



The influence of calcium chloride deicing salt on phase changes and damage development in cementitious materials



Yaghoob Farnam^{a,*}, Sarah Dick^b, Andrew Wiese^a, Jeffrey Davis^c, Dale Bentz^d, Jason Weiss^e

^a Lyles School of Civil Engineering, Purdue University, 550 Stadium Mall Dr., West Lafayette, IN, 47907, USA

^b Lyles School of Civil Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, IN, 47907, USA

^c Materials Measurement Science Division, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8615, Gaithersburg, MD, 20899, USA

^d Materials and Structural Systems Division, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8615, Gaithersburg, MD, 20899, USA

^e Director of Pankow Materials Laboratory, Lyles School of Civil Engineering, Purdue University, 550 Stadium Mall Dr., West Lafayette, IN, 47907, USA

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ABSTRACT

The conventional $\text{CaCl}_2\text{-H}_2\text{O}$ phase diagram is often used to describe how calcium chloride behaves when it is used on a concrete pavement undergoing freeze-thaw damage. However, the chemistry of the concrete can alter the appropriateness of using the $\text{CaCl}_2\text{-H}_2\text{O}$ phase diagram. This study shows that the $\text{Ca}(\text{OH})_2$ present in a hydrated portland cement can interact with CaCl_2 solution creating a behavior that is similar to that observed in isoplethal sections of a ternary phase diagram for a $\text{Ca}(\text{OH})_2\text{-CaCl}_2\text{-H}_2\text{O}$ system. As such, it is suggested that such isoplethal sections provide a reasonable model that can be used to describe the behavior of concrete exposed to CaCl_2 solution as the temperature changes. Specifically, the $\text{Ca}(\text{OH})_2$ can react with CaCl_2 and H_2O resulting in the formation of calcium oxychloride. The formation of the calcium oxychloride is expansive and can produce damage in concrete at temperatures above freezing. Its formation can also cause a significant decrease in fluid ingress into concrete. For solutions with CaCl_2 concentrations greater than about 11.3% (by mass), it is found that calcium oxychloride forms rapidly and is stable at room temperature (23 °C).

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1. Introduction

Concrete pavement and flatwork may degrade when they are exposed to deicing chemicals. The deicing salt solution can be absorbed into the pores of concrete and can alter the cementitious matrix. The interaction between the deicing salt solution and the cementitious matrix may result in damage to the concrete [1]. Physical damage can occur due to a number of processes: 1) exposure of concrete with a high degree of saturation to freeze-thaw cycles [2–7], 2) scaling of concrete surfaces [8–11], 3) crystallization of salt in concrete pores that results in production of an internal stress [12–14], and 4) expansive forces as a result of corrosion of reinforcement when a chloride-based deicing salt is used [15,16]. While the physical attack of deicing salts has been

widely investigated, the chemical reaction between the matrix and the deicing salts has been studied less frequently.

The use of deicing salts can cause damage in cementitious materials even if a concrete does not experience freezing and melting [10,17–22]. This may be caused by the formation of Friedel's salt, Kuzel's salts [18,21–23], and/or calcium oxychloride, changes in the pore solution properties [4,17], or changes in the microstructure of hydration products [19,20,22]. Deicing salt solution, like many external solutions, may also dissolve calcium hydroxide, causing leaching that leads to an increase in permeability and a reduction of concrete alkalinity [16,24].

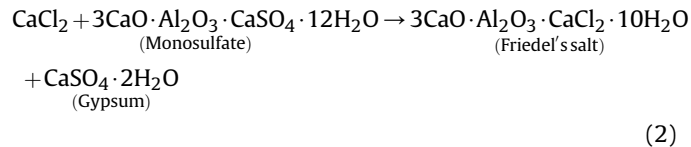
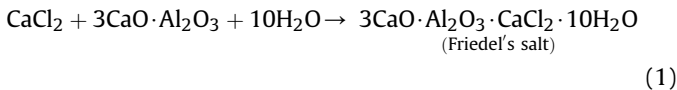
Deicing salts have different chemical and physical interactions with cementitious materials. The use of NaCl deicing salt increases freeze-thaw damage in concrete. This increase in freeze-thaw damage has been explained by the formation of an unexpected phases and the creation of osmotic pressures [4,17,20]. Concrete exposed to CaCl_2 and MgCl_2 de-icing salts also exhibited changes in the concrete microstructure. These changes have been accompanied by a severe cracking and deterioration, even if the concrete did

* Corresponding author.

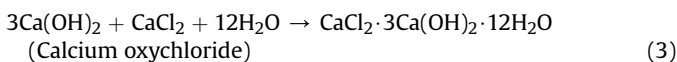
E-mail addresses: yfarnam@purdue.edu (Y. Farnam), dicks@purdue.edu (S. Dick), awiese@purdue.edu (A. Wiese), jeff.davis@nist.gov (J. Davis), dale.bentz@nist.gov (D. Bentz), wjweiss@purdue.edu (J. Weiss).

not experience any freeze-thaw cycles [18,21,22,25].

Chloride-based deicers can result in the formation of calcium chloroaluminate phases such as Friedel's salt and Kuzel's salt that can bind chloride [22,23,26–28]. Possible reactions for the formation of Friedel's salt in the presence of CaCl_2 , for example, are shown in Eq. (1) [28] and Eq. (2). Kuzel's salt ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 0.5\text{CaSO}_4\cdot 0.5\text{CaCl}_2\cdot 11\text{H}_2\text{O}$) may be also produced in the presence of chloride-based deicing salts [23,29].



Colleparidi et al. [19] concluded that CaCl_2 can result in a reaction that leads to damage, even in the absence of freeze-thaw cycles. The chemical reaction is described by the formation of calcium oxychloride (Eq. (3)).



The temperature at which calcium oxychloride forms is above the freezing point of water [18,21,22,26,30,31]. The reaction has also been described as a rapid reaction between calcium hydroxide and calcium chloride, however the rate of this reaction has not been quantified. The reaction between calcium chloride and calcium hydroxide (i.e., solid phases in the reaction) is expansive and can be destructive when it forms in the concrete matrix due to the internal hydraulic pressures that may be generated. Calcium oxychloride is unstable at room temperature and lower levels of relative humidity [18,32]. Calcium oxychloride has been reported with different molar ratios (i.e., $\text{CaCl}_2\cdot 3\text{Ca}(\text{OH})_2\cdot 12\text{H}_2\text{O}$, $\text{CaCl}_2\cdot \text{Ca}(\text{OH})_2\cdot x\text{H}_2\text{O}$, and $\text{CaCl}_2\cdot \text{Ca}(\text{OH})_2$); these phases may coexist and be interchangeable in $\text{Ca}(\text{OH})_2\text{--CaCl}_2\text{--H}_2\text{O}$ systems. However, $\text{CaCl}_2\cdot 3\text{Ca}(\text{OH})_2\cdot 12\text{H}_2\text{O}$ was observed to be destructive and can be simply altered to $\text{CaCl}_2\cdot \text{Ca}(\text{OH})_2$ or $\text{CaCl}_2\cdot \text{Ca}(\text{OH})_2\cdot x\text{H}_2\text{O}$ if the ambient temperature or humidity varies [32–34].

Fig. 1a shows the conventional phase diagram for the $\text{CaCl}_2\text{--H}_2\text{O}$ binary system. Fig. 1b illustrates an isoplethal section from the work of Vol'nov and Latysheva, and Makarov and Vol'nov [35,36] for a ternary system containing $\text{Ca}(\text{OH})_2\text{--CaCl}_2\text{--H}_2\text{O}$. It

should be mentioned that the formation of the different phases in this isoplethal section (Fig. 1b) were reported only as a function of temperature and CaCl_2 concentration. As such, the effect of $\text{Ca}(\text{OH})_2\text{:CaCl}_2$ mass/molar ratio on the formation of the different phases was not considered, but is important. Different phases exist in the $\text{Ca}(\text{OH})_2\text{--CaCl}_2\text{--H}_2\text{O}$ system: CaCl_2 solution, $\text{Ca}(\text{OH})_2$, ice, $\text{CaCl}_2\cdot 3\text{Ca}(\text{OH})_2\cdot 12\text{H}_2\text{O}$, $\text{CaCl}_2\cdot \text{Ca}(\text{OH})_2\cdot x\text{H}_2\text{O}$, and $\text{CaCl}_2\cdot n\text{H}_2\text{O}$ (where n is 2, 4, or 6).

A conventional interpretation of the $\text{CaCl}_2\text{--H}_2\text{O}$ phase diagram (Fig. 1a) shows that using a higher concentration of CaCl_2 can reduce freezing temperature. However, Fig. 1b shows the $\text{Ca}(\text{OH})_2\text{--CaCl}_2\text{--H}_2\text{O}$ isoplethal section that occurs when $\text{Ca}(\text{OH})_2$ is added as a third phase. It can be seen that $\text{Ca}(\text{OH})_2$ from the cementitious matrix in concrete alters the behavior. The interaction between $\text{Ca}(\text{OH})_2$ and CaCl_2 can alter concrete microstructure and pore solution properties resulting in the formation of calcium oxychloride. The formation and precipitation of calcium oxychloride (as an expansive phase) may change transport properties of concrete due to pore blocking and may also cause a severe deterioration due to internal expansion, even when the concrete temperature remains above 0°C , since it forms at a temperature greater than 0°C (Fig. 1b).

The temperature at which calcium oxychloride forms, its relation to the concentration of CaCl_2 solution, and its rate of formation can play an important role in concrete freeze-thaw behavior, concrete degradation, and fluid ingress into concrete.

The main purpose of this study is to provide an improved understanding of the interaction between the calcium chloride deicing salt and cementitious material and to investigate its impact on concrete deterioration. In this paper, several techniques were used to understand the $\text{Ca}(\text{OH})_2\text{--CaCl}_2\text{--H}_2\text{O}$ system and isoplethal sections (varying the concentration of $\text{Ca}(\text{OH})_2$) were used as a model system for a cementitious system. The temperatures at which different phase changes occur were also determined.

2. Experimental program

Mortar freeze-thaw behavior, mortar degradation, and fluid ingress into mortar were evaluated when the specimens were exposed to a CaCl_2 deicing salt. First, a low temperature longitudinal guarded comparative calorimeter equipped with acoustic emission detection (AE-LGCC) was used to investigate the damage (cracking) that occurs during the freezing and melting of mortar specimens saturated with solutions containing different concentrations of CaCl_2 . Micro focused X-ray fluorescence (μXRF) examination was used to study the CaCl_2 solution ingress into these mortar specimens. Low temperature differential scanning

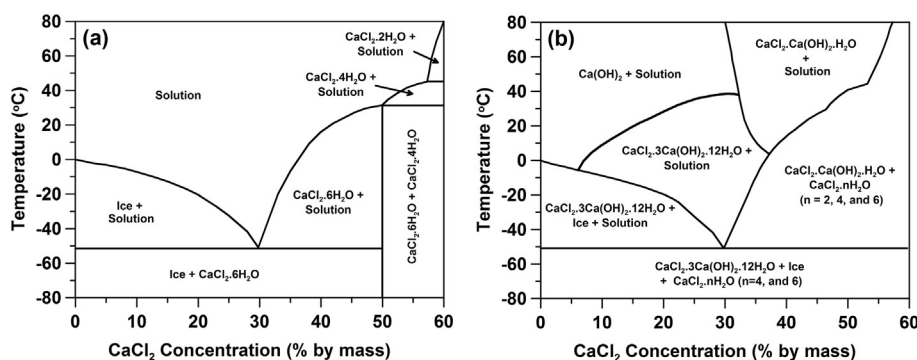


Fig. 1. a) Classical phase diagram for $\text{CaCl}_2\text{--H}_2\text{O}$ system and b) an isoplethal section for a $\text{Ca}(\text{OH})_2\text{--CaCl}_2\text{--H}_2\text{O}$ system developed from Refs. [35,36] ($\text{Ca}(\text{OH})_2\text{:CaCl}_2$ molar ratios ≤ 0.5).

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