



Observations of chloride ingress and calcium oxychloride formation in laboratory concrete and mortar at 5 °C

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ABSTRACT

The combination of chloride deicer exposure and temperatures near the freezing point of water makes for an aggressive environment for many concrete pavements and bridge decks. In laboratory-simulated conditions, the formation of calcium oxychloride hydrate ($3\text{CaO}\cdot\text{CaCl}_2\cdot 15\text{H}_2\text{O}$ or $3\text{CaO}\cdot\text{CaCl}_2\cdot 12\text{H}_2\text{O}$) phases has been associated with the expansion and deterioration of concrete and mortar, but calcium oxychloride phases have yet to be observed in the field. A decomposition path from calcium oxychloride hydrate to $\text{CaCl}_2\cdot\text{Ca}(\text{OH})_2\cdot 2\text{H}_2\text{O}$ to calcite CaCO_3 is proposed here, and offered as an explanation for the lack to date of convincing field evidence for a calcium oxychloride hydrate deterioration mechanism.

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1. Introduction

The list of detrimental chemical reactions involving portland cement concrete is long and varied. In some situations, a chemical reaction may be benign or even beneficial, while in other cases the same chemical reaction may cause damage. Chloride, sulfate, or carbonate salts may occur as efflorescence or subflorescence, either intentionally, as with the standard magnesium/sodium sulfate soundness tests, or through environmental exposure, often combined with drying and wetting cycles and/or partial immersion [1–3]. In some situations the crystallization of salts is harmless, but in others detrimental, especially in cases where salts precipitate in pores under supersaturated conditions [4,5]. Chloride-based salts, when used as deicers, can also participate in frost-scaling damage in situations amenable to the glue-spall mechanism, where stresses are generated due to differences in the coefficient of thermal expansion between an ice layer formed at the surface and the underlying concrete [6]. Aside from glue-spall, another possible detrimental chemical reaction involving chlorides is the formation of calcium oxychloride phases. At temperatures just above the freezing point of water, the precipitation of calcium oxychloride hydrate has been associated with concrete deterioration, but only in artificial laboratory settings [7,8]. It is generally thought

that the high calcium and chloride concentrations necessary for calcium oxychloride hydrate precipitation are never achieved in the field [9]. To further investigate the influence of concentrated deicer solutions on the durability of portland cement concrete, a broad laboratory study was conducted which included an experiment of long-term exposure of concrete and mortar cylinders to deicer solutions at temperatures near 5 °C, and at chloride concentrations within a range of 1 to 4 mol/L [10]. Results pertaining to calcium oxychloride hydrate formation are presented here, and interpreted within the context of calcite deposits observed as efflorescence, or within cracks in concrete.

2. Materials and methods

2.1. Materials

The mortar and concrete mixtures for this study were made with aggregate from Superior Sand & Gravel, Hancock Michigan, USA. The aggregate source consists of sand and gravel derived from glacial till that originated from the Laurentide ice sheet, and is composed primarily of igneous and metamorphic siliceous rock types. All of the mixtures contained a Type I/II portland cement from Lafarge Alpena, Michigan, USA, and VR-90 vinsol resin air entraining admixture from Master Builders/BASF Admixtures. The mortar mixtures were made at two w/cm levels, 0.55 and 0.45, with a target air content of 12 vol.%, and an aggregate content of 52 vol.%. The concrete mixture was made at a w/cm of 0.45, with a target air content of 6 vol.%, and an aggregate

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Table 1
Mix design and fresh concrete/mortar test results.

Mix ID	Mix design (kg/m ³)					Air content (vol.%)			Workability	
	Water	Air entr.	Fine aggr.	Coarse aggr.	Portland cement	Gravimetric ASTM C185/C138	Volumetric ASTM C173	Pressure-metric ASTM C231	Slump (mm) ASTM C143	Flow (%) ASTM C1437
55 M	217	0.43	1420	–	395	12.2	–	–	–	131
45 M	218	0.64	1362	–	486	11.3	–	–	–	106
45 C	157	0.09	794	917	349	9.5	7.5	8.0	75	–

content of 70 vol.%. Table 1 summarizes the mix designs and fresh concrete/mortar test results for the mixtures [11–16].

All specimens were cast in 100 mm dia. × 200 mm length cylindrical molds. Specimens were moist-cured in the molds for one day, demolded, and then wet-cured in lime saturated baths for 27 days. After 28 days the top and bottom of each cylinder were removed by cutting with a water-cooled diamond saw, and the remaining portion cut in half, yielding two cylinders with a height of 75 mm each.

2.2. Chloride exposure

Half of the samples were retained at Michigan Technological University (MTU), and the other half were vacuum packed and shipped to the University of Toronto (U of T). The sides and bases of the U of T samples were sealed with epoxy, leaving only the top surface exposed, and immersed in the various chloride salt solutions at the high concentration levels listed in Table 2. The sample containers were covered to prevent evaporation of the solutions, and stored at a constant temperature of 5 °C. After 35 days of exposure, the mortar samples were removed for chloride profile grinding [17].

The MTU samples were immersed as-is (no epoxy coating) into various chloride solutions at both the low and high concentration levels listed in Table 2. Again, the sample containers were covered to prevent evaporation, but stored at a slightly lower temperature of 4.4 °C (40 °F). At 60 days, mortar samples were removed for chloride profile testing by micro X-ray fluorescence (μXRF). The remaining concrete samples were left in the solutions and removed after 500 days for inspection by stereo-microscope, X-ray diffraction (XRD), petrographic microscope, and scanning electron microscope (SEM) methods.

2.3. Chloride profiling

2.3.1. Profile grinding

A milling machine was used to remove successive thin (mm-scale) parallel layers of mortar, starting from the surface exposed to the chloride solution. The acid-soluble chlorides in the powder samples collected from each layer were determined by titration using a Metrohm 716 DMS Titrino equipped with a 5 ml 0.01 N AgNO₃ titrant exchange unit, an Ag indicator electrode, and an Ag/AgCl reference electrode.

Table 2
Concentrations of chloride solutions.

Salt type	Salt solution concentration (wt.%)		Chloride concentration (mols/L)	
	Low conc.	High conc.	Low conc.	High conc.
NaCl	7.30	17.80	1.35	3.70
MgCl ₂	6.20	15.00	1.38	3.70
CaCl ₂	7.30	17.00	1.43	3.70

2.3.2. μXRF profiles

Since there is no standard procedure for chloride profiling by μXRF, a detailed description of the methodology employed is provided here. Two billets were cut from the middle of each mortar cylinder sample with a kerosene cooled diamond saw as indicated in Fig. 1, to yield cross-sections starting from the top surface exposed to chloride solution, down to a depth of ~40 mm into the mortar.

Each billet was epoxied to a glass slide, the surface of the glass slide fixed to a vacuum chuck, and the opposite face of the billet ground with a mineral oil cooled diamond cup wheel. After a uniformly flat and parallel surface was obtained, each billet was cleaned with kerosene, and oven-dried overnight at 50 °C. After drying, the billets were stored in a dessicator prior to analysis with an OXFORD/HORIBA XGT-2000W X-Ray Analytical Microscope equipped with a Si(Li) EDS. In a μXRF, the billet is stepped on a motorized stage beneath a stationary incoming X-ray flux, and fluoresced X-rays are monitored by EDS [18].

Billets were placed one at a time in the μXRF and analyzed at ambient room temperature and pressure. To ensure a constant geometry between the X-ray source, sample, and detector, the μXRF is equipped with a light microscope at a fixed focal length. The prepared surface of each billet was raised until the features appeared in sharp focus under the light microscope. X-ray spectra were collected from points identified within the paste fraction under the following conditions: 300 μm diameter X-ray guide tube, 30 kV X-ray tube voltage, 1.0 mA X-ray tube current, and 100 s counting time. The number of counts within the Cl K_α range of 2.51 to 2.76 keV was determined for each point and converted to wt.% chlorine values based on calibration curves developed from billets prepared from similar mortar mixtures that had been prepared using mix water spiked with increasing dosages of CaCl₂. Fig. 2 shows the standard addition plots used to develop the calibration curves. To help account for matrix effects, two sets of standards were made at w/cm levels of 0.45 and 0.55 using the same mix designs listed in Table 1. The standards were cast in 50 mm dia. 100 mm cylindrical molds, kept sealed in the molds for 28 days, demolded, and a billet prepared from the middle of each sample.

Fig. 3 shows elemental maps collected from a billet prepared from one of the mortar samples exposed to the high-concentration MgCl₂ solution for 60 days. The chlorine map shows a clear gradient of higher counts for chlorine near the surface exposed to the solution. The elemental map was collected using the same operating conditions as the point analyses, but with a dwell time of 48 μs/pixel, and a pixel size of 56 × 56 μm. The diameter of the X-ray flux (300 μm) exceeds the pixel dimensions, so in this case, the pixel size does not define the resolution. The μXRF does have the capability of 10 μm and 100 μm X-ray flux diameters, but with these smaller diameters also come lower count rates, which prohibited their use in this application. More modern μXRF employs silicon drift detectors (SDD) with higher count rates, and X-ray flux diameter is less of a limitation.

With the μXRF equipment used in this study, the billets are maintained at ambient temperature and pressure throughout the analyses. A thin-film X-ray transparent polyester barrier is present

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