The effect of curing conditions on the durability of high performance concrete

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Abstract. This study researches compressive strength and durability of the high strength self-compacting concrete (SCC) impacted at early stage by the curing conditions. The mixture compositions of metakaolin containing waste and cenospheres as partial cement replacement (15 wt\%) were compared to reference SCC with 100\% cement. The specimens prepared in advance were demoulded 24h after casting of the SCC and the specific curing conditions were applied for up to 28 days: standard water curing at 20°C (i); indoor curing at 20°C, RH 60\% (ii) and low temperature air curing (2°C) at RH 60\% (iii). Results indicate that at early stage (14 days) indoor curing conditions increase compressive strength of the SCC whilst no strength loss has been detected even at a low temperature curing. The further strength gain has been substantially reduced for samples cured indoor and at a low temperature with significant variation observed for long term compressive strength (180 days). The metakaolin containing waste has proved to be an effective partial cement replacement and it has improved strength gain even at a low temperature curing. Meanwhile cenospheres have reduced the SCC strength and with no positive effect on strength observed within the standard term. Freeze-thaw durability and resistance to the chloride penetration have been improved for the SCC cured at low temperature. The SCC with metakaolin containing waste has proved to be the most durable thus demonstrating importance of effective micro filler use.

1. Introduction

The high performance concrete (HPC) plays an increasingly important role in the construction industry due to its improved compressive strength, durability and technological advantages over the traditional concrete of normal strength [1]. Improvement of the HPC technology continues to develop worldwide so that the scale of testing and application of the HPC in laboratory and field trials has been introduced at the level of national standardization and civil engineering. It is generally accepted that micro fillers can be used as supplementary cementitious materials or partial cement replacement in concrete structure and it is self-evident that an integral part of the HPC consists of the micro level fillers that can be much finer compared to the Portland cement [2]. By testing properties of various characteristics of concrete, studies are performed on more effective application of mineral micro fillers to concrete. More and more research focuses on the HPC durability tests with variations of mixture composition. As a result of possible significant decrease in the viscosity of concrete, a max value should be limited for replacing cement with micro filler materials. According to the Zhang report the viscosity of cement pastes can decrease in case of ultrafine powder quantity that is smaller or equal to 15\% while the viscosity can increase significantly with more than 15\% addition [3]. The climatic conditions determine that one of the most important durability properties of concrete is the freeze-thaw...
resistance and chloride penetration, as it is used as protective cover to reinforce the steel protection from corrosion. Traditionally, the durability of freeze-thaw resistance can be improved by using the air entraining agents which can decrease scaling to up to 0.5 kg/m² after 28 salt-scaling cycles for normal strength concrete containing fly ash micro filler (30 MPa) [4]. Another method of influencing the pore size distribution in the HPC is to introduce effective micro fillers thus reducing max pore diameter by 600 μm [5]. The water to binder (W/B) ratio is another important factor affecting durability. The salt-scaling can be affected by various W/B ratios and the W/B ratio of 0.38 could lead up to 6 kg/m² scaling after 58 salt-scaling cycles in the 3% NaCl solution with strength of concrete remaining around 70 MPa [6]. The improvement of properties of hardened concrete can be achieved by choosing the adequate HPC mixture composition whilst the curing conditions remain another important factor after the fresh concrete is casted. The curing conditions have a significant impact on cracking of drying concrete that could lead to increased crack development and to permeability of concrete [7]. Most of the research focus on the increased temperature (20-90 °C) curing that usually has an advantage on strength gain for the HPC [8]. The effect of decreased temperature on the HPC properties has not been studied and these factors based on the conventional concrete research are not considered in current curing requirements; thus it may be necessary to develop new curing requirements for the HPC [9].

This research focuses on studying the strength and durability properties of the high performance SCC in relation to selected micro filler and curing conditions. Cenospheres and metakaolin containing waste have been selected as the partial cement substitution and the air curing conditions at medium and low temperature were applied to the SCC 24h after casting, comparing results to the samples cured at standard conditions.

2. Materials and methods

The Portland cement CEM I 42.5 N produced by Cemex Ltd (Latvia) was used, with characteristics of the oxide composition: SiO₂ – 18.8%, Al₂O₃ – 3.9%, Fe₂O₃ – 3.0%, CaO – 63.2%, MgO – 3.2%, K₂O – 1.1%, Na₂O – 0.2%, the mineral composition C₃S – 57.7%, C₂S – 18.2%, C₃A – 6.4%, C₄AF – 9.8%, the free lime 2.0%, Na₂Oekv – 0.9%, and the Blaine fineness of 3787 cm²/g.

Cenospheres (CS) were used (Biotecha Latvia Ltd, Latvia) with chemical composition of SiO₂ – 53.8 wt%, Al₂O₃ – 40.7 wt%, CaO – 1.4 wt%, and Fe₂O₃ – 1.0 wt%, and smaller amounts of MgO, Na₂O, and K₂O (below 1 wt%). Bulk density was 0.39 g/cm³ based on repeated Scott volumeter measurements according to the ISO 3923-2-81 and the particle size <0.125 mm.

Metakaolin containing by-product (MKW) was used from the production plant of the foam glass granules JSC Stikloporas Ltd. (Lithuania) where kaolin clay is used as a substance for anti-agglutination at the final stage of expanded glass granule production. The MKW has been calcined at 850°C during approx. 40-50 minutes production. The X-ray diffraction (XRD) analysis of the MKW has indicated a halo of amorphous metakaolin in 2θ region of 15 to 30°, and also the crystalline quartz, kaolin, and also small illite and microcline peaks were detected. The MKW with fraction <0.355mm has been used.

Three SCC mixture compositions were created (table 1) including the reference (REF) mixture composition of 500 kg/m³ of cement. Cement has been replaced afterwards by 15 wt% of the MKW or the CS that had proven its effectiveness during the previous studies [10]. The water to cement and pozzolan (P) ratio (W/(C+P) was constant at 0.38 in all the mixture compositions. Performance of the SCC was controlled by using the carboxylate-based superplasticizer Vinplast CL10 (Vincents Polyline Ltd.) to maintain the cone flow of the SCC >600 mm.

Three different curing conditions were applied to each mixture composition testing within 28 days after 24h of initial hardening in moulds at an indoor temperature (20±2°C):

i. standard curing in water at 20±2°C (index H2O);
ii. air curing indoors at 20±2°C, RH 60% (index 60RH);
iii. low temperature (2±2°C) air curing at RH 60% (index 2C).

A mixing procedure was performed in a planetary drum mixer and consisted of the following stages: all dry components were mixed together for 120 s to obtain homogenous mixture of dry
components. Afterwards half of the calculated amount of water was added and the mixing continued for another 120 s. The remaining water with superplasticizer was added and mixing continued for additional 120 s.

Finally, density of the fresh concrete was measured according to the LVS EN 12350-6 and workability performance of the SCC was tested according to the LVS EN 12350-8. The samples were cast in moulds of 100x100x100 mm and 40x40x160 mm. The compressive strength was determined according to the LVS EN 12390-3. The water absorption and open porosity were tested by immersing measured prismatic SCC specimens in water for 72h. The specimens were weighed and then dried at 80°C in an oven to a constant weight for the calculation of water absorption and open porosity.

Durability of chloride penetration was performed according to the NT BUILD 492. Three specimens of Ø100 mm and 50 mm height were created and tested. The freeze-thaw resistance of the SCC was performed according to the CDF to test the capillary suction of de-icing solution and freeze (RILEM TC 117-FDC). Six specimens of each series were tested. 3% NaCl solution was used as the deicing solution.

Table 1. Mixture composition of high strength self-compacting concrete.

| Component                              | Mixture design, kg/m³ |
|----------------------------------------|-----------------------|
|                                        | REF       | MKW       | CS        |
| Cement Cemex CEM I 42.5N               | 500       | 425       | 425       |
| Sand 0.3/4mm                           | 700       | 700       | 700       |
| Fine Sand <0.3mm                       | 118       | 118       | 118       |
| Gravel 4/12 mm                         | 908       | 908       | 908       |
| Water                                  | 190       | 190       | 190       |
| Carboxylate-based superplasticizer     | 4.0       | 5.0       | 7.0       |
| Metakaolin containing by-product       | -         | 75        | -         |
| Cenospheres                            | -         | -         | 75        |
| W/C                                    | 0.38      | 0.40      | 0.42      |
| W/(C+DS)                               | 0.38      | 0.38      | 0.38      |

3. Results and discussion

Results of the fresh SCC properties are given in table 2. Density of fresh concrete was decreased as the MKW partially replaced the cement from 2414 kg/m³ for the REF to 2375 kg/m³ for the MKW. Low density of the bulk CS reduced density of the SCC to 2237 kg/m³. Incorporation of the MKW associated with high surface area in the SCC structure has increased demand for the superplasticizer from 4.0 to 5.0 kg/m³ to maintain the cone flow >600mm, while increasing the time of the cone flow from 25 to 34 s. The CS mixture composition has significantly decreased cone flow. Increase of the superplasticizer was up to 7.0 kg/m³ to obtain the SCC with cone flow >600 mm while the flow time has been increased to 62 s. The porous cenospheres that in addition to decreased density were tented to attract water from cement paste have reduced the SCC performance that was compensated by additional amount of superplasticizer.

Table 2. Properties of fresh self-compacting concrete.

| Mixture design | Fresh concrete density, kg/m³ | Cone flow diameter, [mm] |Flow time, [s] |
|----------------|-------------------------------|--------------------------|---------------|
| REF            | 2414±5                        | 640±20                   | 25            |
| MKW            | 2375±9                        | 645±25                   | 34            |
| CS             | 2237±8                        | 685±15                   | 62            |

In table 3 are presented physical properties of the hardened SCC impacted by the curing conditions during first 28 days. Density has been slightly affected by curing conditions and remained in range of
2302 to 2314 kg/m$^3$ for the REF, of 2271 to 2301 kg/m$^3$ for the MKW and of 2123 to 2135 kg/m$^3$ for the CS. The lowest level of open porosity was in the MKW mixture composition and the highest level was detected in the CS because of the porous nature of the filler. The open porosity was reduced from 11.4 vol% for the REF_H2O and the REF_60RH to 10.6 vol% for the REF_2C. The same result was obtained for the CS mixture composition – the open porosity was reduced 11.9-12.1 vol% to 11.3 vol% for the CS_2C. The impact of curing conditions on the MKW composition was minimal in regard to the open porosity results within range of 10.3 to 10.7 vol%. The same tendencies resulting from the open porosity have been detected in water absorption. The lowest level of water absorption was observed in the MKW composition (4.5-4.7 wt%), in the REF of 4.6 to 5.0 wt% and in the CS – of 5.3 to 5.7 wt%.

Table 3. Physical properties of hardened SCC.

| Composition   | Density, kg/m$^3$ | Water absorption, W$_w$,% | Open porosity, W$_v$,% |
|---------------|-------------------|---------------------------|------------------------|
| REF_H2O       | 2314±14           | 4.9±0.3                   | 11.4±0.7               |
| REF_60RH      | 2302±13           | 5.0±0.3                   | 11.4±0.6               |
| REF_2C        | 2323±20           | 4.6±0.3                   | 10.6±0.5               |
| MKW_H2O       | 2301±22           | 4.7±0.4                   | 10.7±0.9               |
| MKW_60RH      | 2294±21           | 4.5±0.4                   | 10.3±0.7               |
| MKW_2C        | 2271±12           | 4.7±0.1                   | 10.6±0.3               |
| CS_H2O        | 2123±20           | 5.6±0.4                   | 11.9±0.8               |
| CS_60RH       | 2126±13           | 5.7±0.3                   | 12.1±0.5               |
| CS_2C         | 2135±13           | 5.3±0.3                   | 11.3±0.6               |

Development of compressive strength in the SCC is affected significantly by the curing conditions (figure 1). While compressive strength at early stage has been higher for the samples cured in indoor conditions, the increase of compressive strength has been higher for samples cured in standard conditions within 28 days or a longer term (180 days). At stage of 14 days the standard cured samples provided 66 MPa for the REF_H2O, 69 MPa for the MKW_H2O and 48 MPa for the CS_H2O. Samples cured in indoor conditions demonstrated an increase in strength to 70 MPa for the REF_60RH, to 72 MPa for the MKW_60RH and to 45 MPa for the CS_60RH. The low temperature curing conditions provided similar results as the standard curing conditions, except for the mixture CS_2C with strength decrease to 41 MPa. Increase of early strength for the indoor and low temperature cured samples could be explained by low water saturation after curing at standard conditions resulting in higher compressive strength in concrete compared to water saturated samples.

At stage of 28 days the highest strength level was demonstrated by the REF samples cured at standard conditions: the REF_H2O of strength of 72 MPa. Meanwhile strength increase stopped and remained at 70 MPa (the REF_60RH) and 68 MPa (the REF_2C) for the samples cured in indoor and low temperature air conditions. The MKW samples cured at standard conditions demonstrated compressive strength of 73 MPa meanwhile the samples cured in indoor and low temperature conditions still provided strength gain to 78 MPa (the MKW_60RH) and 77 MPa (the MKW_2C). The CS_H2O mixture had strength of 51 MPa in term of 28 days, meanwhile the strength gain was stopped for the samples cured at indoor and low temperature conditions (47 and 46 MPa respectively).

Long term strength gain was the highest for the standard cured samples. At stage of 180 days compressive strength increased to 85 MPa for the REF_H2O and to 87 MPa for the MKW_H2O. No strength gain was detected for the samples cured in indoor and low temperature conditions reaching to 70 and 72 MPa for the REF_60RH and the REF_2C. There was no strength gain for the MKW_60RH at 78 MPa, meanwhile the curing at low temperature provided strength gain similar to that of the
standard conditions – 87 MPa. The CS_H2O reached the highest long term strength gain at 68 MPa which may be the indication of latent CS activity in the SCC proving to be effective only in long term curing.

![Figure 1. Compressive strength results of the SCC in different curing conditions.](image)

Durability results were affected both by curing conditions and micro filler used in the SCC (table 4). The freeze-thaw durability regarding surface scaling in the REF sample was significantly affected by curing conditions. After 52 freeze-thaw cycles the surface scaling for the REF_H2O was 3.3 kg/m² meanwhile the REF_60RH samples were partially collapsed after 44 cycles (scaling of 32.4 kg/m²). Curing at low temperature has increased resistance to freeze-thaw durability and surface scaling was only 0.4 kg/m² after 52 cycles. Since results of porosity and strength have been similar in the REF the high surface scaling can be taken into consideration in developments of pore size distribution during curing which should be studied in the following researches. Lower freeze-thaw scaling in standard curing conditions was detected both for the MKW_H2O and the CS_H2O (1.9 and 1.5 kg/m² respectively). For the samples cured in indoor temperature conditions the surface scaling decreased in the REF_60RH to 0.8 kg/m² after 52 freeze-thaw cycles and in the CS_60RH to 0.3 kg/m² after 44 cycles. Meanwhile during next 8 cycles the surface mass loss increased to 2.6 kg/m². Curing in low temperatures provided similar results and surface scaling decreased to 0.4 for the MKW_2C after 52 cycles whilst in the CS_2C it was 0.3 kg/m² and had increased to 1.6 kg/m² after 52 cycles.

The SCC resistance to chloride ingress in the structure was affected significantly by curing conditions (table 4). The non-steady-state migration coefficient $D_{nssm}$ increased in all cases of application of nonstandard curing conditions. The $D_{nssm}$ for the REF_H2O was $10.9 \times 10^{-12}$ m²/s and increased to $14.3-14.6 \times 10^{-12}$ m²/s for the REF_60RH and the REF_2C. $D_{nssm}$ was significantly reduced when the MKW was introduced in the SCC mixture and has been $1.9 \times 10^{-12}$ m²/s for the MKW_H2O, increased to $4.5 \times 10^{-12}$ m²/s in the MKW_60RH and $3.0 \times 10^{-12}$ m²/s in the MKW_2C. The $D_{nssm}$ has decreased also for the CS_H2O to $8.4 \times 10^{-12}$ m²/s which indicate improvement of the concrete structure despite the increased porosity. Meanwhile, resistance to chloride ingress reduced by drying condition and lead to increase to $14.6 \times 10^{-12}$ m²/s for the CS_60RH and to $16.5 \times 10^{-12}$ m²/s for the CS_2C.
Table 4. Freeze-thaw damage surface scaling and chloride penetration (non-steady-state migration coefficient) test results of SCC.

| Mixture composition | Surface scaling, kg/m² | D_{ssm} \times 10^{-12} m²/s |
|---------------------|------------------------|-----------------------------|
|                     | 44 cycles | 52 cycles |                      |
| REF_H2O             | 3.1       | 3.3       | 10.9±1.0              |
| MKW_H2O             | 1.2       | 1.9       | 1.9±0.3               |
| CS_H2O              | 1.0       | 1.5       | 8.4±0.2               |
| REF_60RH            | 32.4      | 65.0      | 14.3±0.8              |
| MKW_60RH            | 0.4       | 0.7       | 4.5±0.5               |
| CS_60RH             | 0.3       | 2.6       | 18.7±1.1              |
| REF_2C              | 0.2       | 0.4       | 14.6±1.2              |
| MKW_2C              | 0.2       | 0.3       | 3.0±0.2               |
| CS_2C               | 0.3       | 1.6       | 16.5±1.1              |

4. Conclusions
The initial time of standard condition curing of 24h after the casting determined initial strength gain for the SCC. The following indoor or low temperature drying conditions ensured strength increase up to 28 days without any significant strength loss for mixture composition with 100% cement and one with 85% cement and 15% metakaolin containing waste. Even higher strength level in curing at low temperature was detected for the samples with metakaolin compared to the standard curing conditions. Indoor or low temperature curing conditions have been crucial for long term strength gain. Hardening of the air cured sample stopped after 28 days and strength did not increase. In the standard curing conditions strength increased 18-19% in the reference samples and the samples with the metakaolin containing waste. Meanwhile for the samples with cenospheres the strength gain was up to 42% compared to the 28 day strength but the 28 day strength was just 67% that of reference due to high porosity characteristic of cenospheres.

Role of micro filler and curing conditions on durability of the SCC has been significant. Indoor and low temperature conditions have reduced resistance to freeze-thaw damage in the reference samples while durability has increased in other mixture compositions. To better understand effect of micro filler and curing conditions on the freeze-thaw durability, pore size development of the SCC should be tested and researched. Incorporation of the MKW has proven to be advantageous for the SCC in relation to durability both of freeze-thaw resistance and resistance to chloride penetration. Meanwhile cenospheres have improved freeze-thaw durability however they have reduced resistance to chloride ingress in the SCC structure.

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References
[1] Aïtcin P C 2011 High Performance Concrete
[2] Rudžionis Ž, Ivanauskas E and Senkus M 2005 The Analysis of Secondary Raw Materials Usage in Self-Compacting Concrete Production 11 272–277
[3] Zhang X and Han J 2000 The effect of ultra-fine admixture on the rheological property of cement paste Cem. Concr. Res. 30 827–830
[4] Van Den Heede P, Furniere J, and De Belie N 2013 Influence of air entraining agents on deicing salt scaling resistance and transport properties of high-volume fly ash concrete *Cem. Concr. Compos.* **37** 293–303

[5] Vaitkevičius V, Šerelis E, Vaičiukyniene D, Raudonis V and Rudzionis Z 2016 Advanced mechanical properties and frost damage resistance of ultra-high performance fibre reinforced concrete *Constr. Build. Mater.* **126** 26–31

[6] Nowak-Michta A 2013 Water-binder ratio influence on de-icing salt scaling of fly ash concretes *Procedia Engineering* **57** 823–829

[7] Inokuchi K and Iyoda T Effect of Curing Conditions and Exposure Conditions on drying shrinkage of concrete 2–4

[8] Park J S, Kim Y J, Cho J R and Jeon S J 2015 Early-age strength of ultra-high performance concrete in various curing conditions *Materials (Basel)* **8** 5537–5553

[9] Meeks K W and Carino N J 1999 Curing of high-performance concrete: report of the state-of-the-art *Nistir* 6295 1–191

[10] Bumanis G, Bajare D, and Korjakins A 2016 Durability of High Strength Self Compacting Concrete with Metakaolin Containing Waste *Key Eng. Mater.* **674** 65–70