Deterioration in concrete exposed to sodium chloride and heat-cool cycling

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Abstract: Many infrastructure domains required material research as an initial phase of project development life cycle. One such futuristic domain is bridge engineering, where there is a critical need of study of environmental impact and material strength. This paper focuses on the premature deterioration of concrete infrastructures exposed to sodium chloride (NaCl) salts in the presence of thermal cycling. NaCl salts can cause damage and rapid deterioration of concrete due to physical and chemical aspects, including salt scaling, corrosion of rebars, ice and salt crystallizations and/or deleterious chemical reactions. This paper discusses how NaCl solutions can cause damage in concrete in the presence of thermal cycling and how such damage can be mitigated. This paper attempts to provide an advanced thermo-chemo-physical understanding of NaCl salt damage in concrete. This paper also discusses specific structural and chemical alterations during thermal cycling that are caused by NaCl to develop damage to concrete. Results indicates that the heat-cool cycling induces the formation of mirabilite (Na2SO4.10H2O) in concrete exposed to high concentrations of NaCl solution. The mirabilite formation is found to be due to the release of sulfate ions from the concrete matrix.

1. Introduction

Concrete infrastructures subjected to winter conditions are often susceptible to physical and chemical degradations because of the massive utilization of chloride-based salts which are commonly used over the surface of concrete to melt ice and snow. In many cases, these deteriorations are due to the transport of salt ions directly through the concrete pores, which can chemically interact with the cement hydrates and alter their microstructures through various mechanisms [1–3].

The chemical effect of NaCl salts in the concrete durability is negligible according to several studies [4,5]. However, there is a concern regarding the potential leaching of calcium hydroxide (Ca(OH)) and/or the formation of Friedel’s salts (FS) [6–8]. Leaching of CH is believed to have negative impacts on the concrete durability [9].

Several studies have depicted that the reactions amongst such chloride ions as well as cement hydrates, mainly the tri-calcium aluminate (3CaO·Al2O3, C3A) and monosulfate (3CaO·Al2O3·CaSO4·12H2O, AFm), can result in FS formation through ionic exchange mechanisms or dissolution/precipitation mechanism, i.e., direct reactions of chloride ions with residual C3A in the concrete matrix [10–12].

For the dissolution/precipitation mechanism, several equilibrium conditions govern the reaction process, including CH dissolution, formation of calcium chloride, and precipitation of FS. Therefore, equilibrium equations along with solubility products for each condition should be taken into consideration for a complete reaction [13,14].

Some studies have concluded that the ion exchange of chloride with the AFm is the dominant mechanism although both mechanisms can occur [15,16]. The formation reactions of FS through the ionic exchange and the dissolution/precipitation mechanisms can be explained by Eq. (1) [14] and Eq. (2) [12], respectively.

\[
2\text{NaCl} + 3\text{CaO}·\text{Al}_2\text{O}_3·\text{CaSO}_4·12\text{H}_2\text{O} \rightarrow 3\text{CaO}·\text{Al}_2\text{O}_3·\text{CaCl}_2·10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4+2\text{H}_2\text{O} \quad (1)
\]

\[
3\text{CaO}·\text{Al}_2\text{O}_3·\text{CaCl}_2·10\text{H}_2\text{O} + 2\text{NaOH} \rightarrow 3\text{CaO}·\text{Al}_2\text{O}_3·\text{CaCl}_2·10\text{H}_2\text{O} + 2\text{NaOH} \quad (2)
\]

Very few studies have suggested that the formation of FS may create damage to concrete [4,7]. However, there are many studies that have concluded the FS formation, by itself, does not result in significant damage [17–19]. It is believed that the released ions into the pore solution associated with the FS formation can have negative effects on the concrete durability [20–22].

Because of the FS formation through the ionic communication protocol (Eq.1), it has been reported that chloride and sulfate ions can be liberated into the concrete pore solution. The sulfate ions thus released into the pore solution can bind with the free sodium ions, forming aqueous sodium sulfate to balance the charge [23]. This paper evaluates the physical and chemical changes in concrete subjected to NaCl exposure and heat-cool cycling and aims to provide an advanced thermo-chemo-
physical understanding of damage development concerning the chemical changes in concrete exposed to NaCl and heat-cool cycling.

1.1 Aqueous NaCl Phase Diagram

A phase diagram is generally employed to illustrate the impact of deicing salts upon minimizing the freezing temperatures of the solution and expressing the freeze-thaw impairment tendencies of road as well as bridge components. Two thermal cycling paths are shown in Figure-1 (blue arrows) to describe the effect of NaCl concentrations on lowering the freezing temperature of the solution for a typical temperature range during the winter (i.e., +10°C to -10°C). Path 1 describes the thermal cycling in a solution with 10% concentration by mass. The temperature variation between +10°C to -10°C causes ice to start forming in 10% NaCl solution as the temperature passes below the liquidus line. The ice formation results in expansion (9% by volume) and damage to porous materials (e.g., concrete).

To eliminate the physical damage produced by ice formation, the concentration of salt in the solution is increased to lower the freezing point of the solution as illustrated by Path 2 where the concentration of NaCl in the solution reaches 20% by mass. The temperature variation between +10°C to -10°C results in no ice formation in 20% NaCl solution, thereby no freeze-thaw damage is expected to occur in concrete. According to the NaCl-water classical phase diagram (Figure 1 above), the use of high concentrations of NaCl can decrease the freeze-thaw damage in concrete.

Over the past two decades, however, the use of high concentrations of NaCl (Figure 2b) has been reported to create severe damage in concrete pavements and bridges in cold regions (Figure 2a). Serious premature deteriorations of concrete infrastructure have been observed in regions where NaCl deicing salts are used heavily and the observed deteriorations have become a growing concern among governmental transportation agencies and academia.

2. Experimental Program

2.1 Materials and Sampling

Type I standard Portland cement (ASTM C150-17) was utilized to make cement pastes. The chemical composition concerning the cement is detailed in Table 1. Cement pastes were generated that had a water-to-cement ratio of 0.42 by mass. The blending was conducted based on ASTM C305-14 [24] employing a typical mixing a standard laboratory mixer. Pastes were moulded into rectangular prism forms of 1x1x11 in³ (25x25x279 mm³) and then treated in covered plastic bags intended for 28 days at room temperature (23°C). After the curing, the samples were cut using a table-saw to dimensions of 1x1x2 in³ (25x25x50 mm³). The samples were consequently vacuum saturated with NaCl solution and prepared for the LGCC-AE test following procedures mentioned elsewhere [25,26].

Powder samples were also prepared by grinding the hydrated cement to a fineness of 75-μm (Passing Sieve No.200). The powder was subjected to NaCl solutions for the LT-XRD study.

2.2 Methods

Several experiments were conducted in this paper. Damage and associated phase changes in specimens were monitored using longitudinal guarded comparative calorimeter geared (LGCC) and acoustic emission (AE). The detailed experimental procedures of the LGCC setup are mentioned elsewhere [26–35]. Low-temperature X-ray diffraction (LT-XRD) was employed to discover and define chemical phase transformations within the heat-cool cycling. Analytical calculations were also performed to study the chemical of the concrete pore solution.

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

<table>
<thead>
<tr>
<th>Items</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.2</td>
</tr>
<tr>
<td>CaO</td>
<td>62.6</td>
</tr>
<tr>
<td>SO₃</td>
<td>4.0</td>
</tr>
<tr>
<td>MgO</td>
<td>3.4</td>
</tr>
<tr>
<td>Na₂O(eq)</td>
<td>1.02</td>
</tr>
<tr>
<td>Insoluble Residue</td>
<td>0.24</td>
</tr>
<tr>
<td>LOI</td>
<td>1.4</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.15</td>
</tr>
</tbody>
</table>
3. Results and Discussion

As per the experimental evaluation, impact of thermal variables on chemical integrations and performance parameters are discussed. The performance was also evaluated for mechanical damage due to impact of thermochemical integrations. Detection concerning the chemical phase transformation examines the variables for damage leading to elements along with the theoretical evaluation of NaCl and Na2SO4. This section should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

3.1. Damage Development

During the LGCC-AE experiment, the thermal response of the specimen was linked to the AE activities to understand the damage development during the chemical phase transformation. Fig.3 explains the temperatures of the sample, the temperature circulation, AE events, as well as the total energy of AE occurrences as a function of time for cement paste samples saturated with 20% NaCl. In the first cycle, a sudden increase in the temperature (shown by zoom boxes) accompanied by a development of chemical phase change was discovered during cooling at a temperature close to -5°C. Many AE events associated with an increase in the cumulative energy were also observed which coincided because of the development of the chemical phase transformation. The AE occurrences as well as the boost within the total energy are most likely associated with cracking due to the development of such chemical phase change. It should be mentioned that the applied temperature range does not prompt the freezing of the salt solution, that is, no ice is expected to form in the samples. Therefore, AE events (i.e., cracking) observed are mainly due to the chemical phase transformation.

3.2 Phase Change Identification

The XRD patterns during cooling and heating for cement pastes mixed with 20% NaCl solution are shown in Fig.5 as the temperature varied between 20°C and -7°C. Different peaks were observed, which correspond to ettringite, portlandite, calcite, periclase and FS [12]. In addition, peaks corresponded to halite (NaCl) were observed, which started to appear at 15°C during the cooling. Also, peaks corresponding to mirabilite (Na2SO4.10H2O) were observed, which appears and
disappears on passing 5 °C during cooling and heating. The observations from LT-XRD are in line with the results obtained from the LGCC-AE concerning the chemical phase transformations. The damage detected from the LGCC-AE corresponds mainly to the formation of mirabilite. The formation of mirabilite is a well-known destructive phenomenon in porous materials [36–38].

Fig. 5. XRD patterns for hydrated cement paste exposed to 20% NaCl solution at different temperatures between 20°C and -7°C. Phases identified are E= ettringite, FS= Friedel’s salt, CH=calcium hydroxide (portlandite), NaCl=sodium chloride, and M= mirabilite (Na2SO4.10H2O)

3.3 Pore solution chemistry

This section provides theoretical calculations to estimate the final concentrations of Na2SO4 and NaCl in the pore solution formulated on the primary quantity of NaCl, the content of the sulfate in the cement, as well as the level concerning hydration of the cement. Chemical interactions between NaCl solutions and hydrated cementitious materials can release sulfate ions in the concrete pore solution, which can form Na2SO4 aequous solution in the concrete pores as described in Eq. (1) in the previous section.

The solid (i.e., dry) mass of hydrated cement (W_HC) consists of reacted cement (m_RC) (including initial cement plus the chemically combined water) and unreacted cement (m_UC). The solid mass of the hydrated cement can be calculated using the following equations:

\[ W_{HC} = m_{RC} + m_{UC} \]  
(3)

\[ m_{RC} = [\alpha(W_h W_C + W_C)] \]  
(4)

\[ m_{UC} = [(1 - \alpha)W_C] \]  
(5)

where \( \alpha \) is the cement degree of hydration, \( W_h \) is the chemically combined water of major cement phases [39] (taken as 0.230 gwater/ghydrated cement, formulated as per the Bogue composition of the cement), and \( W_C \) is the pilot mass of cement prior to the initialization of hydration. The mass fractions of reacted (\( f_{RC} \)) and unreacted cement (\( f_{UC} \)) per total solid mass of hydrated cement can then be expressed as follows:

\[ f_{RC} = \frac{m_{RC}}{m_{RC} + m_{UC}} = \frac{1}{1 + \frac{1 - \alpha}{\alpha(W_h W_C + W_C)}} \]  
(6)

\[ f_{UC} = \frac{m_{UC}}{m_{RC} + m_{UC}} = \frac{1}{1 + \frac{\alpha(W_h W_C + W_C)}{(1 - \alpha)W_C}} \]  
(7)

Further, the volume of sulfate in the solid mass of hydrated cement may be accustomed to estimate the concentration of Na2SO4 in the pore solution. The following equation can be then used to calculate the amount of sulfate per total mass of hydrated cement \( C_S \):

\[ C_S = \frac{w_s}{W_{HC}} \]  
(8)

Where, \( w_s \) is the content of sulfate in the cement (in wt.%) (Table-2) For simplification, a complete release of all sulfates available in the cement is assumed in this equation.

Table shows the calculated final concentrations of NaCl and Na2SO4 in the pore solution as a function of the initial concentration of NaCl solution. It is found that the initial concentration of NaCl solution significantly influences the final concentrations of Na2SO4 and NaCl in the solution. The final concentration of NaCl solution reduces with respect to the initial NaCl concentrations. This occurs due to the partial consumption of chloride ions from the solution to form Friedel’s salt [12].

For the range of 15 % to 25 % initial NaCl solutions, the average predicted concentrations of Na2SO4 are calculated as 9.14 % ± 0.04 %. The higher Na2SO4 explains the presence of mirabilite in the LT-XRD test. It should be also mentioned that in these calculations, the maximum possible concentrations of Na2SO4 are calculated assuming that the entire sulfate from cement will be released into the pore solution [40,41].

<table>
<thead>
<tr>
<th>Initial concentration of NaCl in the solution (% by weight)</th>
<th>Final estimated concentration of salt in the solution (% by total weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 %</td>
<td>NaCl 10.69</td>
</tr>
<tr>
<td>18%</td>
<td>13.43</td>
</tr>
<tr>
<td>20 %</td>
<td>14.95</td>
</tr>
<tr>
<td>25%</td>
<td>19.71</td>
</tr>
</tbody>
</table>

Table 2: Initial and final Concentrations in pore solution
4. Conclusions

The chemical relationships amongst excessive concentrated salt solution (> 10% by mass) and the concrete matrix can form a chemical phase transformation. The development concerning the chemical phase transformation is damaging to concrete. It was discovered that the chemical phase transformation is the development of mirabilite (Na₂SO₄·10H₂O).

Mirabilite can be formed through releasing sulfate ions from the matrix of concrete as a result of chemical interactions with the NaCl solutions. The crystallization-volume expansion of mirabilite formation can induce stresses sufficient to damage concrete.

The findings from this study can recommend limiting the contents of the sulfate in the cement to reduce the damage. This research can further be utilized for material testing of massive infrastructure concrete project exposed to NaCl and thermal cycling.

References


