Pore Distribution and Water Uptake in a Cenosphere–Cement Paste Composite Material

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Abstract. Alumina silicate cenospheres (CS) is a significant waste material from power plants that use a coal. Use CS as Portland cement replacement material gives opportunity to control physical and mechanical properties and makes a product lighter and more cost-effective. In the frame of this study, Portland cement paste samples were produced by adding CS in the concentration range from 0 to 40 volume %. Water uptake of hardened samples was checked and pore size distribution by using the mercury porosimetry was determined. In a cold climate where the temperature often falls below 0 °C, it is important to avoid the amount of micrometer sized pores in the final structure and to decrease water absorption capacity of material. In winter conditions, water fills such pores and causes additional stresses to their walls by expansion while freezing. It was found that generally water uptake capacity for cement paste samples decreased up to 20 % by increasing the concentration of CS up to 40 volume %, at the same time, the volume of micrometer sized opened pores increases.

1. Introduction

Coal combustion ashes are one of the key materials in research and practice related to concrete [1]. Cenospheres (CS) are fine spherical particles (microspheres, micro-balloons), formed in coal
combustion process in a furnace. Such property of CS like bulk density in the range between 300 to 700 kg/m$^3$ allows for easy design and building of simple furnaces with separators for different ashes by using the effect of gravity. Therefore, it is not necessary to ensure additional cleaning of CS [2], [3]. An outer diameter of CS may vary from ~1 to 500 µm [4]. Types of CS are classified depending on their chemical composition and raw material. The chemical and mineralogical composition can change the colour of CS from brown to grey or even black, depending on concentration of unburned carbon. According to standard ASTM C618, depending on raw coal, CS is divided into class F (made by burning anthracite and other older coals) and class C (from burning of brown lignite or half-bituminous coals). As required in the standard, content of SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ for class F (70 %) and class C (50 %) plays the main role in activity of CS, exhibiting a higher pozzolanic activity for class C [5]. Additionally to the type of raw materials, processing temperature, flow rate and other factors in the furnace influence the result regarding the size, type and density of the final spherical ash particles. The models of such particles can be: a) spherical ash particles with an outer diameter, b) a shell type single wall spherical particles (CS), filled with gas, c) a shell type single wall spherical particles filled with smaller particles inside (plierospheres), d) spherical particles with a complex network structure inside [6], [7].

Popular way for utilization of CS is its use in production of lightweight constructions of Portland cement mortar and concrete [8]. Due to the fact that particle sizes of CS can be similar or even smaller than particle sizes of Portland cement and sand, their spherical shape can also reduce the amount and size of the opened pores. Additionally, pozzolonic effect consumes free Ca(OH)$_2$ from hydrated Portland cement by filling pore volume between particle surfaces of CS and Portland cement with insoluble silicate hydrates. All these effects can allow producing a concrete or cementing mortar with less permeability to various gases, vapour and fluids [2], [9]–[11].

As observed by Barbare, Shukla, and Bose in their work [12], the equilibrium moisture content of cenospheres used in their work is about 18 times higher than that of sand, reflecting the porous nature of cenospheres. The flux of water vapour away from both the cenosphere–concrete and the normal concrete shows nonlinear change with moisture content throughout the drying cycle, implying that the pore structure within the concrete strongly influences the drying behaviour. Sorption usually takes place in case of contact of two phases, but sorbents (solid phase) link gases or liquids. In case of dry hardened Portland cement paste immersed into water, chemisorptions occur in addition to physical absorption by forming crystal hydrates. Due to great variety of pores in a Portland cement paste structure, depending on the sizes of pores and related frost resistivity, these are divided into a) small pores (or gel pores) with sizes below 0.04 millimetres and freezing point of water at ~ 50 ºC; b) average size of pores with the diameter between 0.04 to 0.3 mm (micrometer sized or capillary pores) with the water freezing point close to 0 ºC and can cause formation of new cracks; c) pores larger than 0.3 mm that are not filled with water fully and do not significantly cause the formation of new cracks [13], [14]. Depending on different experience, scientific medium, deepness of research work and other factors, in different reviews and research works, different pore classifications with similar (but not equal) assessment of pore impact on water absorption capacity and frost resistance of Portland cement pastes, concrete and mortars are considered and proposed [15]–[17].

2. Materials and methods
The Aalborg White CEM I 52.5R cement (Germany) and the mullite containing CS from electric power station “Troitskaja” (Russian Federation), supplied by Biotecha Latvia (Latvia) were used. The chemical composition and size distribution (determined by using CONTROLS Model 15-D0407 with
Glenammer sieves) are shown in table 1 and table 2. Cement paste samples with water to cement ratio of 0.4 were prepared by mixing fresh cement paste using a laboratory mixer, filled into concrete moulds and vibrated for 10 seconds on the vibration table. Mix compositions are summarised in table 3.

### Table 1. Chemical composition of mullite containing cenospheres.

| Compound | Mass % |
|----------|--------|
| SiO₂     | 55.8   |
| Al₂O₃    | 37.9   |
| Fe₂O₃    | 1.5    |
| CaO      | 1.9    |
| MgO      | 0.9    |
| Na₂O     | 0.7    |
| K₂O      | 0.3    |

Loss of ignition – LOI

| Temperature, °C | Loss of Ignition, % |
|-----------------|---------------------|
| 20-400          | 0.5                 |
| 400-1000         | 0.1                 |

### Table 2. Sieve analysis of used cenospheres CS5 (BS/ISO 3310).

| Sieve opening size, mm | Residuals, % |
|------------------------|--------------|
| 0                      | 0            |
| 0.063                  | 0.8          |
| 0.075                  | 1.5          |
| 0.150                  | 1.9          |
| 0.3                    | 95.8         |
| 0.6                    | 0            |

### Table 3. Mix design of cement pastes (for production of 1m³ cement paste).

| Material   | Portland cement, kg | Cenospheres CS5, kg | Water, kg |
|------------|---------------------|---------------------|-----------|
| CS5-CP-0   | 1370                | 0                   | 545       |
| CS5-CP-5   | 1296                | 20                  | 518       |
| CS5-CP-10  | 1226                | 41                  | 490       |
| CS5-CP-20  | 1087                | 81                  | 435       |
| CS5-CP-30  | 947                 | 122                 | 379       |
| CS5-CP-40  | 808                 | 162                 | 323       |

Cylindrical shape samples with the diameter of 45.5 ± 0.2 mm and height of 41.2 ± 0.3 mm were made for test. After 28 days hardening in water, samples were dried for 24h at 80 ± 5°C by using drying oven MEMMERT ULE 400 until the constant mass and cooled down to room temperature in desiccators. As observed in this test, application of higher temperature for drying is limited for this material due to formation of new cracks by possible decomposition of hydrated compounds. Densities of dried specimens were recorded before the test (see table 4). Dried samples were fully immersed into
a container filled with water. Depth of the water was 45 mm above the top of the samples, while the samples were totally immersed in water. Two plastic wires with the diameter of 2 mm were placed under the samples to ensure maximum contact area with water. Depth of water was controlled and adjusted during every measurement test. Test was executed at 20 ± 5 °C. During the first 60 minutes of the test, the weight of samples was recorded by using scale Kern EW600-2M (±0.01g) every 10 minutes. After 60 minutes of test, the weight of samples was recorded every 30 minutes. After 240 minutes, the weight of samples was recorded every 1440 minutes (24 h). Test duration was 12960 min (9 days). Tests were repeated 3 times.

Content of absorbed water $W_{Abs}$ was calculated according to the following equation:

$$\frac{\Delta M}{M_0} \times 100 \%$$  \hspace{1cm} (1)

Where,

- $M_w$ – Mass of the sample with water;
- $M_0$ – Mass of the dried sample;
- $\Delta M$ – Increase in weight of the sample, %.

Pore size distribution and total opened pore volume was determined for 28 days cured samples by using the mercury porosimetry with a porosimeter Pore Master 33 Quantachrome Instruments according to ISO 2738.

An important note in this work is that the mercury porosimetry is useful only for determination of a limited range of pore volume (10$^{-2}$ to 950 µm) and there is no reaction between mercury and cement paste samples.

3. Results and discussions

3.1. The influence of concentration of CS on density and water uptake behaviour of cement pastes

Average densities of dried samples are summarised in table 4. Replacing 40% of Portland cement by cenospheres decreases material density up to 23% (from 1.79 to 1.45 T/m$^3$). As shown in figure 1, all samples filled with CS in the first 10 minutes have uptake more than 50% of total absorbed water in this test. The rate of water uptake for cement paste samples CS5-CP-0 has changed the curve from vertical to horizontal only after 20 minutes from the start moment of the test.

| Material    | Average densities, T/m$^3$ |
|-------------|---------------------------|
| CS5-CP-0    | 1.79                      |
| CS5-CP-5    | 1.71                      |
| CS5-CP-20   | 1.64                      |
| CS5-CP-30   | 1.54                      |
| CS5-CP-40   | 1.45                      |

According to the reviewed literature, a non-linear water uptake curve can be expected in this test, exhibiting a complex path for water trip into a CS containing cement paste pore system. However, in this work the non-linearity has been observed only in first 20 minutes. An observed difference between Portland cement pastes with and without CS could be explained by higher capillary forces into CS containing samples.
After 20 minutes, the remaining unfilled pores and other spaces into structures cement paste samples have uptake water slowly, by increasing the mass by maximum up to 3.5% in cases of CS5-CP-30 and CS5-CP-40. The total amount of absorbed water decreased with increasing the concentration of CS from 20 to 40 volume %, as compared to Portland cement paste samples without CS, exhibiting up to 3% less water absorption capacity at the same test duration. No significant effect was observed to the sample with 5 volume % of CS, which exhibited a higher water absorption capacity as compared to other samples.

![Figure 1. The dynamics of water uptake.](image-url)

3.2. The influence of concentration of CS on pore size distribution of cement paste

As shown in table 5, the total opened porosity increased by 7.38% by increasing the concentration of CS up to 40 volume %. Exception is observed for sample CS5-CP-5, exhibiting similar content of opened porosity as compared to CS5-CP-20. It could be concluded that the cement pastes even with small concentrations of CS significantly reduce the air and vapour discharge ability by using the same preparation method.

As shown in figure 2 (a) and (c), for CS5-CP-0 and CS5-CP-20, similar increase in the total volume of pore with sizes in the range up to 2·10⁻¹ μm (with a highest volume of pores of 5.16·10⁻³ cm³/g in this range) was observed. For other samples (see figure 2 (b), (d) and (e)), the pore size range was higher, exhibiting pore diameters up to 1.00·10⁻¹ cm³/g.

| Material     | Total opened porosity, % |
|--------------|--------------------------|
| CS5-CP-0     | 2.00                     |
| CS5-CP-5     | 5.37                     |
| CS5-CP-20    | 5.11                     |
| CS5-CP-30    | 7.21                     |
| CS5-CP-40    | 9.38                     |
For all samples, a significant increase in content of opened pores was observed in the range of pore sizes from 10 to 500 µm with a clear trend to increase pore volume by increasing the concentration of CS.

In general, an increased volume of micrometer sized pores (in diameter range between 1 to 100 µm) appears for samples with concentration of CS from 20 to 40 volume % (see figure 2 (c), (d) and (e)). As shown in figure 2 (b), a relatively small concentration of CS (5 volume %) decreased the total volume of micrometer sized pores close to 0 cm$^3$/g.

![Figure 2](image)

**Figure 2.** Pore size distribution in the tested samples.

According to the obtained results, it could be concluded that by increasing the concentration of CS in the range from 0 to 40 volume %, the total volume of the opened pores increases. It is expected that by increasing the concentration of CS up to 20 volume %, frost resistance of concrete can be improved due to decreased volume of micrometer sized opened pores. An increase of CS from 30 to 40 volume % can decrease the cement paste durability due to the full filling of micrometer pores with water that could break the pore walls causing the cracks in a cement paste system. Increased porosity may be
affected by shrinkage micro cracks in the hydrated cement paste, especially in the contact zone cenosphere – cement paste. A significant factor in mercury porosimetry is relatively high pressure in the work chamber reaching up to 400 MPa. Such pressure can lead to opening of the closed pores and possible collapse of weaker or thinner walls in the pore system.

By comparing the results from pore distribution and water uptake test results, it could be concluded that high relative amount of CS in a Portland cement paste structure provides less water absorption, it is a positive factor for improving frost resistance. On the other hand, high amount of CS in the cold climate can lead to faster formation of new cracks due to increased volume of micrometer sized pores.

4. Conclusions
Generally, replacing Portland cement by cenospheres (CS) (up to 40% by volume) contributes to the reduction of density (up to 23%) and decreasing water absorption capacity up to 3% (by mass) at the same test duration as compared to cement paste sample without CS. Initial water uptake rates for all cement paste samples with CS were higher (have uptake more than 50% of total water in 10 minutes), as compared to Portland cement paste sample without CS (in 20 minutes). Decreased water absorption can have a positive impact on providing durability and frost resistance.

At the same time, by increasing the concentration of CS in the range from 0 to 40 volume %, the total volume of opened micrometer pores determined by mercury porosimetry is higher. An increased volume of “dangerous” (micrometer) pores can cause faster formation of new cracks during the freezing/thawing of wet structures in the cold climate.

Small concentration (5 volume %) of CS did not influence the water uptake capacity and did not increase the volume of “dangerous” (micrometer) pores.

This study has been carried out on a cement paste, which does not fully reflect the behaviour of real concrete, which contains multi-sized aggregate system and surface active admixtures. In the next step of study, durability of real concrete mixtures containing cenospheres would be investigated.

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