Damage Development in Cementitious Materials Exposed to Magnesium Chloride Deicing Salt

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ABSTRACT

Magnesium chloride (MgCl$_2$) is used in deicing applications due to its capability to depress freezing temperatures to a lower point than other salts such as sodium chloride (NaCl). The constituents of concrete (i.e., pores solution, calcium hydroxide, aluminate phases, and calcium silicate hydrate gel) can alter the MgCl$_2$–H$_2$O phase diagram when it is used to interpret the performance of concrete. Different chemical reactions may concurrently occur between MgCl$_2$ and cementitious constituents to form Brucite, Friedel's salts, magnesium silicate hydrate, magnesium oxychloride, and/or secondary calcium oxychloride. In this study, it was observed that MgCl$_2$ can be entirely consumed in concrete by the chemical reactions and produce CaCl$_2$. As such, it was found that MgCl$_2$ interacts significantly with a cementitious material and it follows a response that is more similar to the Ca(OH)$_2$-CaCl$_2$-H$_2$O phase diagram than that of the MgCl$_2$–H$_2$O phase diagram. Mortar samples exposed to low concentration MgCl$_2$ solutions (<10% by mass) for a short duration of freezing and thawing showed damage due to ice formation, while for higher concentrations (≥10% by mass), the damage was most likely due to the chemical reactions between MgCl$_2$ and cementitious constituents at room temperature (23 °C). These chemical reactions occurred rapidly (within 5-10 min) and caused a significant decrease in subsequent fluid ingress into exposed concrete.

Keywords: Brucite, Concrete, Deicing Salt, Freeze-Thaw, Damage, Magnesium Oxychloride, Magnesium Silicate Hydrate (M-S-H), Phase Change, Calcium Oxychloride.
1.0 Introduction

The widespread use of deicing salt is considered to be a primary cause of the deterioration of concrete structures in cold climates, resulting in costly repairs and early replacement of concrete infrastructure elements. Deicing salts can penetrate into the concrete and cause corrosion of reinforcement, as well as changing the concrete microstructure by participating in aggressive chemical reactions. Changes in concrete microstructure due to aggressive chemical reactions are often accompanied by a decrease in the mechanical properties, a change in transport resistance of concrete, and damage and degradation. The formation of expansive phases and salt crystallization in concrete pores are thus two major sources of damage and cracking in a concrete exposed to deicing salts [1–7].

Among the most common deicing chemicals, MgCl$_2$ is perceived as being particularly effective in melting ice and snow due to: 1) its ability to depress the freezing temperature of a solution to a lower temperature than other salts (Figure 1) and 2) dissolution of MgCl$_2$ itself can produce heat that can be further used to melt ice or snow (enthalpy of hydration = -2653 kJ/mol). However, concrete exposed to MgCl$_2$ de-icing salt typically exhibits changes in its microstructure due to chemical reactions, including formation of brucite, Friedel's salts, magnesium silicate hydrate (M-S-H), magnesium oxychloride, and/or secondary calcium oxychloride; these changes can be accompanied by severe cracking, even if the concrete does not experience any freezing and thawing cycles [5,8–10].
Figure 1 – a) Phase diagram for MgCl$_2$-H$_2$O and b) comparison of freezing temperature for aqueous MgCl$_2$ with NaCl, CaCl$_2$, and KAc (potassium acetate) deicing chemicals.

MgCl$_2$ deicers can react with the cement paste to produce M-S-H and brucite (Mg(OH)$_2$).

As described in Eq. 1, non cementitious magnesium silicate hydrate is formed by replacing the calcium from the cementitious calcium silicate hydrate (C-S-H) with magnesium. The formation of M-S-H was reported to produce damage in concrete and it appears to be a gradual and slow reacting product [8,11].

\[
\text{C-S-H + MgCl}_2 \rightarrow \text{CaCl}_2 + \text{M-S-H} \quad (\text{M-S-H}) \quad \text{Eq. 1}
\]

The formation of brucite is caused by MgCl$_2$ reacting with Ca(OH)$_2$ as shown in Eq. 2. In the presence of reactive dolomite aggregate, brucite formation resulted in mechanical distress [12]. The brucite usually forms on the surface of concrete samples as an outer layer product [5,8,13–15]. The brucite appears to be a dense and homogeneous product [15]. It is also reported that the brucite layer can slow down concrete deterioration due to deicing salt exposure by hindering ingress of the chloride solution into the concrete [8].

\[
\text{Ca(OH)}_2 + \text{MgCl}_2 \rightarrow \text{CaCl}_2 + \text{Mg(OH)}_2 \quad (\text{Brucite}) \quad \text{Eq. 2}
\]
Formations of magnesium oxychloride and calcium oxychloride were also reported in concrete with MgCl₂ as secondary reactions [5,7,10], since CaCl₂ and Mg(OH)₂ should be formed first by reactions described in Eq. 1 and Eq. 2. Two common phases of magnesium oxychloride are typically reported to exist, containing either 3 or 5 Mg(OH)₂ molecules, so called the 3-form and 5-form, respectively (Eq. 3) [7,16–18]. The addition of small quantities of hydraulic aluminate minerals (such as CA, C₃A, and C₄AF) can convert the 5-form magnesium oxychloride to 3-form magnesium oxychloride (3Mg(OH)₂•MgCl₂•8H₂O) [18]. It was also reported that the 5-form phase can alter to 3-form over time and that the 3-form is more stable than the 5-form [17]. In concrete exposed to MgCl₂, therefore, it is expected that 3-form magnesium oxychloride exists due to the usual presence of C₃A and C₄AF. The 3-form magnesium oxychloride is unstable and can dehydrate and lose water at temperatures around 65 ºC [17].

\[
(3 \text{ or } 5)\text{Mg(}OH\text{)}₂ + \text{MgCl}_₂ + 8\text{H}_₂\text{O} \rightarrow (\text{3 or 5})\text{Mg(OH)}₂\text{•MgCl}_₂\text{•8H}_₂\text{O} \\
(\text{Secondary Magnesium Oxychloride})
\]

The formation of calcium oxychloride can be described as in Eq. 4. Calcium oxychloride was found as platey-shaped crystals in concrete exposed to MgCl₂ [1,5,10,19]. The formation of calcium oxychloride has been reported to be very expansive and destructive within the cementitious matrix [1,5]. Calcium oxychloride can form at temperatures above the freezing point of water [1,20] and is unstable at room temperature and lower levels of relative humidity [9,21–23].

\[
3\text{Ca(OH)}₂ + \text{CaCl}_₂ + 12\text{H}_₂\text{O} \rightarrow 3\text{Ca(OH)}₂\text{•CaCl}_₂\text{•12H}_₂\text{O} \\
(\text{Secondary Calcium Oxychloride})
\]
MgCl₂ deicers can also cause formation of calcium chloroaluminate phases such as Freidel's salt [8,24–27]. A possible reaction for the formation of Freidel's salt in the presence of MgCl₂ salt, for example, is shown in Eq. 5 [27]. The formations of magnesium oxychloride, calcium oxychloride, and M-S-H were reported as primary sources for severe deterioration. In contrast, brucite, magnesium sulfate, and Freidel's salt are not generally reported as very destructive components [5,7,8,10,14,28].

\[
\text{MgCl}_2 + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O} + \text{MgSO}_4 \cdot 2\text{H}_2\text{O} \\
\text{(Monosulfate)} \quad \text{(Freidel's salt)} \quad \text{(Magnesium Sulfate Hydrate)} \quad \text{Eq. 5}
\]

In previous studies [1–4,29–31], the influence of NaCl and CaCl₂ deicing salts on damage development in cementitious materials has been investigated. It was found that chemical reactions between the matrix and salt solution can result in the formation of additional phases that can cause severe damage in cementitious materials. For NaCl, the source of this chemical phase transition appears to be most likely due to the presence of aluminate phases within the concrete. In the CaCl₂ case, the additional phase change was mainly due to the formation of calcium oxychloride, and calcium hydroxide was the main source of this reaction. While the use of NaCl and CaCl₂ deicing salts are relatively common practices to remove ice and snow from the surface of roadways and pavement, MgCl₂ is also used in some regions. For MgCl₂, there have been attempts to investigate the potential physical and chemical changes that may be caused by MgCl₂ deicing salts and lead to damage development [5,7,8,10,14,28]. However, the interaction between MgCl₂ and the cementitious material constituents (i.e., pore solution, calcium hydroxide, aluminate phases, or C-S-H) has not been fully understood.

The current research attempts to improve the understanding of the contributions that MgCl₂ deicing salt may have in cementitious materials to produce damage. It is hypothesized...
that the conventional MgCl\textsubscript{2}–H\textsubscript{2}O phase diagram is not fully descriptive of what occurs in
cementitious materials when MgCl\textsubscript{2} is used. Therefore, it is necessary to develop a phase
diagram that is applicable for concrete exposed to MgCl\textsubscript{2} deicing salt; this phase diagram can
be further used to interpret the damage development in concrete exposed to MgCl\textsubscript{2} deicing
salts.

2.0 Experimental Program

Experiments have been performed on mortar samples and hydrated cement powders (or
ground cement paste). These experiments are 1) longitudinal guarded comparative calorimeter
(LGCC) equipped with acoustic emission measurement, 2) micro focused X-ray fluorescence
(\textmu XRF), 3) low temperature differential scanning calorimetry (LT-DSC), and 4) isothermal micro-
calorimetry (IMC). The LGCC experiment was performed to evaluate damage development in
mortar samples due to phase changes under thermal cycling. \textmu XRF was performed to evaluate
MgCl\textsubscript{2} fluid ingress and resultant chloride ion profiles in mortar samples. LT-DSC was performed
to detect possible phase transitions and to develop a phase diagram that can be used for
cementitious materials exposed to MgCl\textsubscript{2} deicing salts. IMC was used to evaluate the rate of
reaction that may occur between cementitious materials and MgCl\textsubscript{2} deicing salt.

2.1 Materials, Mixture Proportioning, Specimen Preparation, and Conditioning

Type I ordinary portland cement (OPC) was used in this study. This cement had a
calculated Bogue phase composition of 60 % tricalcium silicate (C\textsubscript{3}S), 10 % dicalcium silicate
(C\textsubscript{2}S), 9 % tricalcium aluminate (C\textsubscript{3}A), and 10 % tetracalcium aluminoferrite (C\textsubscript{4}AF) by mass,
and a reported Blaine fineness of 375 m\textsuperscript{2}/kg. The total equivalent alkali was 0.86 % originating
from 0.35 % of Na\textsubscript{2}O and 0.77 % of K\textsubscript{2}O, by mass. Aggregates used to prepare mortar
specimens consisted of natural sand with a maximum size of 4.75 mm, specific gravity of 2.61, fineness modulus of 2.89, and an absorption value of 2.2 % by mass.

To perform LGCC and µXRF experiments, mortar specimens were prepared using a sand volume fraction of 55 % and a water-to-cement ratio (w/c) of 0.42 by mass. The mass of cement, water, and sand (in saturated-surface-dry (SSD) condition) were 612 kg, 257 kg, and 1435 kg per m$^3$ of total material volume, respectively. The mortar was cast in 25.4 mm × 25.4 mm × 300 mm (1 in × 1 in × 11.81 in) molds and the samples were demolded after 24 h. All mortar bars were then sealed in double plastic bags and cured for 28 d in these sealed conditions at 23 °C ± 0.5 °C. After 28 d of curing, the mortar bars were cut using a wet saw to 25.4 mm × 25.4 mm × 50.8 mm (1 in × 1 in × 2 in) specimens. These specimens were then placed in a vacuum oven at 65 °C ± 1 °C and a pressure of 20 mm Hg ± 5 mm Hg for 7 d to remove moisture (the ± 1 °C and ± 5 mm Hg are indicative of the nominal operating range encountered when running the experiment). These samples were then vacuum saturated with DI water or MgCl$_2$ solutions before performing experiments.

To perform LT-DSC and IMC experiments, powders of hydrated cement paste and calcium hydroxide were used. Cement paste with a water-to-cement ratio (w/c) of 0.42 by mass was prepared. The cement paste was cured for one year in a sealed condition. After one year, the cement paste specimens were ground in a mortar and pestle and the 75-μm (No. 200) sieve was used to separate out larger particles. The hydrated cement powder was then stored in a vacuum oven at 65 °C ± 1 °C and a pressure of 20 mm Hg ± 5 mm Hg for 3 d to remove moisture. To perform an LT-DSC experiment, a synthetic pore solution ([K+] = 0.65 mol/L, [Na+] = 0.45 mol/L, and [OH-] = 1.10 mol/L) was also prepared in addition to powder samples. This solution concentration was calculated using software for estimation of pore solution properties developed previously (http://concrete.nist.gov/poresolncalc.html) [32] for the cement used in this study (assuming 100 % degree of hydration in a sealed condition).
2.2 Testing Procedure

As mentioned before, four types of experiments were conducted in this study: 1) longitudinal guarded comparative calorimeter (LGCC) equipped with acoustic emission measurement, 2) micro focused X-ray fluorescence (µXRF), 3) low temperature differential scanning calorimetry (LT-DSC), and 4) isothermal micro-calorimetry (IMC).

The LGCC, equipped with acoustic emission measurement, was used to perform the freeze-thaw experiments described in [3,4]. A temperature gradient was generated in the test specimen to produce a one-dimensional heat flow. Two meter bars with known thermal properties were used on the top and bottom of the mortar specimens; and temperatures at different locations were monitored to calculate the heat flow through the specimens. Since acoustic emission (AE) has shown promise in quantifying damage (i.e., cracking) [33], acoustic activity was detected during test by one acoustic sensor attached to the specimen. Wave speed (pulse velocity) was also measured on specimens using a pulsed wave generated by two coupled AE sensors through the length of the specimen before and after the freeze-thaw test to measure the damage index. Samples saturated with 0 %, 0.9 %, 3 %, 5 %, 8 %, 10 %, 13 %, and 15 % (by mass) MgCl₂ solutions were used to perform LGCC experiments. The temperature of mortar specimens was varied from 24 °C to -40 °C by using a cold plate. The cooling and heating rates were -2 °C/h and 4 °C/h, respectively. At 24 °C and -40 °C, the temperature was kept constant for 1 h and 4 h, respectively, to allow the specimen to reach thermal equilibrium.

The test was complete after one cycle.

The µXRF was used to estimate the penetration depth of chloride ions into the specimens through the use of hyperspectral X-ray imaging. After imaging, a full X-ray spectrum for the chloride concentration was obtained over its respective spectral range. This imaging technique is described in [34]. For µXRF experiments, one mortar specimen saturated with DI
water (as a reference sample) and one mortar specimen saturated with 20 % (by mass) MgCl₂ solution were used. They were then broken, exposing a cross section surface of their interior for μXRF imaging.

The LT-DSC was used to study possible chemical phase transitions in powder-solution samples. The initial temperature of the test was set to equilibrate at 25 °C. After the initial temperature became stable, the LT-DSC cell was cooled to -90 °C at a cooling rate of -5 °C/min. The specimen temperature was kept constant at this temperature (-90 °C) for one min to allow the specimen to equilibrate. A cycle of heating and cooling was established between -90 °C and 70 °C. The specimen was equilibrated again at -90 °C for 5 min; and the temperature of the specimen was increased to 70 °C at a heating rate of 5 °C/min. For the LT-DSC, four different series of experiments were performed: Series I) development of a phase diagram for the MgCl₂-H₂O system, Series II) development of a phase diagram for pore solutions and MgCl₂, Series III) development of a phase diagram for Ca(OH)₂–MgCl₂-H₂O, and Series IV) development of a phase diagram for a cementitious material exposed to MgCl₂ solution (using the hydrated cement powder). For Series I and Series II, a total solution mass of 3 mg to 5 mg was used in LT-DSC. For Series III and Series IV, a 9 mg to 11 mg powder sample was mixed with 9 mg to 11 mg of MgCl₂ solution and the mixture was tested in the LT-DSC immediately after mixing (0 d), 1 d after mixing, and 7 d after mixing.

The isothermal micro-calorimeter was used to measure the heat released during the reaction between hydrated cement paste powder or calcium hydroxide powder and MgCl₂ solution under constant temperature (23 °C ± 0.1 °C). The heat release can be used to determine the rate of reaction. An internal admix ampoule was used to determine the heat of reaction as soon as MgCl₂ solution was introduced to and mixed with powder by stirring. For these IMC experiments, 2 g of powder was mixed with 2 g of MgCl₂ solution.
3.0 Results and Discussion

3.1 Thermal Response of Mortar samples (LGCC Experiment)

During the LGCC experiment, the thermal response of mortar samples was evaluated. Figure 2 indicates the temperatures at different locations of the specimen and the meter bars.
Using the measured temperatures and the thermal properties of the meter bars, the heat flow inward or outward of the mortar samples [3] was calculated and is plotted in Figure 2. During freezing, an increase in the temperature and an exothermic behavior (shown by an arrow in this figure) were observed due to ice formation. During thawing, the specimen temperature remains constant near 0 °C, until the melting of ice concludes, as an endothermic behavior was observed.

Figure 2- Temperature at different locations ($T_1$ & $T_2$: temperature between cold plate and bottom meter bar; $T_3$ & $T_4$: temperature between bottom meter bar and specimen; $T_5$ & $T_6$: temperature between specimen and top meter bar; and $T_7$: temperature at the top surface of top meter bar), and heat flow versus time during freeze-thaw cycle for specimens saturated with (a) DI water, and (b) 10 % MgCl$_2$.
The temperatures associated with the exothermic/endothermic behaviors (i.e., freezing/thawing temperatures) were obtained for all samples and are compared with the conventional MgCl₂-H₂O phase diagram in Figure 3. A relatively constant difference between the freezing and thawing temperatures was observed; this is mainly due to supercooling during freezing. A reduction in freezing and thawing temperatures was observed as the solution concentration increases; however, the rate of reduction is less than the one expected from the MgCl₂-H₂O (pure) phase diagram (Figure 3). This may be due to MgCl₂ being consumed by a replacement of magnesium for calcium in Ca(OH)₂ and C-S-H, resulting in the formation of CaCl₂, M-S-H, brucite, and magnesium/calcium oxychloride (Eq. 2, Eq. 1, Eq. 3, and Eq. 4); thereby diluting the original solution. For 13 % and 15 % concentrations, the freezing points were even above the liquidus line of conventional MgCl₂-H₂O. A considerable reduction in fluid ingress into mortar samples during vacuum saturation was observed as the salt concentration increased, which will be discussed in Section 3.3. As a result, the LGCC experiment was not performed for concentrations of MgCl₂ greater than 15 % (by mass).
Figure 3 - Freezing and thawing points of solution in mortar samples saturated with MgCl₂ solutions obtained by LGCC with comparison to the phase diagram of MgCl₂ solution (the uncertainty for this measurement was previously measured in [1,3] and the average coefficient of variation was determined to be 9.2 %).

3.2 Damage Detection (AE Measurement and LGCC Experiment)

Acoustic emission activity (produced primarily due to cracking) was monitored during the LGCC experiment to determine freeze-thaw damage. The AE activity (amplitude of events) is shown in Figure 4 as a function of temperature for specimens saturated by DI water and 10 % MgCl₂ solution, as examples. At the freezing temperature, clusters of AE events develop due to cracking (~ -5 °C for DI water and ~ -10 °C for 10 % MgCl₂). During cooling, the AE activities are mainly due to hydraulic and osmotic pressures caused by the ice formation. For sample saturated with 10 % MgCl₂, the AE events during cooling spread out after freezing while for sample saturated with DI water they are more concentrated. This is mainly due to the gradual additional damage caused by increasing osmotic pressure as the temperature decreases.
AE activity is also seen during heating which may be attributed to cracking development/propagation due to stress relaxation and thermal expansion of the specimen during ice melting. The damage on thawing is significantly lower than the damage on freezing. During heating, a cluster of AE events was observed at the moment of ice melting for sample saturated with DI water while no cluster was observed for sample saturated with 10% MgCl₂.

A damage index (a measure of the reduction in dynamic elastic modulus) was also determined using the ASTM C597-09 procedure [35] for specimens in two conditions: a) damage caused during immersion time, and b) damage caused during the freeze-thaw cycle. Figure 5a shows the damage index as the MgCl₂ concentration increases. Mortar specimens saturated with high concentration MgCl₂ solutions (≥10% by mass) indicated damage before the freezing and thawing began, during the time when the samples were immersed in solution. This
damage appears to correspond to the chemical reactions occurring between MgCl$_2$ and cementitious constituents (Eq. 2, Eq. 1, Eq. 3, and Eq. 4). In contrast, these samples did not show considerable damage due to the freeze-thaw cycle itself. This may be attributed to the fact that a large portion of solution in concrete pores was consumed by the chemical reactions to form magnesium/calcium oxychlorides (solid phases at room temperature, i.e., 23 °C). As a result, further ingress of solution would be prevented due to pore clogging; and thus, the sample would remain unsaturated during the subsequent freeze-thaw cycle.

Mortar specimens saturated with low concentration MgCl$_2$ solutions (<10 % by mass) showed a relatively small reduction in dynamic elastic modulus during immersion time, while they showed considerable damage during the subsequent freeze-thaw cycle. For these samples, the hydraulic and osmotic pressures caused by ice formation during freezing and thawing may be the main source of cracking. Figure 5b shows the total cumulative AE signal strength as a function of solution concentration. The samples saturated with 3 % and 5 % MgCl$_2$ solution (by mass) showed a relatively higher level of freeze-thaw damage and a greater cumulative AE signal strength. This can be attributed to the critical damage caused by a combination of hydraulic pressure and osmotic pressure during freezing and thawing [36,37].
Figure 5 – (a) Change in the relative dynamic elastic modulus (damage index) due to freeze-thaw damage for samples saturated with different dosages of MgCl₂ solution (the uncertainty was previously measured in [1,3] and the average coefficient of variations were determined to be 6.2 % and 15.6 % for damage index and cumulative AE signal strength, respectively).

3.3 MgCl₂ Fluid Ingress and Chloride Profile (µXRF Experiments)

During vacuum saturation of mortar specimens for the LGCC experiment, a reduction in fluid absorption into mortar specimens was observed for specimens saturated with high concentration solutions (≥8 % by mass). As the concentration of solution increased, the amount of fluid ingress decreased. Therefore, the reduction in degree of saturation (DOS) for mortar samples tested in the LGCC experiment was determined using Eq. 6 and it is shown in Figure 6 as a function of MgCl₂ concentration.

$$\text{Reduction in DOS} = 1 - \frac{V_{abs}}{V_{max}} \quad \text{Eq. 6}$$
where $V_{\text{abs}}$ is the volume of the solution absorbed by the samples and $V_{\text{max}}$ is the maximum volume of a solution that can be absorbed by the mortar samples used in this study (obtained from the sample saturated with DI water). The reduction in DOS for specimens saturated with MgCl$_2$ solutions with concentrations greater than 8 % (by mass) is most likely attributed to the enhanced formation of brucite, and magnesium/calcium oxychloride that can fill in the pores near the surface of specimens and block the fluid ingress into the mortar samples. In fact, higher volumes of brucite and magnesium/calcium oxychloride should be produced as the solution concentration increases.

![Graph showing reduction in DOS vs MgCl$_2$ concentration]

Figure 6 - Reduction in degree of saturation (DOS) for mortar specimens saturated with different concentrations of MgCl$_2$ solutions (the uncertainty was measured in [1,3] study and the maximum standard deviation was determined to be 3 %).

To better understand the MgCl$_2$ fluid ingress into mortar samples, two mortar specimens were saturated using only DI water and 20 % MgCl$_2$ solution; and the chloride profile within their
depth was determined using µXRF. Figure 7 indicates color-coded image maps for chloride. Yellow and white colors indicate higher concentrations of chlorides, while a black color indicates areas with relatively no chloride. In addition, red color shows areas with relatively lesser intensity of chloride ions than the yellow and white colors. The normalized color intensity within the depth of each sample was also determined using the average value for the middle third of the sample section and is plotted in Figure 7. The core of the specimen is free of chloride while the edges of samples have a higher level of chlorides. This can again provide confirmatory evidence that pores near the specimen surfaces may be blocked by the possible chemical reactions between the cement matrix and MgCl$_2$, thereby preventing further fluid ingress into the sample saturated with the 20 % MgCl$_2$ solution. Aggregates appeared in black color since they have quite small porosity and chloride ions cannot penetrate into aggregates.
Figure 7 - X-ray fluorescence images of mortar samples saturated with DI water and 20% MgCl₂ solution and average normalized color intensity within the depth of mortar specimens.

3.4 Phase Diagram Development (LT-DSC Experiment)

Four series of experiments were performed using powder/solution samples in the LT-DSC to determine the temperature at which phase changes associated with the formation of ice, eutectic solid, calcium oxychloride, and magnesium oxychloride occur. This was done to develop a phase diagram for 1) MgCl₂ solution, 2) pore solution and MgCl₂, 3) Ca(OH)₂ and MgCl₂ solution (Ca(OH)₂-MgCl₂-H₂O), and 4) cementitious material (hydrated cement) and MgCl₂ solution.
3.4.1 MgCl$_2$–H$_2$O solution and Pore Solution Containing MgCl$_2$

For the MgCl$_2$–H$_2$O solution, two endothermic peaks were observed corresponding to eutectic solid and ice melting as the temperature of the sample increased. The eutectic and liquidus peaks for MgCl$_2$ solution are shown in Figure 8a as a function of salt concentration. The experimental results followed the conventional MgCl$_2$–H$_2$O phase diagram.

For the pore solution and MgCl$_2$ system, in addition to the eutectic and ice peaks, two additional endothermic peaks were detected during the sample heating as shown in Figure 8b. For pore solution, the liquidus and eutectic temperatures showed relatively a different behavior than that shown in the MgCl$_2$–H$_2$O phase diagram. As indicated in Figure 8b, a reduction in the freezing temperature depression was observed for temperatures at which ice forms as the salt concentration increases. In addition, it appears that the eutectic concentration changed to a higher concentration (~ 27 % by mass) than expected from the MgCl$_2$–H$_2$O phase diagram (21.6 % by mass). Two additional endotherms were observed from phase changes associated with the presence of NaOH and KOH in the pore solution. Endothermic 1 and endothermic 2 temperatures most likely reflect the formation of KCl·H$_2$O (transition temperature at -10.7 °C) and NaOH·7H$_2$O (transition temperature at -28.0 °C), respectively [38,39].
Figure 8 - Comparison of temperatures associated with different phase changes observed in LT-DSC with conventional phase diagram for MgCl₂ solution: a) MgCl₂ solution, b) low alkali pore solution containing MgCl₂ salt (calorimetric reproducibility is reported to be within ± 0.05 % using reference indium metal [40]).

3.4.2 Ca(OH)₂-MgCl₂-H₂O

For Ca(OH)₂ powder with MgCl₂-H₂O solution, two endothermic peaks were observed during the heating of the samples in LT-DSC. The results are shown in Figure 9 and are compared with the phase diagrams for MgCl₂-H₂O, and CaCl₂–H₂O, and the calcium oxychloride formation line. The endotherm that was observed at temperatures greater than 0 °C is most likely due to the formation of calcium oxychloride since its formation temperature follows the calcium oxychloride liquidus line. The endotherm observed at 0 °C is compatible with pure ice melting. It appears MgCl₂ was consumed through a very rapid chemical reaction between MgCl₂ and Ca(OH)₂ to form Mg(OH)₂ (brucite) and CaCl₂ (Eq. 2); the produced CaCl₂ reacted with the remaining Ca(OH)₂ and calcium oxychloride was formed.
Mg(OH)$_2$ is a relatively stable material and does not decompose until the temperature reaches approximately 400 °C. There is a possibility that magnesium oxychloride was also formed and it can decompose (lose some of its water) during the temperature range applied in this study. However, no endotherm was observed associated with magnesium oxychloride decomposition. This may be due to the fact that the reaction between MgCl$_2$ and Ca(OH)$_2$ to form Mg(OH)$_2$ (brucite) and CaCl$_2$ was very fast (Section 3.5) and no MgCl$_2$ remained to form magnesium oxychloride. It should be noted that mixing calcium hydroxide powder with MgCl$_2$ solution with a concentration greater than 15 % could not be achieved, due to a very fast reaction and near immediate solidification.

Figure 9 - Phase diagram for a system containing MgCl$_2$, Ca(OH)$_2$, and H$_2$O (the liquidus line for the formation of calcium oxychloride was obtained from [1] as shown liquidus$_{Ca-Oxy}$; CaCl$_2$-H$_2$O phase diagram and liquidus$_{ca-oxy}$ are plotted as a function of CaCl$_2$ concentration while MgCl$_2$-H$_2$O phase diagram is plotted as a function of MgCl$_2$ concentration).
3.4.3 Cementitious Material Exposed to MgCl₂ solution

Hydrated cement powder (ground paste) and MgCl₂ solution behaved quite differently than the conventional MgCl₂–H₂O phase diagram. Three endothermic peaks were observed during the heating of the samples in LT-DSC. The results are shown in Figure 10 and are compared with the phase diagrams for MgCl₂–H₂O, and CaCl₂–H₂O, and the calcium oxychloride formation line. As expected, hydrated cement powder and MgCl₂ solution did not follow the conventional MgCl₂–H₂O phase diagram. Instead, the detected eutectic and liquidus lines matched quite well with what would be expected from the CaCl₂–H₂O phase diagram [1].

An additional endothermic behavior that was observed at temperatures greater than 0 °C is most likely due to the dehydration of magnesium oxychloride, since its temperature does not completely follow the liquidus line for the formation of calcium oxychloride. However, for lower concentrations (≤15 % by mass), it seems that magnesium oxychloride is not stable and can convert to calcium oxychloride at later ages (7 d, Figure 10b) since the temperature at which oxychloride was detected moved to a lower temperature (i.e., liquidus line associated with calcium oxychloride formation) as the exposure time increased.

For higher concentrations (>15 % by mass), the additional endothermic peak was not observed immediately after mixing the hydrated cement powder and MgCl₂ solution (Figure 10a); it was only detected after 7 d (Figure 10b). For concentrations greater than 15 % by mass, the quick formation of brucite may consume whole calcium hydroxide and prevent the formation of calcium oxychloride. At later ages (7 d), brucite can react with remained MgCl₂ in the solution and form magnesium oxychloride. At lower concentrations (<15 % by mass), however, the amount of MgCl₂ in the solution may not be sufficient to consume whole calcium hydroxide for brucite formation. Therefore, remained calcium hydroxide may react with produced CaCl₂ to form calcium oxychloride. At lower concentrations, the conversion between calcium oxychloride
and magnesium oxychloride at later ages may show that magnesium oxychloride may be a more stable material than calcium oxychloride.

A logarithmic trend line was fitted to the data points associated with the dehydration of magnesium oxychloride (i.e., when magnesium oxychloride loses some water) and is presented in Eq. 7 and shown as the Mg-Oxy line in Figure 10.

\[ T = 25.32 \ln \frac{C_o}{C^*} \quad R^2=0.97 \quad \text{Eq. 7} \]

where \( T (°C) \) is the temperature at which magnesium oxychloride begins to dehydrate, \( C_o (% \text{ by mass}) \) is the initial concentration of \( \text{MgCl}_2 \) solution, and \( C^* (= 2.58 \%) \) is the theoretical minimum concentration of \( \text{MgCl}_2 \) solution at which the magnesium oxychloride begins to dehydrate (as \( 3\text{Mg(OH)}_2\cdot\text{MgCl}_2\cdot8\text{H}_2\text{O} \) loses some of its water (see Section 1.0)).

Figure 10 - Comparison of temperatures associated with different phase changes for hydrated cement powder and \( \text{MgCl}_2 \) solution in LT-DSC with phase diagrams for \( \text{MgCl}_2\cdot\text{H}_2\text{O}, \text{CaCl}_2\cdot\text{H}_2\text{O}, \)
calcium oxychloride (shown by liquidus$_{\text{Ca-Oxy}}$), and magnesium oxychloride (shown by Mg-Oxy) 
at different exposure ages: a) immediately after mixing the solution and powder, and b) 7 days 
after mixing the solution and powder.

3.5 Reaction Rate between Powder and MgCl$_2$ Solution (IMC Experiment)

To assess the rate of reaction between hydrated cement paste or calcium hydroxide and MgCl$_2$ solutions, isothermal calorimetry experiments were performed. The heat flow was measured as soon as MgCl$_2$ solution was mixed with dry powder (hydrated cement paste or Ca(OH)$_2$) and it is shown in Figure 11. Blending the Ca(OH)$_2$ powder with DI water showed a very small amount of heat release. This may be attributed mainly to the heat release caused by internal mixing and the heat of wetting. A considerably higher heat release was observed during blending hydrated cement powder and DI water that is most likely associated with internal mixing, heat of wetting, and the heat of hydration of any unreacted cement (or unreacted C$_3$A).

As the concentration of the solution increased, the heat release increased for both Ca(OH)$_2$ and hydrated cement powders. The majority of the heat release occurred within the first 10 min, illustrating the high rate of reaction between Ca(OH)$_2$ or the hydrated cement powder and MgCl$_2$ solutions to form brucite and/or calcium/magnesium oxychloride. As the salt concentration increases, the increase in the heat release appears to be higher for the hydrated cement powder than for pure calcium hydroxide (assuming 25 % calcium hydroxide in the hydrated cement powder). This additional heat release for the hydrated cement powder may be due to the reaction between aluminate phases in the hydrated cement powder and MgCl$_2$ to form magnesium sulfate hydrate and Freidel’s salt (Eq. 5).
Figure 11 - Heat flow curves (normalized by the amount of powder) measured at 23 °C as a function of time for (a) \(\text{Ca(OH)}_2\) powder and MgCl\(_2\) solution, and (b) hydrated cement powder and MgCl\(_2\) solution. (Percentages indicate MgCl\(_2\) solution concentration by mass, the precision is reported within ± 20 µW [41]).

4.0 Conclusions

This paper shows that the chemical reactions between MgCl\(_2\) and cementitious constituents can result in the formation of additional chemical phases such as CaCl\(_2\), brucite, magnesium oxychloride, and calcium oxychloride in concrete. The additional chemical phases can result in damage in concrete, as well as changes in the behavior of the remaining solution in concrete under thermal variations.

Thermal evaluation of cementitious samples showed that the MgCl\(_2\)-H\(_2\)O solution in concrete does not behave as expected from the pure MgCl\(_2\)-H\(_2\)O phase diagram. This is mainly due to the chemical reactions between MgCl\(_2\) and concrete constituents and the formation of additional chemical phases. A phase diagram was proposed for a cementitious material exposed to MgCl\(_2\). It was observed that it is relatively similar to the pure CaCl\(_2\)-H\(_2\)O phase diagram, with additional phase changes associated with the formation of magnesium oxychloride and calcium oxychloride phases.
Damage of mortar samples was also evaluated when they were exposed to thermal cycling and MgCl₂ solutions. The damage observed in mortar samples saturated with low concentration MgCl₂ solution (<10% by mass) was mainly due to hydraulic pressure and osmotic pressure caused by ice formation. Exposure to high concentration MgCl₂ solutions (≥10% by mass) showed damage (reduction in dynamic elastic modulus) prior to any thermal cycling (before freeze-thaw testing, when the samples were immersed in the solution). This may be due to the formation of magnesium oxychloride or/and calcium oxychloride at room temperature (23 °C). The further change in dynamic elastic modulus after one freeze-thaw cycle was not considerable for specimens saturated with high concentration MgCl₂ solutions (≥10% by mass). This may be due to the fact that a large portion of solution in concrete pores was consumed by the formations of calcium/magnesium oxychloride and brucite, and the sample remained unsaturated. The formation of M-S-H may also be another source of damage or change in fluid ingress into mortar samples. However, more research is needed to understand the influence of M-S-H formation on damage development and fluid ingress in cementitious materials exposed to MgCl₂ solutions.

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6.0 References


A. Mesbah, M. François, C. Cau-dit-Coumes, F. Frizon, Y. Filinchuk, F. Leroux, et al., Crystal structure of Kuzel’s salt 3CaO·Al2O3·1/2CaSO4·1/2CaCl2·11H2O determined by


[38] W. van der Tempel, Eutectic Freeze Crystallization: Separation of Salt and Ice, Delf University of Technology, 2012.

