposed to NaCl brine or to tap water.¹⁷ In Fig. 2, the strains are plotted as a function of time for specimens exposed outdoors. The ambient temperature variation results in large variations in the strains. Nevertheless, it is clear from the data that the NaCl brine produces lower strains than MgCl₂ brine.

Effect of Exposure to Brines on Compressive Strength

The question remained on how these strains would affect the mechanical properties of the concrete. Consequently, at the request of the Ministry of Transportation of Ontario (MTO), concrete cylinders were cast, exposed to brines, and subsequently tested in compression. Specifically, 400 cylinders (100 x 200 mm [4 x 8 in.]) were cast from the same batch of concrete and consolidated on a vibratory table. The MTO now uses performance specifications, so the ready mixed concrete companies are reluctant to divulge their full (proprietary) mixture designs. Thus, we specified a “typical MTO highway structure mixture” with a cementitious (75% Type I cement + 25% slag cement) content of 355 kg/m³ (598 lb/yd³), a 0.42 water-cementitious materials ratio (*w/cm*), and a specified compressive strength of 30 MPa (4350 psi). Because of the length of time required to cast all the cylinders, it was necessary to add a second dose of polycarboxylate high-range water-reducing admixture, approximately two-thirds of the way through the casting, to maintain the fluidity of the mixture.

All cylinders were demolded after 24 hours and left in a fog room for a further 27 days. They were then randomly divided into five sets of 80 cylinders each. One set was kept in the fog room, and one set was immersed in each of four anti-icing brines. Thereafter, every 2 months for

5 years, three cylinders were removed from each of the four brines and from the fog room and tested in compression. While it is understood that immersion is not characteristic of a practical application and does not produce the same rate of chloride ingress as would be produced by continual wetting and drying cycles,¹⁸ immersion was selected as a more feasible testing environment. Furthermore, the cylinders did not contain cracks and defects that would be present in a typical structure.

It should be noted that the brines were commercial anti-icing agents and, unlike the reagent-grade salts used in many research experiments, these were natural solutions with many components. The amounts of the major components of the brines used in this project, determined by inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectroscopy, and ion chromatography, are listed in Table 1.

Figure 3 shows the compression test data plotted as a function of time of exposure to the brines. Initially, all specimens exhibited approximately the same strength gain, reaching about 38 to about 40 MPa (about 5510 to about 5800 psi) at 6 months. Over the next 6 months, the strength of specimens stored in the fog room increased to as high as 48 MPa (6960 psi). Over the remainder of the 5-year program,

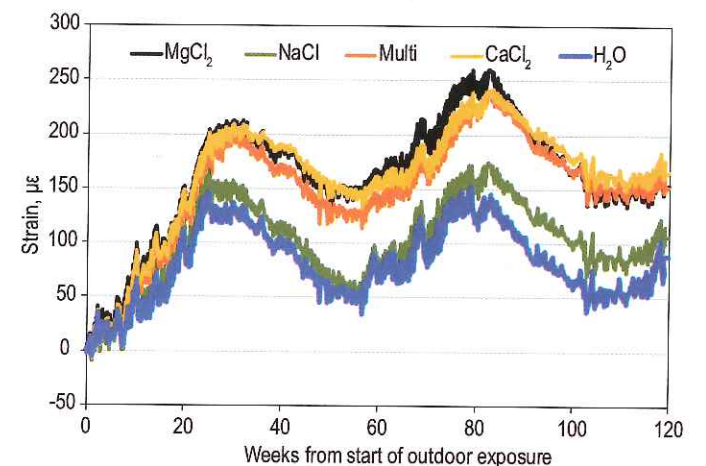


Fig. 2: Internal strains in concrete due to exposure to anti-icing brines outdoors in Waterloo, ON, Canada, compared with that of the same concrete exposed to water¹⁷

Table 1: Major components of the commercial anti-icing brines used in the current study

Brine	Ca, mol/L	K, mol/L	Mg, mol/L	Na, mol/L	S, mol/L	Sr, mol/L	Cl, mol/L	Cl, wt.%
Calcium	3436	123	—	106	50	21	7603	26.9
Sodium	—	17	—	5733	20	—	5010	17.8
Magnesium	60	33	3497	108	22	—	6523	21.4
Multi	2006	129	425	1598	36	18	6040	23.1

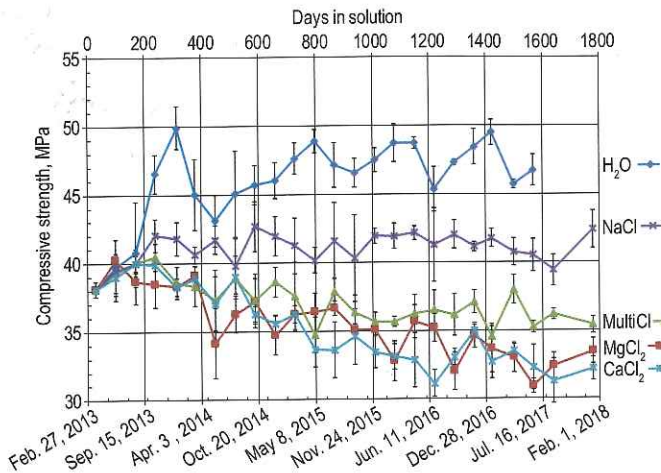


Fig. 3: The average compressive strength of three replicate cylinders exposed to either water or commercial NaCl, CaCl₂, MgCl₂, and multichloride brines from February 2013 until the day of testing

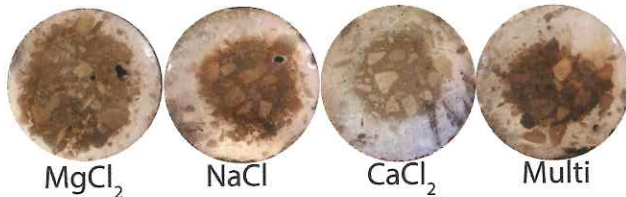


Fig. 4: Cross sections of cylinders after immersion in the different salt brines for 5 years and sprayed with a 0.1 M silver nitrate solution. The depths of chloride penetration are indicated by the light gray or white precipitates on the cut surfaces

specimens stored in the fog room had test strengths between 42 and 48 MPa (6090 and 6960 psi). The compressive strengths of specimens immersed in NaCl remained approximately constant at 40 to 42 MPa over the whole 5-year exposure period. In contrast, the compressive strengths of specimens exposed to the other brines steadily decreased over the 5-year exposure period, to about 30, 34, and 35 MPa (4350, 4930, and 5080 psi) for the MgCl₂ brine, the multichloride brine, and the CaCl₂ brine. These findings are in agreement with earlier results from Collepardi et al.¹⁹

After 2000 days in brines, sections of the remaining specimens were dry cut and sprayed with either a pH indicator or a 0.1 M solution of silver nitrate. The silver nitrate spray serves as an indicator of soluble chlorides in the cement paste by forming a precipitate of silver chloride that appears light gray or white on the cut surface. The soluble chloride concentration at the color change border indicated by the silver nitrate spray has been found to be approximately 0.15% by weight of cement.²⁰

All cylinders were found to have a pH exceeding 11. Examples of the surfaces sprayed with silver nitrate solution are shown in Fig. 4. The lowest amount of chloride ingress was observed for the MgCl₂ brine. The lower penetration of MgCl₂ has been observed by others,²¹ and it has been

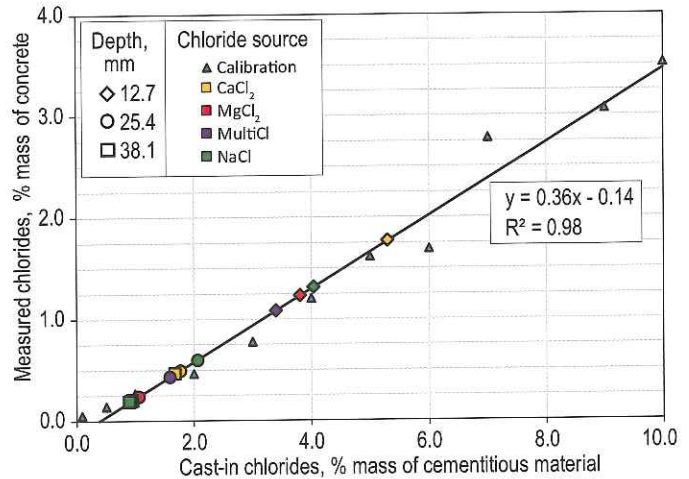


Fig. 5: Results of XRF analyses of chlorides in concrete. The small blue triangles correspond to the average of 100 measurements on concretes with known chloride concentrations. Other symbols correspond to XRF measurements on the cylinders exposed to brines in the current study (Note: 1 mm = 0.04 in.)

attributed to the precipitation of Mg(OH)₂ in the pores of the concrete, which limits further ingress. This precipitation did not, however, prevent the reduction in strength of the concrete, as shown by the data in Fig. 3.

X-ray fluorescence analysis (XRF) was used to analyze eight locations at each of three depths from the exposed surface, 12.7, 25.4, and 38.1 mm (0.5, 1.0, and 1.5 in.). The XRF had been calibrated previously by taking 100 measurements in different areas of each of 11 concrete mixtures that had been cast with known amounts of NaCl. The average values of the XRF measurements are plotted (as small blue triangles) against the admixed chloride content in Fig. 5. The data from the current measurements are superimposed on the graph. The chloride concentrations at various cylinder depths, obtained from the graph, are plotted as a bar chart in Fig. 6.

Summary and Conclusions

The compressive strengths measured for specimens exposed to the CaCl₂, MgCl₂, and multichloride brines were about 20 and 25% lower than the strengths of specimens exposed to NaCl brine or cured in a fog room, respectively. The observation that NaCl is the most benign of the four brines studied is in agreement with strain measurements presented in previous work.¹⁷

It should be emphasized that the cylinders were constantly immersed in the brines, whereas concrete structures in the field would be exposed intermittently and only for a few months every year. Nevertheless, the repeated drying between deicing applications in the field would allow much faster ingress of the brines by absorption than experienced by diffusion during continuous immersion. Moreover, cracks in concrete structures would be expected to exacerbate the ingress of deicing salts and lead to more significant decreases in strength.

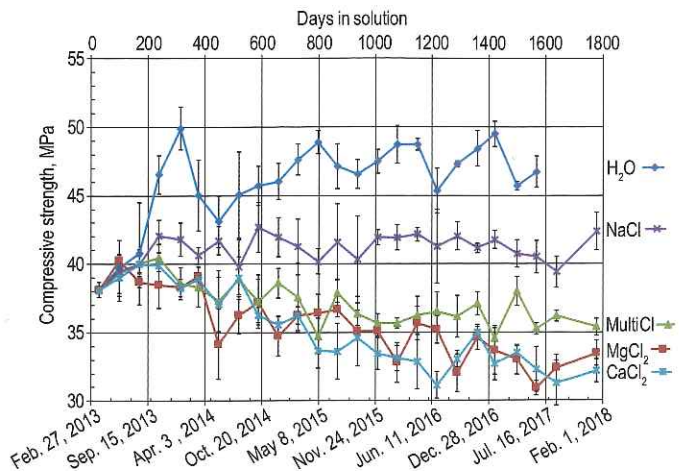


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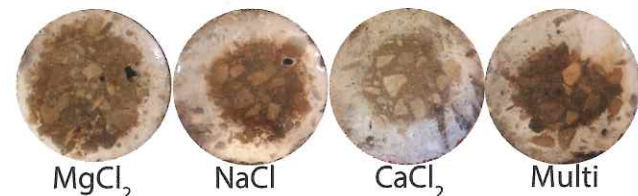


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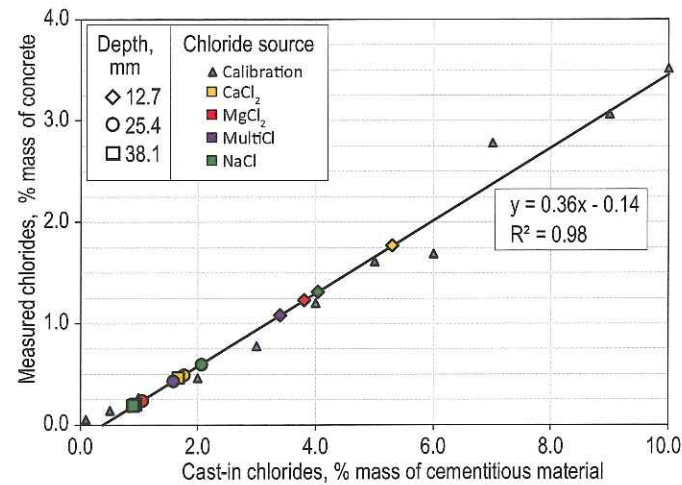


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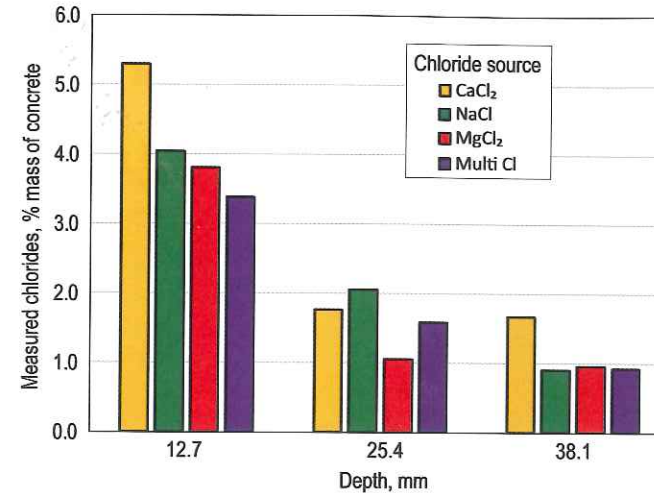


Fig. 6: Chloride concentrations by mass of concrete, determined at depths of 38.1, 25.4, and 12.7 mm from the exposed surface of test cylinders. Chloride concentrations were obtained from the calibration curve shown in Fig. 5 (Note: 1 mm = 0.04 in.)

Acknowledgments

The authors wish to acknowledge the financial support for this project provided by the Province of Ontario and the Natural Science and Engineering Research Council of Canada, the material support supplied by CRH Canada, and colleagues and technicians at the University of Waterloo who helped cast the 400 cylinders.

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Received and reviewed under Institute publication policies.



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