

## ABSTRACT

Air-entraining agents (AEA) were introduced in the 1930s to improve concrete's resistance to cyclic freezing-thawing exposure. Over the past 90 years, there has been extensive discussion about how traditional AEA contribute to durability improvements. However, the issue of strength loss associated with conventional AEA use remains unresolved unless the cement is overdosed. Moreover, the effectiveness of traditional AEA in entraining air voids has proven inconsistent, as it is influenced by various factors. As a result, the increased costs and carbon footprint associated with AEA use continue to be ongoing concerns for the industry.

Hollow polymeric microspheres have emerged as a promising solution for enhancing concrete's cyclic freezing-thawing resistance by providing encapsulated air without compromising mechanical performance or durability. In this study, the hydration, fresh properties, hardening performance, and freezing-thawing resistance of air-entrained cement mortar and concrete were investigated using the novel hollow polymeric microspheres and a traditional aqueous AEA, respectively. Additionally, the dynamic modulus of elasticity change and surface spalling damage of concrete beams following cyclic freezing-thawing exposure were evaluated. The air-void system and capillary pore structure of cement mortar and concrete, air-entrained with the traditional AEA and microspheres, respectively, were examined through various characterization methods, including optical microscopy (OM), scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and 3D X-ray microscopy (micro-CT, or XCT). The properties of mortar and concrete with varying dosages of AEA and microspheres were assessed, and the mechanisms behind the enhanced freezing-thawing resistance were explored.

The microspheres used in this study were found to have a 'curing' effect, enhancing the hydration, workability, and mechanical strength of the mortar compared to both plain mortar without air entrainment and mortar air-entrained with the traditional aqueous AEA. Evaluating the mechanical strength changes and mass loss of mortar specimens demonstrated that the freezing-thawing resistance of mortar air-entrained with microspheres was superior to that achieved with aqueous AEA. The small size and compressibility of the microspheres resulted in a fine and well-distributed air void system, offering improved freezing-thawing resistance in the mortar specimens.

Additionally, due to the potential 'curing' and nucleation effects of the microspheres, the strength of air-entrained concrete with microspheres was slightly higher than that of plain concrete without air entrainment. In contrast, the traditional air-entraining method led to a 7.0% to 8.4% strength loss in concrete with 1% entrained air. Furthermore, concrete air-entrained with microspheres exhibited significantly less surface spalling damage compared to plain concrete, thanks to its well-distributed air void system and enhanced strength. On the other hand, although traditionally air-entrained concrete maintained its dynamic modulus throughout the 300 cycles of freezing-thawing exposure, it still suffered severe surface spalling damage, likely due to its reduced strength.

This study provides valuable insights into the practical application of polymeric microspheres for enhancing the freezing-thawing resistance of concrete.