

# Examining Freeze-Thaw Damage at the Microscopic Scale

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## PROBLEM

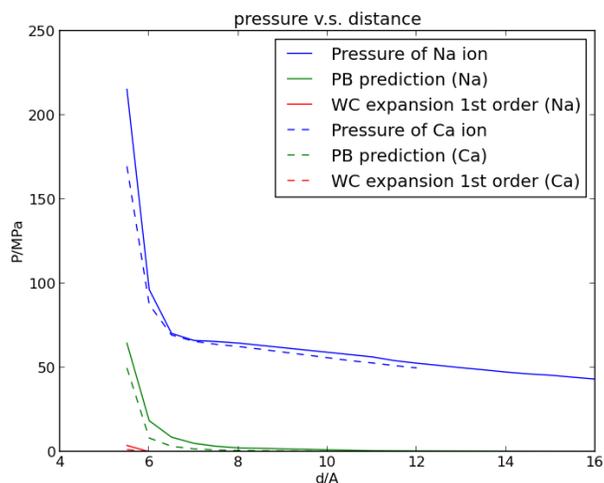
Freeze-thaw damage is a potentially serious deterioration process that occurs in concrete structures in cold climates. When the temperature cycles below and above the freezing point of water in the cement pore solution (a freeze-thaw cycle), some of the water will turn into ice, an expansive process, and then turn back into liquid when thawing. Whether this expansion and contraction of water leads to enough pressure on the cement paste matrix to cause cracking is debated, but it is known that using certain deicing salts can aggravate the damage and that appropriately distributed entrained air bubbles can prevent damage. Previous experiments where mortar samples' capillary pore solutions are replaced with benzene (which, unlike water, shrinks when freezing) showed freeze-thaw damage similar to conventional samples; this suggests that water volume expansion may not be the direct cause of cracking. We conducted both theoretical and numerical studies on the microscopic phenomena in cement paste pores to reveal the important roles that ions and electrolytes play in freeze-thaw damage.

## APPROACH

From theoretical calculations, it is understood that a liquid layer remains between the ice core and the solid C-S-H matrix even when most of the water inside a pore is frozen. We conducted molecular simulations on the liquid layer with ions modeled as individual particles interacting with each other, as well as with the surfaces of C-S-H and ice. The motions of the ions were calculated according to these interaction forces. In these simulations we are able to tune the size, valence, interaction strength and surface effects of the ions assuming different conditions, and our results showed the stresses generated under these conditions.

## FINDINGS

The C-S-H surface layer is negatively charged and the concentration of ions is very high ( $> 1 \text{ MM}$ ) in the liquid layer. Within the confined system of ice and C-S-H, the concentrated ions display interesting behavior and interactions: we find that ions and electrolytes in this system are capable of generating large stresses which then transfer to the surface of the solid. These stresses are potentially the origin of micro-cracking and also of damage to the C-S-H matrix. Additionally, we find that the type, valence, size and polarization of the ions can affect the stresses, which indicates that it may be possible to tune the chemical recipe of cement paste pore solution, and to tailor the selection of deicing salts, to mitigate damage.



Stress measured in molecular simulations for Na and Ca ions (blue lines) with theoretical approximations (PB for Poisson-Boltzmann in green, and WC for Strong coupling expansion in red). On the X-axis  $d$  is the distance between the C-S-H surface and neutral ice surface in unit of Angstroms.

## WHY DOES THIS RESEARCH MATTER?

- Freeze-thaw damage is one of the top destroyers of concrete in colder climates, but the origins of the damage are not well understood.
- CSHub researchers have identified stresses resulting from ion behavior in the cement paste pore solution.
- The research sheds new light on electrolyte behavior in cement paste pores, and may provide new solutions to combating freeze-thaw damage.