

Effects of Chloride Deicing Chemicals on Pavement Concrete Deterioration.

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INTRODUCTION

Durability of concrete is possibly related to externally-induced chemical attacks in addition to internally-induced deterioration. Externally-induced chemical attacks can be derived from various sources such as local contaminated groundwater, seawater, deicing salts, sulfate salts, and dilute and strong acids. Among these external sources, the application of deicing salts is most important for pavement concretes in Iowa. The adverse effects of various deicing salts on concrete pavements and bridges have concerned concrete researchers worldwide. Deterioration by deicers is related to complex processes associated with physical and chemical alteration in cement paste and aggregates, which is affected by factors such as the cation composition of the deicer, aggregate type, and aggregate reactivity. The present study examined the effects of NaCl, CaCl₂, and MgCl₂ solutions on the deterioration of concretes from Iowa concrete pavements and on dedolomitization reaction originally caused by reactive dolomite coarse aggregates. Special attention was paid to the secondary minerals that were formed and the mineral changes that occur as a direct result of deicers.

EXPERIMENTAL METHODS

Cores were taken from existing seven Iowa highway concretes of different service records. Small 3cm x 1.5cm x 1.5cm blocks were cut from cores. Two blocks from each core were immersed in 100 ml of solution and sealed in cleaned polymethylpentene containers that were stored for 132 hours at 58°C in a constant temperature chamber. The solutions used were 0.75 M CaCl₂·2H₂O, MgCl₂·6H₂O, NaCl, and distilled water. All solutions contained 0.01% sodium azide to control bacterial growth. Laboratory simulations of environmental conditions (wet/dry and freeze/thaw cycling) were conducted on highway concrete with various deicer chemicals

Wet/Dry (W/D) Experiments: After being immersed in 58°C solutions for 132 hours, blocks were removed from the solutions, dried 58°C (≈135°F) for 24 hours, air cooled to 25°C, returned to their immersion solutions at 25°C, and again stored at 58°C for 132 hours.

Freeze/Thaw (F/T) Experiments: Samples removed from the 58°C solutions after 132 hours were air cooled to 25°C and stored for 24 hours in a freezer at -4°C (25°F). The blocks were air warmed to 25°C, returned to their receptive solutions at 25°C, and stored at 58°C for 132 hours.

Analytical Methods and Instrumentation: All experiments were continued until visual signs of deterioration were detected in samples. Petrographic analyses of thin-sections were conducted with both transmitted and reflected light utilizing a standard petrographic polarizing microscope. Petrographic examination was used to identify specific areas to be studied by scanning electron microscope and to supplement observations of features difficult to observe with scanning electron microscopy such as color changes on coarse aggregate margins.

A Hitachi S 2460 reduced-vacuum scanning electron microscope was used in this study. Back-scattered images were taken and energy dispersive analytical x-ray (EDAX) area mapping was performed for Si, Al, K, Na, O, Ca, Mg, S, Cl, and Fe. EDAX point analyses were obtained at high magnification for qualitative mineral identification. An accelerating voltage of 15 kV was generally used for imaging whereas EDAX point analyses were obtained at 20 kV.

RESULTS AND DISCUSSIONS

Secondary Minerals in Solution and on Concrete Surfaces

Crystals that precipitated in the saline immersion liquids and on the walls of containers were also analyzed by x-ray diffraction. Visually-detected surface coats of secondary minerals from blocks treated with CaCl₂, NaCl, and MgCl₂ were removed with care taken not to include underlying concrete. X-ray diffraction analyses detected the minerals shown in Table 1.

Table 1. Secondary minerals in solutions and on concrete surfaces.

Solutions	Crystals in Solution	Crystals on Concrete Surfaces
Water	calcite	no coating
CaCl ₂	calcite+minor brucite	aragonite+brucite+gypsum(tr.)
NaCl ₂	calcite	calcite+halite
MgCl ₂	brucite+minor calcite	brucite+Mg ₂ (OH) ₃ Cl·3H ₂ O+calcite

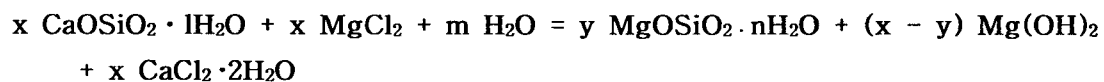
The presence of calcite in solution was attributed to atmospheric carbonation of calcium leached from the concrete or added as a reagent. Formation of brucite, Mg(OH)₂, in magnesium-rich solutions indicated that the leached component was a

hydroxide from the cement paste.

Effects of Chloride Solutions

Calcium chloride: Calcium chloride deicing salts caused characteristic deterioration in concretes with reactive dolomite aggregates by enhancing dedolomitization reactions that release magnesium to form destructive brucite and MSH (Magnesium Silicate Hydrate). Reaction rims observed after wet/dry and freeze/thaw conditions appear similar to the original dedolomitization reaction rim patterns seen in untreated concrete, but significant difference occurred at dolomite aggregate rim. The EDAX element maps (Fig. 1) show a decrease in Ca and a significant concentration of Mg in rim Zone Ce. In pre-experiment rims, considerable volumes of calcite existed without significant quantities of brucite, but in the post-experiment rims abundant brucite and less calcite were observed. In durable concrete with non-reactive dolomite aggregate, no new reaction rims occurred after wet/dry and freeze/thaw cycles in calcium chloride. Critical changes occurred in cement paste of both durable and non-durable concrete.

Magnesium chloride: In $MgCl_2$ -treated samples, distinctive dedolomitization reaction rims were formed at the margins of reactive dolomite aggregate. A considerable amount of brucite formed in the outer light-colored dolomite rim, a feature not seen in the rims of untreated dolomite (Fig.2). Brucite also formed in air entrainment voids and at the interface between the fine aggregate and cement paste (Fig.2)) where it weakened the integrity of the bond between paste and fine aggregate and caused popping out of quartz grains when thin sections were made. Calcite formed in association with brucite at the inner and outer margins of void-rim brucite in the air entrainment voids. Magnesium chloride produced significant concrete crumbling because of widespread replacement of CSH (Calcium Silicate Hydrate) by non-cementitious MSH. Formation of MSH resulted from reaction between magnesium ions and the CSH phase of the cement, with replacement of CSH by MSH (Fig.2). Abundant shrinkage cracks developed in the MSH phase. Using a modification of Bonens (1992) equation, the general reaction for the formation of MSH from CSH in Mg-chloride solution can be written as follows:



$$\text{where } 1 + m = n + 3x - y$$

From this reaction, displaced Ca^{2+} leaches out into cement paste because CaCl_2 is highly soluble and can form portlandite (Ca(OH)_2), or calcite/aragonite (CaCO_3). Calcite associated with brucite in air voids or in cracks in some samples supports this concept. Needles of calcium carbonate and brucite precipitated on the surface of a $MgCl_2$ -treated sample.

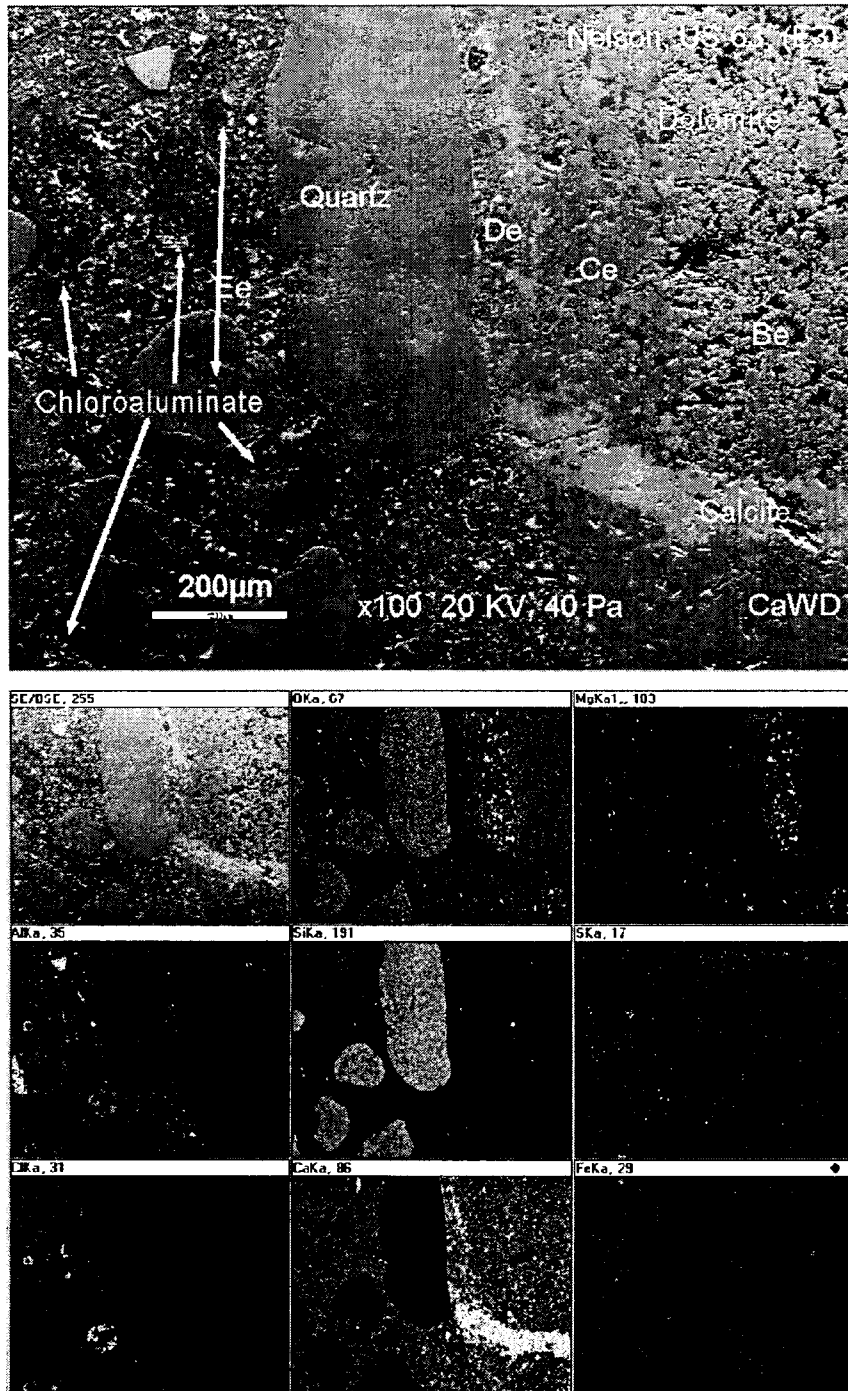


Fig. 1. SEM micrograph and EDAX element maps showing experimentally-induced deterioration after wet/dry cycling in CaCl_2 of Nelson quarry concrete, US 63. Abundant brucite precipitated in the interstitial voids of the light-colored dolomitization reaction rim (Ce). In air entrainment voids, areas rich in Ca, Al, and Cl probably are chloroaluminate. The limited S concentrations at the margins of air-entrainment voids indicate that chloroaluminates have replaced ettringite which occurs abundantly in untreated concrete voids.

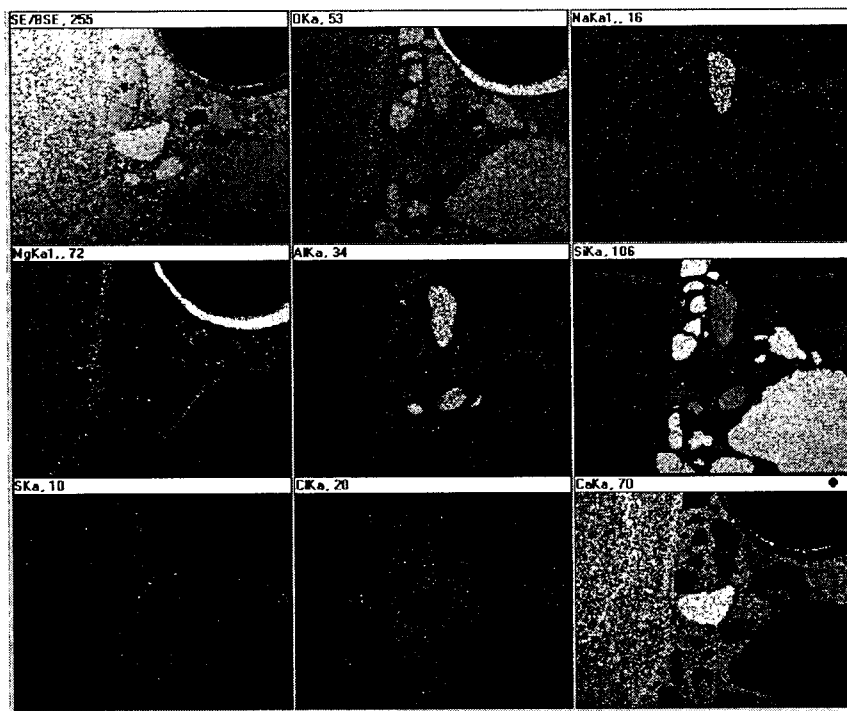
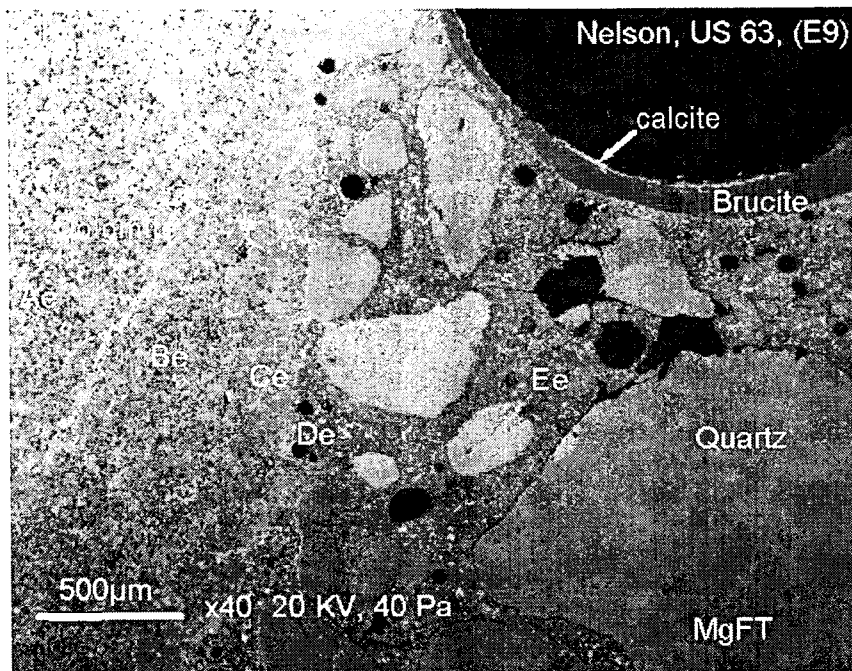
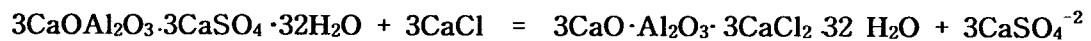


Fig. 2. SEM micrograph and EDAX maps showing experimentally-induced deterioration after freeze/thaw cycling in MgCl₂. Post-experimental dedolomitization reaction rims, Be, Ce, De, are well developed at the aggregate-paste interface. Significant Mg concentrations indicate that interstitial brucite precipitated in the dedolomitization reaction rim Ce as a result of the experimental treatment. A thin layer of Ca-rich material indicates calcite (Cal) which precipitated at the outer and inner margins of the brucite rim which lines the air void. Increased Mg concentration in the cement paste is probably due to the formation of magnesium silicate hydrate (MSH) as well

Sodium Chloride: After NaCl treatment in wet/dry and freeze/thaw experiments, no enhanced or new rim were evident in either dolomite aggregate or cement paste in non-durable concrete. No reaction rims were observed in durable concrete.

Formation of Chloroaluminate

All the chloride containing solutions cause the formation of chloroaluminate. Chloroaluminate (Freidels salt = monochloroaluminate, $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ + trichloroaluminate $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaCl}_2\cdot 32\text{H}_2\text{O}$) forms from reactions between the chloride solutions and C_3A (Ramchandran et al. 1976; Chatterji 1978; Ftikos and Parissakis 1985; Worthington et al. 1988; Day 1992; Kurdowski et al. 1994). Its morphology and occurrence in air-entrainment voids suggest that the chloroaluminate formed in concrete treated with chloride solutions is tri-chloroaluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaCl}_2\cdot 32\text{H}_2\text{O}$) resulting from the transformation of pre-existing ettringite (Day, 1992). This transformation produces a substitution of Cl^- ions for SO_4^{2-} ions in the ettringite chemical formula:



The trace of gypsum detected in the surface coat of the sample block may be the result of sulfate released during ettringite conversion (Table 1). All chloride solutions, also, appears to cause paste deterioration by decalcification of cement paste. The released calcium ions believed to form calcite in concrete, which is evidenced by the detection of calcite from leachate and on the concrete surface (Table 1). Brucite in cement paste appears to be stable in chloride treated concrete.

CONCLUSIONS

Magnesium chloride produced significant concrete crumbling because of widespread replacement of CSH by non-cementitious MSH. Calcium chloride deicing salts caused characteristic deterioration in concretes with reactive dolomite aggregates by enhancing dedolomitization reactions that release magnesium to form destructive brucite and MSH. Sodium chloride solutions did not cause significant change in reaction rims.

All the chloride containing solutions cause the formation of chloroaluminate. Its morphology and occurrence in air-entrainment voids suggest that the chloroaluminate formed in concrete treated with chloride solutions is tri-chloroaluminate resulting from the transformation of pre-existing ettringite.

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