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Damage in cement pastes exposed to NaCl solutions

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HIGHLIGHTS

- More Friedel's salt forms in post-exposure cement pastes before staying constant.
- Little volume change is associated with the formation of Friedel's salt.
- Cement pastes with a higher FA level shows a smaller flexural strength reduction.
- The damage may be due to the crystallization pressure of Friedel's salt in pores.

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ABSTRACT

Friedel's salt forms in cementitious materials exposed to NaCl solutions. This paper quantifies the amount of Friedel's salt that forms and relates the formation of Friedel's salt to the damage. Thermogravimetric analysis (TGA) is used to quantify the amount of Friedel's salt. The volume change associated with the formation of Friedel's salt is measured. Flexural strength is measured for cement pastes exposed to NaCl solutions using the ball-on-three-ball test. While Friedel's salt was observed, no calcium oxychloride was detected in cement pastes exposed to NaCl solutions. As the NaCl concentration increases, the amount of Friedel's salt formed in the cement pastes increases before remaining constant at high concentrations. For the same NaCl concentration, similar amounts of Friedel's salt are obtained in cement pastes with varying water-to-cementitious materials ratios (w/cm), while a greater amount of Friedel's salt exists in cement pastes with a higher fly ash replacement level. As the NaCl solution concentration increases, the flexural strength of the cement paste decreases. There is a greater flexural strength reduction in the cement pastes with higher w/cm. For cement pastes with a higher fly ash replacement, the flexural strength shows a smaller decrease when exposed to NaCl. Since TGA confirmed little leaching of $Ca(OH)_2$ in the cement paste, the strength reduction appears to be mainly due to the formation of Friedel's salt. Little volume change is associated with the formation of Friedel's salt, which indicates that the damage may primarily be attributed to the crystallization pressure associated with the formation of Friedel's salt in pores.

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1. Introduction

Chloride-based deicers such as sodium chloride (NaCl), calcium chloride ($CaCl_2$), and magnesium chloride ($MgCl_2$) are widely applied on concrete flatwork and pavements to melt ice and improve driving and walking conditions in cold regions during winter [1–3]. When chloride ions, coupled with the corresponding cations (Na^+, Ca^{2+}, and Mg^{2+}), penetrate the cementitious materials, they interact with the hydrated and unhydrated phases through several different mechanisms [4]. For the NaCl, the common interaction mechanisms between cement paste and chloride include the adsorption of chloride ions onto the surface of calcium silicate hydrate (C-S-H) [5], and the reaction of chloride ions with aluminate and aluminoferrite phases to form Kuzel's salt ($Ca_4Al_2(OH)_{12}Cl(SO_4)_{0.5}\cdot 5H_2O$, KS) [6] and Friedel's salt ($Ca_4Al_2(OH)_{12}Cl_2\cdot 4H_2O$, FS) [7–9].

However, in addition to the absorption of chlorides and the formation of Friedel's and Kuzel's salt, concrete exposed to $CaCl_2$ and $MgCl_2$ has been observed to develop an additional potential reaction [10–12]. $CaCl_2$ reacts with calcium hydroxide ($Ca(OH)_2$) to form calcium oxychloride ($3Ca(OH)_2\cdot CaCl_2\cdot 12H_2O$) [10,11], which results in cracks [12,13] and strength reduction [14–16]. When cementitious materials are in contact with $MgCl_2$, Mg^{2+} ions react with $Ca(OH)_2$ and C-S-H to form brucite ($Mg(OH)_2$), calcium oxychloride, and magnesium silicate hydrate (M-S-H), respectively

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[17–20] resulting in damage and strength reduction [20]. Cracking and damage have been detected using acoustic emission [19]. While much of the recent work on salt damage to concrete has focused on $CaCl_2$ and $MgCl_2$ in contrast, fewer studies have focused on the potential damage to cementitious materials exposed to NaCl solutions [3,21–23].

Studies indicate that exposure to NaCl has a relatively small negative effect on the dynamic modulus of concrete [21]. Calcium leaching [22] and the formation of Friedel's salt [23], have previously been claimed to cause damage to cementitious materials exposed to NaCl. The solubility of $Ca(OH)_2$ increases with increasing concentrations of NaCl solutions, especially at concentrations above 0.5 mol/L [24]. This could potentially lead to dissolution and leaching of $Ca(OH)_2$ and C-S-H. Leaching of calcium at the surface of the mortar samples has been experimentally and numerically confirmed [25]. It should be noted that calcium leaching and the extent to which it occurs depends on the experimental procedure used. It is important to determine calcium leaching in different specific scenarios and discuss its relation to the potential damage.

The crystallization of Friedel's salt has been reported to cause expansion in cement paste exposed to NaCl solutions, which leads to cracks in the paste [23,26]. The crystallization of Friedel's salt can occur through a dissolution and precipitation mechanism as shown in Eq. (1) [9]:

$$C_3A(s) + 2CH(s) + 2NaCl(aq) + 10H_2O(aq) \\ \rightarrow FS(s) + 2NaOH(aq) \tag{1}$$

There is another mechanism that can potentially result in the formation of Friedel's salt: ionic exchange between the chloride from the exposure solution and sulfate ions from the hydrated monosulfoaluminate ($C_3A{\cdot}CaSO_4{\cdot}12H_2O$, AFm) [7,9]. The ionic exchange progress is shown in Eq. (2) [27]:

$$AFm(s) + 2NaCl(aq) \rightarrow FS(s) + Na_2SO_4(aq) + 2H_2O(aq) \tag{2}$$

It has been shown that in cementitious materials, it is only the formation of Friedel's salt by dissolution and precipitation that causes damage to the cementitious materials [23]. The relationship between the volume change due to the formation of Friedel's salt and the strength reduction is not known.

There are very few studies focusing on the quantification of Friedel's salt [25,28]. These studies that quantify the formation of Friedel's salt are important to link the formation of Friedel's salt to the damage of cementitious materials exposed to NaCl solutions. The influence of supplementary cementitious materials on the formation of Friedel's salt also still remains unclear.

This paper aims to relate the reaction between cement pastes and NaCl solutions, with a focus on the quantification of Friedel's salt, to the corresponding reduction in flexural strength. The influence of varying exposure conditions (NaCl concentrations) and mixture proportions (water-to-cementitious materials ratios, and fly ash replacement levels) will be examined. Other potential damage mechanisms, such as calcium leaching and the formation of calcium oxychloride, are also considered. The volume change associated with the formation of Friedel's salt is measured to help explain the damage mechanism.

2. Materials and experimental methods

2.1. Materials

2.1.1. Cement paste

Type I ordinary Portland cement and class C fly ash were used in this study. Their chemical and mineral compositions are listed in Table 1. The type I cement has a Blaine fineness of 392 m^2/kg. The specific gravity of the cement and fly ash is 3.15 and 2.66, respectively.

Cement pastes were made with three water-to-cementitious material ratios (w/cm) (0.36, 0.42, and 0.50) and four fly ash replacement levels by volume (0%, 20%, 40%, and 60%). The mixture proportions are listed in Table 2. A programmable vacuum mixer was used to provide a constant high vacuum level during mixing, which minimizes the presence of entrapped air. The mixing procedure is described elsewhere [29]. After mixing, the paste was cast into cylindrical molds (50.8 mm in diameter and 101.6 mm tall) and sealed with lids. The cylinders were cured at 23 ± 1 °C for 3 days and then maintained at 50 ± 1 °C for 25 days, as an accelerated curing regime, to reach an equivalent age of 91 days (at 23 °C), based on the previous maturity calculations [30].

2.1.2. NaCl solutions

Granular NaCl (EMD Millipore Inc., reagent grade) was dissolved in deionized water to make NaCl solutions with concentrations of 5.3%, 10.6%, 16.0%, 21.4% and 26.7% w.t, respectively. They have the same chloride molar concentrations as 5%, 10%, 15%, 20% and 25% w.t. $CaCl_2$ solutions previously studied [14], which makes the flexural strength reduction comparable in cement pastes exposed to NaCl and $CaCl_2$ solutions in further work.

2.2. Experimental methods

2.2.1. Low temperature differential scanning calorimetry (LT-DSC)

A LT-DSC instrument (Q20, TA Instruments) was used to measure the heat flow in the cement paste-NaCl solution system. Approximately 10 mg hydrated cement paste powder (with an equivalent age of 91 days at 23 °C as discussed in Section 2.1.1) was mixed with 10 mg NaCl solutions with varying concentrations (5.3%, 10.6%, 21.4% and 26.7% by mass). Mixing was done in high volume stainless steel pans, and the pans were then sealed and placed in the LT-DSC chamber. The samples were then exposed to the following temperature cycle [14]: isothermal at 25 °C for one hour; 3 °C/min cooling until −90 °C; low temperature loop from −90 °C to −70 °C and back to −90 °C at 3 °C/min; and 0.25 °C/min heating until 50 °C.

2.2.2. Volume change measurement

Approximately 10 g of ground cement paste powder placed in a glass vial (a capacity of 24 ml, VWR Inc.). The 21.4% NaCl solution was added to the ground cement paste powder and the amount of NaCl solution was calculated to fit the volume of the glass vial, as shown in Table 3. After filling the glass vials with cement paste and NaCl solution, a rubber stopper was placed in the container with a

Table 1
Composition of raw materials (in wt.%).

	Type I cement	Fly ash
Chemical Data		
SiO_2	20.20	38.97
Al_2O_3	4.60	21.43
Fe_2O_3	3.30	5.42
CaO	63.40	22.31
MgO	0.80	4.58
SO_3	3.10	1.11
$Na_2O_{eq.}$	0.54	1.80
Loss on ignition	2.70	0.64
Bogue Phase Calculation		
C_3S	60	–
C_2S	12	–
C_3A	7	–
C_4AF	10	–

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