



## Resistance of concrete to different exposures with chloride-based salts



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### ABSTRACT

Formation of complex salts (oxychlorides) has been suspected for causing chemical degradation of concrete in cold regions. In this study, conditioned mode (controlled temperature and relative humidity) environmental scanning electron microscopy was specifically used to minimize changes in the crystal structures of oxychlorides phases and thus reliably capture their unaltered morphology and existence/effects on concrete exposed to different de-icing salts under two different environmental conditions (constant low temperature and wetting/drying (W/D) cycles). Formation of acicular flattened blades of 3- and 5-form magnesium oxychloride (MOX) and tiny fibrous crystals as well as subhedral pseudo-hexagonal calcium oxychloride plates (COX) were found in deteriorated concrete specimens, depending on the type of solution. The reversible formation of hydrous and anhydrous COX during W/D cycles had a significant effect on aggravating the kinetics of damage of concrete in this exposure. The combined salt ( $\text{MgCl}_2 + \text{CaCl}_2$ ), which simulates using a synergistic maintenance and protective strategy for concrete pavements in winter, was the most aggressive solution; thus, this practice should be cautiously reconsidered. The incorporation of 30% fly ash had a pronounced effect on improving the concrete resistance to damage as reflected by sound mechanical properties and longevity. Also, the performance of concrete was much enhanced when an innovative supplementary cementitious material, nanosilica, was incorporated in the cementitious system.

### 1. Introduction

Historically, the damage of concrete due to the presence of de-icing salts was linked to physical mechanisms such as frost damage, scaling, and salt crystallization (e.g. [1–3]). While these physical mechanisms have been widely investigated, the chemical interactions between de-icing salts and hydrated cement paste in concrete have been studied less frequently, especially with direct microscopy techniques. At high concentrations, chloride ( $\text{Cl}^-$ ) ions and cations (e.g.  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) in de-icing salts can enter into chemical reactions with cement-based materials forming complex salts. Formation of calcium oxychloride ( $x\text{Ca}(\text{OH})_2 \cdot y\text{CaCl}_2 \cdot z\text{H}_2\text{O}$  [COX], where  $x:y:z$  can be 3–4:1:8–15, depending on  $\text{Ca}(\text{OH})_2/\text{CaCl}_2$  molar ratio, surrounding temperature and relative humidity (RH), and pH of the pore solution [4–6]) and magnesium oxychloride ( $m\text{Mg}(\text{OH})_2 \cdot n\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ , where the ratio of  $m:n$  is 3:1 or 5:1, termed as 3- or 5-form MOX, respectively) were suspected for causing chemical degradation of hardened concrete exposed to concentrated deicer solutions ( $> 3 \text{ mol/l}$ ) [4,5,7–12]. The formation of COX/MOX has mostly been studied in synthetic hydrated materials using inferred trends from longitudinal guarded comparative calorimetry (e.g. [9]), low-temperature differential scanning calorimetry and thermogravimetric analysis (e.g. [10]). However, the explicit

occurrence and exact nature and morphology of these phases were not unequivocally established in deteriorating concrete systems due to their instability when subjected to conditions (e.g., sawing, polishing, washing, filtering, coating) normally applied for sample preparation before direct microstructural tests [4–9]. Drying and elevated temperatures lead to losing some of or all their combined water resulting in changes in their crystal structure [6–8]. The sensitivity of these phases to vacuum drying in the scanning electron microscope makes it difficult to observe their unaltered morphology [6]. Also, the instability of these phases might be the reason that fewer studies could successfully correlate the physico-mechanical damage of concrete to the formation of these complex salts [5,9].

On the other hand, the impact of environmental conditions such as wetting/drying (W/D) cycles on the formation/stability of COX/MOX in cementitious matrices is not adequately documented so far. Galan et al. [6] reported conversion of synthetic COX (3:1:12) to anhydrous salt  $\text{Ca}(\text{OH})_2\text{-CaCl}_2$ , or  $\text{CaClOH}$  by drying and wetting, respectively and this conversion was reversible [6]. However, the effect of this conversion between hydrous and anhydrous oxychloride phases on the damage manifestations of concrete remains unknown. Most of the reported investigations did not show the formation of such phases in field concrete exposed to highly concentrated chloride solutions (e.g. 25%

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salt by mass) (e.g. [12]). Actually, in many of the cores taken from aged and damaged concrete pavements exposed to high concentration de-icing salts, conspicuous ettringite formation was found in-filling the majority of voids as well as interfacial transitional zones in hydrated cement paste [12,13]; however, the mechanism by which chlorides influence ettringite formation and its role in the damage process are still uncertain.

Many approaches focused on improving the durability properties of concrete exposed to de-icing salts by: (i) using topical treatments (sealers) to provide a physical barrier between salt and concrete, (ii) carbonation of the concrete to form a barrier of calcite, and (iii) improving the performance of such concrete by replacing part of the cement with a pozzolan such as fly ash. The pozzolanic reaction refines the pore structure of the cementitious matrix, which reduces its permeability and ionic diffusivity. Furthermore, portlandite consumption in this reaction helps alleviating the chemical attack by chloride ions. Despite the benefits of fly ash concrete, the use of fly ash as a cement replacement in concrete pavements in North America is optional and typically limited by departments of transportation to dosages < 15–20% [14,15]. The delay in setting time, strength gain, and micro-structural development at early ages of fly ash concrete as well as vulnerability to surface scaling are considered to be the major technical issues, which deter its wider acceptance [16,17]. Nevertheless, these performance limitations associated with the use of slowly reactive supplementary cementitious materials [SCMs] (e.g. Class F fly ash) can be mitigated by incorporation of nanoparticles (size scale of 1–100 billionth of a meter) in this concrete [18–21]. Nanoparticles (e.g. nanosilica) have been applied in the production of concrete and proven to enhance fresh and hardened properties by modifying the structure of the cementitious matrix at the nano and micro levels. Therefore, their application in concrete may have a great potential to produce innovative types of fly ash concrete with superior performance for concrete pavements exposed to high concentrations of de-icing salts. Yet, this needs to be experimentally verified.

Given the aforementioned research needs in this area, the objective of this study was to directly investigate the formation/stability of oxychloride phases in concrete under different exposure conditions when combined with chloride-based de-icing salts. Conditioned mode (controlled temperature and relative humidity) ESEM was specifically used to minimize changes in the crystal structure of these reaction products to explicitly capture their unaltered morphology and existence in deteriorating concrete. In addition to normal/reference concrete, concretes incorporating nanosilica without and with different dosages of fly ash were tested in order to substantiate the potential benefits of SCMs, if any, in mitigating this type of damage.

## 2. Experimental program

### 2.1. Materials and mixtures

General use (GU) portland cement and fly ash (Class F), which meet the requirements of the CAN/CSA-A3001 standard [22], were used as the main components of the binder. Their chemical and physical properties are shown in Table 1. In addition, a commercial nanosilica sol (50% solid content of SiO<sub>2</sub> dispersed in an aqueous solution, Table 1) was incorporated in some binders. The target consistency of fresh concrete was achieved by high-range water reducing admixture (HRWRA) based on polycarboxylic acid and complying with ASTM C494 [24], Type F. This HRWRA was added at variable dosages (0 to 475 ml per 100 kg of the binder) to the mixtures in order to maintain a slump range of 50 to 100 mm. In addition, an air-entraining admixture was used to obtain a fresh air content of 6 ± 1%. The coarse aggregate used was mostly natural gravel (max. size of 9.5 mm) with a small proportion of carboniferous aggregate; its specific gravity and absorption were 2.65 and 2%, respectively. The fine aggregate was well-graded river sand with a specific gravity, absorption, and fineness

**Table 1**  
Chemical composition and physical properties of cement and SCMs.

	GU	Fly ash	Nanosilica
Chemical composition			
SiO <sub>2</sub> %	19.21	55.20	99.17
Al <sub>2</sub> O <sub>3</sub> %	5.01	23.13	0.38
Fe <sub>2</sub> O <sub>3</sub> %	2.33	3.62	0.02
CaO %	63.22	10.81	–
MgO %	3.31	1.11	0.21
SO <sub>3</sub> %	3.01	0.22	–
Na <sub>2</sub> O <sub>eq</sub> %	0.12	3.21	0.20
Physical properties			
Specific gravity	3.15	2.12	1.40
Mean particle size, μm	13.15	16.56	35 × 10 <sup>-3</sup>
Fineness, m <sup>2</sup> /kg	390 <sup>a</sup>	290 (1.41 × 10 <sup>3</sup> ) <sup>a</sup>	80000 <sup>b</sup>
Viscosity, Cp	–	–	8
pH	–	–	9.5

<sup>a</sup> Blain fineness.

<sup>b</sup> Fineness was determined by titration with sodium hydroxide [23].

modulus of 2.53, 1.5% and 2.9, respectively. Six concrete mixtures were tested in this study; the total binder (GU cement, fly ash and nanosilica) content in all mixtures and the water-to-binder ratio (*w/b*) were kept constant at 400 kg/m<sup>3</sup> and 0.4, respectively. Single binder (control) mixtures were prepared from 100% GU cement, representing typical concrete pavements in North America. Fly ash was used to prepare blended binders with GU cement without or with nanosilica, at dosages of 20% and 30% by the total binder content (i.e. 80 and 120 kg/m<sup>3</sup>, respectively). Finally, the nanosilica was added at a single dosage of 6% by the total binder content (i.e. solid content of 24 kg/m<sup>3</sup>), as a replacement of the GU cement component in the binder, to prepare binary (comprising GU and nanosilica) and ternary binders (comprising GU cement, fly ash and nanosilica). Table 2 shows the mixture design proportions of the concrete tested in this study.

Constituent materials were mixed in a mechanical mixer and cast in prismatic molds (50 × 50 × 285 mm) to prepare triplicates for each mixture. Also, eight replicate cylinders (100 × 200 mm) were prepared in order to evaluate the compressive strength (Table 2) according to ASTM C39 [25], and the penetrability of chloride ions into concrete mixtures. The specimens were demoulded after 24 h and then cured for 28 days at standard conditions (22 ± 2 °C and 98% RH) according to ASTM C192 [26].

### 2.2. Exposures

To evaluate the durability of the tested mixtures to chloride-based de-icing salts, two exposure regimes were adopted:

- Exposure I is a continuous immersion exposure in which prismatic specimens were fully immersed in high concentration solutions of various de-icing salts at 5 °C up to 540 days. Sodium chloride (NaCl), dihydrate form of calcium chloride (CaCl<sub>2</sub>·2H<sub>2</sub>O) and hexahydrate form of magnesium chloride (MgCl<sub>2</sub>·6H<sub>2</sub>O) with purity of 99, 96 and 96%, respectively were used to prepare the solutions. In addition, combined salts (MgCl<sub>2</sub>·6H<sub>2</sub>O and CaCl<sub>2</sub>·2H<sub>2</sub>O) were applied to simulate anti-icing and de-icing strategies. Table 3 shows the concentrations of the de-icing solutions used in the present study. These types and concentrations of de-icing salts are comparable to that applied by different transportation agencies in North America (e.g. [28,29]) based on factors such as the availability of the de-icing salt and effective freezing temperature in each region. Also, for better comparison between the de-icers used, an equal number of chloride ions (~160,000 ppm) among the four solutions was used. The solutions were renewed every four weeks to keep a continual supply of de-icing salts, thus providing aggravated damage conditions.

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