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## Modeling of frost salt scaling

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## Abstract

This paper discusses the numerical modeling of deterioration in cement-based materials due to frost salt scaling (FSS). Several aspects of FSS are investigated such as carbonation, microstructure, mechanical properties and testing conditions. Mainly blast-furnace slag cement (henceforth *slag cement*) systems are of interest in this paper since several reports have been indicated that cementitious materials bearing slag-rich cement are critically vulnerable under combined attack of frost and de-icing salts.

In the first part, the paper deals with the effect of carbonation on the micromechanical properties and FSS resistance of 1-year-old slag cement and ordinary Portland cement pastes with W/C 0.45. The micromechanical properties were evaluated by the nano-indentation technique and the results are used to evaluate the behavior of these pastes under frost salt attack. FSS damage on the paste samples is modeled according to the *glue-spall* theory with the aid of Delft Lattice Model. Additionally, the carbonated cement paste microstructures are characterized by ESEM/BSE.

In the second part, parameters that are varied in the investigation are the salt concentration in the external water layer and ice-layer thickness on the surface. Again the lattice type model is used to simulate the mechanism in which the material structure is implemented using digital images of the real material. Both experiments and the simulation with the model show that the amount of scaling increases with increasing thickness of the ice layer on the surface. Furthermore it is shown that with the model the well known pessimum effect for salt concentration in the water (which causes maximum damage at 3% salt) can be reproduced.

The outcome of the model indicates that *glue-spall* theory can successfully explain FSS. © 2007 Elsevier Ltd. All rights reserved.

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## 1. Technical background

The modeling of FSS has been a difficult issue due to its complex physical and chemical mechanisms [1]. Plain frost action has attracted relatively more attention and thanks to its less complicated mechanism, we increased our knowledge during the past few decades. The works of Powers, Litvan, Pigeon, Marchand, Setzer [2–5], and many other researchers have drawn the frame of the issue substantially. Unfortunately, similar arguments could not be made for frost salt attack. There have been a number of questions, which could not be answered by a single theory [6]. Due to having insufficient knowledge about the phenomenon, modeling attempts have been restricted to black-box type [7]. However, recently an interesting theoretical explanation of the mechanism of frost

\* Corresponding author. *E-mail address:* o.copuroglu@citg.tudelft.nl (O. Çopuroğlu). salt attack was introduced by Valenza and Scherer [8,9]. The researchers proposed a mechanism called *glue-spall*. According to this theory the cracking of the ice/brine layer is the origin of FSS. They put forward a theoretical explanation for the greater damage of pessimum salt concentration under frost which has been known as a mystery so far. The principle idea is that following the ice formation on top of the concrete surface, ice starts to shrink due to further cooling. The shrinkage creates tensile stresses in the ice and causes three consequences depending on the solute concentration of the liquid. These are:

- 1. Weak salt concentration (*i.e.* 0.1%): Due to the ice formation and further cooling of the ice, the exerted tensile stress cannot exceed the tensile strength of ice; hence no cracking occurs (in ice and concrete).
- 2. Pessimum salt concentration (1-3%): Due to the ice formation and further cooling of the ice, the exerted tensile

stress exceeds the tensile strength of ice and breaks the ice, which triggers surface scaling.

3. Strong salt concentration (10-20%): In this case the ice layer is too soft to exert enough stress to the underlying cementitious material, hence only the ice cracks and no scaling occurs.

Therefore, tensile strength of a cement-based material seems to be an essential indicator concerning the FSS resistance of cement-based materials. The study of the glue-spall theory has shown that scaling occurs due to the cracking of the external ice layer and consequent generation of tensile stress on the surface layer. However, simply considering the global tensile strength of a cementitious material may not be an appropriate approach to the problem since the tensile strength highly depends on the strength of the weakest link in the specimen under tensile stress (see Fig. 1a). In case of FSS, the picture is a bit more complex where the micromechanical properties of the phases in different locations determine the scaling resistance throughout the material surface (Fig. 1b). Therefore assessment of local micromechanical properties seems to be much more crucial than evaluation of global tensile strength in order to predict the FSS resistance of a particular material.

For the measurement of local micromechanical properties, depth-sensing nano-indentation has been shown to provide a useful tool, especially for measuring hardness and elastic modulus of local phases/materials on the submicron scale [10]. This has been achieved principally through the development of instruments capable of continuously measuring load and displacement throughout an indentation. With this method and high precision instrument, the mechanical properties can be determined directly from indentation load and displacement measurements without the need to image the indent impression. Details of such a technique, which was used successfully to study properties of the interfacial transition zone (ITZ) in practical concrete and individual phases in cement paste, have been given elsewhere [11–13].

The FSS modeling is very much restricted by the lack of data concerning the mechanical properties (*i.e. E*-modulus, strength) of the micromaterials and more specifically, by the lack of data obtained *in situ*. Very little information is found on the micromechanical properties of cementitious materials in the

literature [14]. Constantinides and Ulm [13] reported the elastic modulus of C–S–H, decalcified C–S–H, calcium hydroxide and unhydrated clinker ranging between 19.5 and 31.8 GPa, 2.2 and 13.2 GPa, 33 and 43 GPa and over 100 GPa, respectively. The tensile strength cannot be measured directly but could be estimated from the elastic modulus of the phases.

Furthermore, the properties of the above mentioned cement paste phases appear to be influenced by different cement types as well as environmental conditions, which affects various aspects of cement-based materials, including FSS. It is reported that slag-rich cement concrete and ordinary Portland cement (OPC) concrete perform differently when subjected to carbonation [15]. While carbonation leads to a slight densification of the microstructure in OPC concrete, in slag cement concrete the microstructure becomes coarser. The percentage of capillary pores increases with carbonation in slag cement concrete, while in the case of OPC it decreases. More recent electron microscopy and mercury intrusion porosimetry studies have further confirmed that carbonation causes remarkable coarsening of the slag-rich cement paste microstructure [16,17]. The visual findings from the electron microscopy imply that there could be a significant decrease in tensile strength of the slag cement paste which could be the reason for increased vulnerability of the concrete surface against the attack of frost and de-icing salts.

Among the influencing parameters, a high priority has to be given to carbonation since the mechanical properties (and indirectly FSS performance) of a cement-based material can be significantly influenced by this environmental issue. Only a small number of researchers reported the strength sensitivity of slag cement-based materials to carbonation [18–20]. Manns and Wesche investigated the effect of carbonation on the flexural strength of the high-slag (82% slag m/m) cement mortars with W/C 0.50. They concluded that the higher the degree of carbonation, the lower the rupture modulus of high-slag cement mortars. They also observed that flexural strength of OPC and low-slag cement mortars were not negatively affected by the carbonation [21].

This paper discusses the numerical and visual modeling of the FSS phenomenon according to the *glue-spall* theory. Various experimental results are used as an input for the model and the validation of the model is also discussed with the

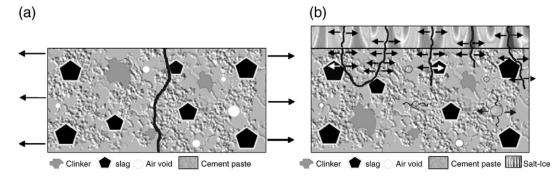


Fig. 1. Schematic description of a cement paste under global tensile stress and of the cracks induced by the cracking of external ice layer.

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