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Internal curing of high performance concrete using cenospheres

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ABSTRACT

This study explores a novel internal curing agent, perforated cenospheres. Cenospheres are hollow fly ash particles produced from coal burning power plants. The shell of the cenospheres is inherently porous that is sealed by a thin layer of glass-crystalline film. By removing this film through chemical etching, the pores on the shell can be exposed, perforating the cenospheres and providing paths for water propagating into the internal volume of cenospheres. The perforated cenosphere were found to have water absorption as high as 180 wt%. The loaded water can be readily released from the cenospheres under high relative humidity (95%). When incorporating saturated cenospheres into cement mortar for internal curing, the autogenous shrinkage of the mortar was almost eliminated. The internal curing also improved the compressive strength of the cement mortar. All these results suggest that perforated cenospheres can be used as an efficient internal curing agent for HPC.

1. Introduction

Autogenous shrinkage is an important phenomenon in early age concrete, in which water can be rapidly drawn into the hydration process and the demand for more water creates very fine capillaries. The surface tension within the capillaries causes autogenous shrinkage which can lead to premature cracks, making the concrete more vulnerable to the ingress of potentially aggressive species and thus severely reducing the durability of concrete. Early age cracking due to autogenous shrinkage is especially serious for high-performance concrete (HPC) because of its low water to cement ratio [1]. These cracking problems cannot be mitigated through conventional full water curing due to HPC's compact structure and very low permeability. To combat this problem, internal curing method has been developed in which water-filled internal curing agents are added to concrete mixture. These internal curing agents are used as water reservoirs which can gradually release its water during the hydration process. The released water can maintain a high relative humidity inside the concrete pores to prevent self-desiccation in concrete [1]. As a result, autogenous shrinkage of concrete can be reduced or eliminated, which will ultimately minimize cracking and significantly promote the durability of structural concrete [2,3]. More complete cement hydration is also achieved by internal curing due to extra curing water provided by the internal curing agent, creating a denser cement paste, reducing permeability [1,4,5]. As a result, the service life of concrete structures can be significantly increased and the life-cycle cost can be significantly reduced [6].

The key element in internal curing technique is to choosing a proper internal curing agent to load and release water in concrete as needed. An ideal internal curing agent should release most of its absorbed water uniformly at high relative humidity within an appropriate time [1] in order to optimize internal curing of concrete [7]. The most often used internal curing agents are pre-wetted high porosity lightweight aggregates (LWAs) and super absorbent polymers (SAPs) [1]. LWAs include lightweight coarse aggregates (LWCAs) with a particle size > 6.35 mm and lightweight fine aggregates (LWFAs) with a particle size smaller than 6.35 mm. Pre-wetted LWFAs are more suitable than LWCAs because of two reasons [8]: 1) LWFAs can produce better distribution of moisture; and 2) LWCAs don't have the approximate gradation of the natural aggregate being replaced. SAPs can expand to absorb thousands of times their dry weight in water without dissolving, although commercially available SAPs generally exhibit absorbency below 20 g/g. When used in cement to entrain water, the high pH environment of the concrete mixture can substantially reduce the absorption extent of SAPs compared to pure water. Nevertheless, the SAPs can absorb much more water to be used in internal curing than LWAs.

Although great success has been achieved by these two internal curing agents, they can be further improved to minimize the adverse effect on the mechanical properties [9,10] induced by the internal curing agents. This is because in nature the internal curing agent is much weaker than normal aggregates. To this end, the amount of necessary internal curing agent should be minimized [7]. By using the concept of protected paste volume, Bentz and Snyder [11] found that cement paste should lie within a sufficiently small distance from the internal curing water reservoir so that the internal water could penetrate. Within this distance, the cement paste is protected by the internal curing water from self-desiccation. Clearly, smaller spacing between internal curing agent particles

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is more desirable because more cement paste can be protected by the internal curing water. To achieve this, the internal curing agent particle size should be as small as possible [7]. Some experimental studies [12] did show that smaller internal curing agent particles perform better than the larger ones. Zhutovsky et al. [13] also found that reduction of the internal curing particle size down to 4–2 mm can improve the curing efficiency. However, further reduction of the internal curing agent particles led to reduction of internal curing efficiency, instead of increase. Zhutovsky et al. [7] found that this apparent discrepancy was caused by two competing mechanisms taking place upon reduction of the particle size of the internal curing agent: i) small spacing factor can increase the internal curing efficiency; while ii) small particles have smaller pores which tend to hold water more tightly, making them unavailable for internal curing. When the particle size is sufficiently small, the second mechanism overrides the first mechanism, leading to reduction in internal curing efficiency. Therefore, to obtain optimal internal curing result, only reducing the spacing between particles is not sufficient. The structure of the internal curing agent particles must be optimized too. To make water more available to internal curing, the size of the pore in the internal curing agent particles should be as large as possible. Theoretically, the largest size for a pore should be the size of the particle itself. However, the currently used internal curing agents, neither LWAs nor SAPs can have such a pore structure.

In this study, a novel internal curing agent with such an optimal pore structure, perforated cenospheres is proposed for internal curing of HPC. Cenospheres are hollow fly ash particles generated in coal burning power plants, which have sizes ranging from a few to hundreds of micrometers (Fig. 1(a)). Cenospheres are much smaller than LWAs, thus they can provide better distribution of curing water. Since they have only one large pore, which is very close to their own size, as shown in Fig. 1(b), water can be loaded into and released from them easily. Moreover, cenosphere particles have an aluminosilicate shell with high stiffness and strength and a thickness of just a few micrometers. The potential of using cenospheres to deliver water was noticed by Jensen and Lura [14] 10 years ago. They stated that "If water-filled, the capsule wall (of cenosphere) could have beneficial pozzolanic properties whereas the water might serve as internal curing water." However, they have never been implemented because the shell of cenospheres is covered by a glass-crystalline nanosize film (Fig. 1(a)). Without removing this thin film, the inner volume of the cenosphere is inaccessible to water, as shown in Fig. 1(a). Jensen and Lura [14] also pointed out that "no method to induce the water into the particles or to ensure its proper release when needed seems to be available."

In this work, this barrier has been removed through removing the thin film by a simple chemical etching process. Water can then be easily induced into or released out of cenospheres through the holes perforating the shell of the cenospheres. It is found from this research that perforated cenospheres have a water absorption as high as 180 wt%, and the loaded water can be readily released from cenospheres under high relative humidity of 95%. When mixing the saturated cenospheres into mortars, the autogenous shrinkage can be eliminated without compromising the compressive strength. These findings suggest that the perforated cenospheres have a great potential to be used as an efficient internal curing agent for HPC.

2. Materials and methods

2.1. Materials

In current study, reagent grade ammonium fluoride (NH_4F) and hydrochloric acid (HCl) were used. Calcium gluconate gel was always present during handling of hydrofluoric based acid solution (1.0 M NH_4F-1.2 M HCl-H_2O).

Cenospheres used have sizes between 10 and 200 μm. Table 1 shows the chemical composition of cenospheres, gained by X-ray fluorescence (XRF) analysis. The composition of Type I Portland cement used for casting mortar is also listed in Table 1. It has to be pointed out that XRF technique can provide excellent quantification for many elements in the periodic table except those with low atomic weights, e.g., oxygen. In an effort to compensate for the matrix effects of the compounds routinely compromising the solids, the XRF software offers the option to represent the elemental concentrations as oxides. For cement-based materials, comparing and contrasting 'oxide equivalent' within a sample can provide a more helpful and representative metric relative to a comparison of elemental concentrations [19,20,27]. Thus in this paper, the XRF data is reported as oxide compositions.

2.2. Production of perforated cenospheres with acid etching

Cenosphere particle has an aluminosilicate shell with a thickness in a few micrometers (Fig. 1(a)). The shell has a porous structure formed by gas inclusion and is covered by a glass-crystalline nanosize film, which is shown in Fig. 1(b). To make the internal volume of cenospheres accessible for water, the film should be removed. This can be done by etching the cenospheres with acids [15]. Approximately 12 g of cenospheres were soaked into 250 mL of 1.0 M NH_4F-1.2 M HCl-H_2O solution for 2 h with occasional stir. By the end of this treatment, >95% of cenosphere sank to the bottom of container, which were floating on the surface of acid solution at the beginning. The settlement of cenospheres indicates the completion of perforation. After etching, the perforated cenospheres were vacuum filtered and rinsed with 1500 mL of water, followed by being dried in an oven at 110 °C.

The morphology and microstructure of as-received (Fig. 1) and the produced perforated cenospheres were investigated using a JOEL 7000 FE scanning electron microscope (SEM). The microscope was operated at low accelerating voltage (1–3 kV) and 10 mm working distance with a spot size of medium 8. Before being put into SEM chamber, cenospheres were coated with a layer of gold, in order to mitigate the charging effect.

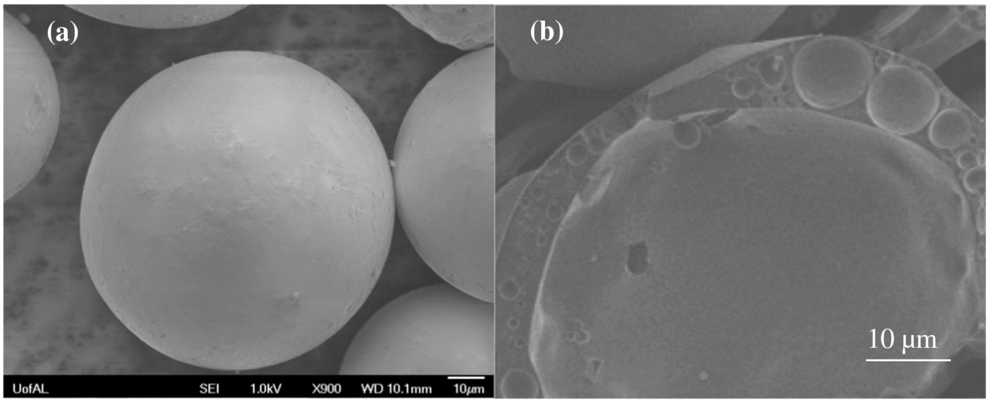

Fig. 1. Microstructure of cenospheres under SEM observation: (a) a cenosphere with impermeable shell; (b) porous shell of the cenosphere.