Proposed mechanism for the formation of oxychloride crystals during sodium chloride application as a deicer salt in carbonated concrete

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ABSTRACT

Even though freeze and thaw performance for uncarbonated concrete may be considered good, its resistance may be considerably affected by carbonation and the presence of deicing salts.

Besides the general belief that the major single mechanism that contributes to frost-scaling damage is purely mechanical and due to stresses caused by the differences in thermal expansion coefficients between ice and the underlying concrete, there is also experimental evidence of scaling deterioration on concrete that has been exposed to chloride deicers at temperatures just above freezing without the influence of ice formation. This fact is suggestive of another deterioration mechanism occurring at low temperatures.

Blast furnace slag (BFS) and ordinary Portland cement (OPC) concretes with different slag/binder ratio and a high sulfate resistant cement concrete (HSR) were wet cured during a short period, followed by additional exposure to accelerated and natural CO_2 environments. It was found that carbonation predisposition depends on amount of BFS replacement and cement type. Vaterite and Calcite were the two types of carbonated minerals identified by XRD analysis. The carbonated face of concrete was exposed to freeze and thaw cycles under deicing sodium chloride salt solution. It was noticed that the deicing scaling resistance of carbonated concrete decreases, as the ratio between carbonates coming from CSH decomposition over the ones coming from available CH (carb. ratio CSH/CH) increases.

The presence of a well packed net of oxychloride minerals of prismatic and platey shape and growing underneath a crust of cement paste were observed in polarized microscopy after the freezing cycle. The crystallization pressures caused by these minerals below the surface are believed to contribute to concrete scaling.

The mechanism is started with the dissolution of calcium bearing minerals from the carbonated concrete paste at the low temperatures occurring during the freezing cycle. The available calcium hydroxide present in the pore solution combines with chloride ions to form temporary oxychloride crystals. The crystal growth caused by these salts causes paste disruption. During the thaw cycle oxychlorides dissolve releasing calcium hydroxide, thus potentially contributing to calcium leaching from concrete in every cycle and also maintaining calcium availability for subsequent oxychloride formation during the next cycle. CO_2 equilibrium in the pore solution is crucial for mineral stability; therefore the reactions are temperature and pH dependent.

1. Introduction

Chlorides of sodium, magnesium or calcium are amongst the most common salts chosen to melt ice in roads and bridges thanks to their high efficiency and low cost, but the positive factors that these salts produce are in contrast with the negative effects on the durability of concrete that they cause. The salt scaling damage has been well identified and consists of progressive exfoliating flakes released from concrete that has been partially saturated with salt solutions and subjected to freezing. The worst condition for damage occurs at moderate salt concentration, usually 3% by weight.

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There are several theories that attempt to explain the causes of the deterioration of concrete exposed to frost with deicing salts. Among the best known is the theory of Powers [1] (published in 1945, but later withdrawn by Powers himself), who mentions the effect the hydraulic pressure exerted on a saturated concrete. When the water freezes within the concrete it experiences an increase of 9% of its volume, and the unfrozen water has to be expelled to the remaining pores exerting pressure. Besides, as ice starts to form, concentration gradients are generated in the remaining unfrozen solution; this mechanism is also believed to provoke osmotic pressures that further contribute to the damage.

Hansen [2] proposed the mechanism of salt solution oversaturation in larger pores. At these sites salt crystals start to form and keep attracting more salt during their growth. The continuing salt crystallization provokes inner pressures in the concrete microstructure.

Snyder [3] proposed that the surface and inner layers of concrete are initially frozen leaving an unfrozen high concentration solution in-between these two layers. When this latter layer starts to freeze the remaining unfrozen water exerts pressure on the top layer causing scaling.

More recently Valenza II and Scherer [4] presented a mechanism that they called the Glue-Spall theory in which the salty ice attached to the underlying concrete, at temperatures below its freezing point, undergoes higher contraction than the latter material due to its thermal expansion coefficient which is about 5 times larger. The stresses to which ice is submitted produces cracks; these crack are further propagated to the concrete which exfoliates producing flakes.

Abovementioned mechanisms are mainly physical in nature, nevertheless the deleterious mechanism of chloride attack on cementitious materials at low temperatures from a chemical point of view has not been clearly proposed. Moreover, the amplified damage that chloride attack could develop in combination with carbonated materials has barely been analyzed.

There are several forms in which chlorides react with cement compounds to form other salts. Some of the products are considered beneficial to concrete as the formation of Friedel's salt (FS) $3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$ which chemically binds chlorides and somehow keeps them from reaching the steel [5]. Another form of chloride binding is in Kuzel's salt $3CaO\cdot Al_2O_3\cdot 1/2CaSO_4\cdot 1/2CaCl_2\cdot 10H_2O$ and a modified form of iron containing FS, $3CaO\cdot (Al,Fe)_2O_3\cdot CaCl_2\cdot 10H_2O$ [6]. Other chlorides can be bound as calcium oxychloride with a general formula $3Ca(OH)_2\cdot CaCl_2\cdot nH_2O$ ($3:1:n$, where $n = 13, 10$ or 11), depending on temperature [7]. A similar mineral where $n = 12$, is cited in the bibliography by Robbins [8]. Several investigators identified oxychloride of $n = 15$ as being responsible for concrete damage after being exposed to $CaCl_2$ attack [9–11] (Eq. (1)):

$$3Ca(OH)_2 + CaCl_2 + 12H_2O \leftrightarrow 3CaO\cdot CaCl_2\cdot 15H_2O \qquad (1)$$
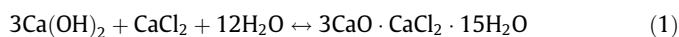
At temperatures just above freezing this reaction progresses fast; under these conditions the solubility of the oxychloride mineral is considerably decreased assuring mineral stability.

Most of the studies about oxychloride formation and its deleterious role on deicing scaling damage to concrete have been performed on pure OPC materials. Limited information on this matter is found for BFS/OPC blends and the leading part that carbonation has in catalyzing the attack is not well understood. This research tries to match relations between the two damaging mechanisms.

2. Experimental procedure

Four concrete mixtures without special properties regarding deicing resistance (the research purpose was to compare materials behavior without analyzing specification compliance) were prepared for this investigation, as presented in Table 1. The aggregates were gravel and a natural sand of siliceous nature. The utilized binders are presented in Table 2 and are composed of an ordinary Portland cement (OPC) with no special durability properties and a high sulfate resistant cement (HSR), both materials complying with type CEM I 52.5 N according to European Standards. A (ground granulated) blast furnace slag addition was also used to replace 50 and 70% by weight of the OPC. In order to improve the fresh concrete properties (slump between 160 and 210 mm) a superplasticizer (polycarboxylic ether based) was used in amounts between 0.2% and 0.4% by weight of the total binder content.

After mixing, concrete was cast in cylindrical molds (diam. 100 mm, h. 100 mm). Subsequently, 7 days of wet curing at 20 °C and RH > 95% was applied and additional, by 21 days at 20 ± 2 °C and 60 ± 5%. This curing condition mostly resembles a real curing situation on site.

After curing, adhesive aluminum foil was glued to the external cylinders surfaces, leaving only 2 faces (top and bottom faces) uncovered to permit free CO_2 exposure for only these two opened faces.

At least 18 cylinders representing each type of concrete were exposed to a 10% CO_2 concentration in a carbonation chamber, while a similar number were exposed to natural carbonation, in a climate controlled room. For both exposure conditions, the samples were maintained at 20 ± 2 °C and 60 ± 5% RH until the time for testing. For each testing age, 3 cylinders were taken out from the curing place (accelerated and normal carbonation), each sawn parallel to the exposed surfaces into 2 half cylinders (diam. 100 mm, h. 50 mm) and the aluminum foil was removed. Half of the carbonated discs were utilized to measure the carbonation depth in a freshly split surface made perpendicular to the exposed face. The carbonated front identification was done using phenolphthalein solution. Pictures that illustrate procedures have previously been reported [12].

After one year of CO_2 exposure, carbonated and non-carbonated concrete's hardened paste was extracted for mineral composition determination, this was done by separating by wet cutting the samples at the location of the carbonated front after phenolphthalein identification. The non-carbonated paste was extracted from cubic samples corresponding to the same concrete batch. Here a core (diam. = 70 mm, h = 150 mm) was extracted from the center of one face. Afterward the two 40 mm edges of the core were removed to avoid carbonated paste contamination. The paste was obtained by crushing the remaining core using a hydraulic press followed by wet grinding in plastic cylindrical containers on two moving rollers; the purpose of wet grinding was to loosen the hardened concrete paste through friction and rubbing action between aggregates and its adhering paste while keeping the crushed concrete's particles immersed in isopropanol. Afterwards fine particles were separated by wet sieving in isopropanol solution using a sieve of 63 μm size opening. The obtained paste (finer than 63 μm) was treated by vacuum drying; the collected

Table 1
Materials for concrete's mix design, kg/m³.

Material	S_o	S_{50}	S_{70}	HSR
CEM I 52.5 N	345	173	102	0
CEM I 52.5 N SR	0	0	0	347
BFS	0	173	238	0
Water	156	156	154	157
Sand 0/4	771	771	759	774
Gravel 2/8	611	611	601	614
Gravel 8/16	474	473	466	476