

Farnam, Yaghoob. Ph.D., Purdue University, May 2015. Damage development, phase changes, transport properties, and freeze-thaw performance of cementitious materials exposed to chloride based salts. Major Professor: Jason Weiss.

ABSTRACT

Recently, there has been a dramatic increase in premature deterioration in concrete pavements and flat works that are exposed to chloride based salts. Chloride based salts can cause damage and deterioration in concrete due to the combination of factors which include: increased saturation, ice formation, salt crystallization, osmotic pressure, corrosion in steel reinforcement, and/or deleterious chemical reactions. This thesis discusses how chloride based salts interact with cementitious materials to (1) develop damage in concrete, (2) create new chemical phases in concrete, (3) alter transport properties of concrete, and (4) change the concrete freeze-thaw performance.

A longitudinal guarded comparative calorimeter (LGCC) was developed to simultaneously measure heat flow, damage development, and phase changes in mortar samples exposed to sodium chloride (NaCl), calcium chloride (CaCl₂), and magnesium chloride (MgCl₂) under thermal cycling. Acoustic emission and electrical resistivity measurements were used in conjunction with the LGCC to assess damage development and electrical response of mortar samples during cooling and heating.

A low-temperature differential scanning calorimetry (LT-DSC) was used to evaluate the chemical interaction that occurs between the constituents of cementitious materials (i.e., pore solution, calcium hydroxide, and hydrated cement paste) and salts. Salts were observed to alter the classical phase diagram for a salt-water system which has been conventionally used to interpret the freeze-thaw behavior in concrete. An additional chemical phase change was observed for a concrete-salt-water system resulting in severe damage in cementitious materials.

In a cementitious system exposed to NaCl, the chemical phase change occurs at a temperature range between -6 °C and 8 °C due to the presence of calcium sulfoaluminate phases in concrete. As a result, concrete exposed to NaCl can experience additional freeze-thaw cycles due to the chemical phase change creating

cracks and damage to concrete under freezing and thawing. In a cementitious system exposed to CaCl_2 , the chemical phase change is mainly due to the presence of calcium hydroxide (CH) in concrete. Calcium hydroxide can react with CaCl_2 solution producing calcium oxychloride. Calcium oxychloride forms at room temperature (i.e., 23 °C) for CaCl_2 salt concentrations at or above ~ 12 % by mass in the solution creating expansion and degradation in concrete. In a cementitious system exposed to MgCl_2 , it was observed that MgCl_2 can be entirely consumed in concrete by reacting with CH and produce CaCl_2 . As such, it followed a response that is more similar to the concrete- CaCl_2 -water system than that of the MgCl_2 -water phase diagram. Formation of calcium/magnesium oxychloride is most likely the main source of the chemical phase change (which can cause damage) in concrete exposed to MgCl_2 .

During the LGCC testing for CaCl_2 and MgCl_2 salts, it was found that the chemical reactions occur rapidly (~ 10 min) and can cause a significant decrease in subsequent fluid ingress into exposed concrete in comparison to NaCl. Isothermal calorimetry, fluid absorption, oxygen permeability, oxygen diffusivity, and X-ray fluorescence testing showed that the formation of calcium oxychloride in concrete exposed to CaCl_2 and MgCl_2 can block or fill in the concrete pores on the surface of the specimen; thereby decreasing the CaCl_2 and MgCl_2 fluid ingress into the concrete.

To mitigate the damage and degradation due to the chemical phase transition, two approaches were evaluated: (1) use of a cementitious binder that does not react with salts, and (2) use of a new practical technology to melt ice and snow, thereby decreasing the demand for deicing salt usage. For the first approach, carbonated calcium silicate concrete (CCSC) was used and the CCSC mortar showed a promising performance and resistance to salt degradation than an ordinary portland mortar does. For the second approach, phase change materials (PCM), including paraffin oil and methyl laurate, were used to store heat in concrete elements and release the stored heat during cooling to reduce ice formation and snow accumulation on the surface of concrete. PCM approach also showed a promising performance in melting ice and snow, thereby decreasing the demand for salt usage.