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CHLORIDE PENETRATION COEFFICIENT AND FREEZE-THAW DURABILITY OF WASTE METAKAOLIN CONTAINING HIGH STRENGTH SELF-COMPACTING CONCRETE

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Abstract

Traditional ordinary concrete testing methods are still applied to characterize self-compacting concrete (SCC). This allows comparing properties of two types of concrete, however, the efficiency of such testing methods is still under question due to superior properties of SCC. In the present research high strength SCC using metakaolin containing waste as partial cement replacement was created and its durability characterized. Constant amount of water was used in all mixtures and workability (>600 mm by cone flow) was ensured by changing the amount of superplasticizer. The compressive strength was tested at the age of 7, 28 and 180 days. The chloride penetration was tested according to NT BUILD 492 and freeze-thaw test was performed according to LVS 156-1:2009 annex C respectively. The compressive strength of SCC at the age of 28 days was from 68-70 MPa. The results indicate that the chloride penetration test method NT BUILD 492 is a fast and progressive test method which could effectively characterize SCC, while freeze-thaw resistance test of SCC could take up to 6 months to reach 150 freeze-thaw cycles using 5% NaCl solution as de-icing solution for concrete specimens and more rapid and reliable testing method should be used instead.

1. Introduction

Chloride penetration coefficient and freeze-thaw resistance of concrete could affect service life of concrete structures which are exposed to marine environment as well as in road infrastructure, where salty water is present and together with freezing and thawing could cause significant deterioration of the concrete [1]. Industries working under such conditions are continuously demanding improved construction durability in these conditions. Well known ordinary concrete (OC) has proved that durability of such concrete provides an average performance; therefore new concrete types and production methods are introduced [2]. Chicker et. al. indicated that W/C and silica fume content are the main parameters affecting the durability results of chloride penetration depth of the ordinary and self-compacting concrete (SCC) and in general SCC mixes presented better durability results compared to OC [3]. This gives significant advantage of using SCC instead of OC not only because of high durability results but also due to the fact that improved workability of SCC reduces construction costs. SCC is associated with high binder and chemical admixture volumetric content; therefore there have been attempts to produce SCC with high volumes of supplementary cementitious materials such as silica fume or metakaolin to make SCC cost-effective and more durable [4]. Ganesh et. al has detected that rapid chloride penetration, water sorptivity and water absorption durability of high strength concrete can be improved by replacing cement with nanosilica by up to 2wt.% [5]. Using metakaolin high performance concrete can be obtained having higher resistance to sulphuric acid comparing to the reference mix [6].

In addition, metakaolin proves to be one of the most effective among available natural pozzolanic materials because metakaolin reactivity is 1050 mg $Ca(OH)_2$/g pozzolan compared to 427 g of silica fume and 875 g of fly ash respectively [7]. The incorporation of metakaolin in concrete mixture usually reduces workability of conventional concrete; however, if it is compared to silica fume additive, metakaolin requires from 25 to 35% less superplasticizers [8]. Ouyang et al. has reported that optimal amount of cement replacement with metakaolin was 15% and this could lead to 20% improvement of compressive strength; however, superplasticizers must be used to ensure workability of mortar replacing cement by metakaolin [9].

Metakaolin can be obtained by the endothermic reaction of kaolin as dihydroxylation of kaolin begins at 450 °C and continues up to 900 °C and amorphous metakaolin $Al_2Si_2O_7$ is obtained when exceeding 925 to 950 °C. The metakaolin transforms to spinel $Si_3Al_4O_{12}$ and mullite at 1050 °C [10]. Not only metakaolin derived from naturally occurring minerals can be successfully used in concrete. An artificial kaolinite can be obtained by utilizing paper sludge coming from paper industry. By burning paper sludge at 700 to 800 °C metakaolin and calcium hydroxide can be produced which exhibit pozzolanic reactivity similar to commercially available metakaolin [11]. Metakaolin can also be derived from coal mining wastes which can contain up to 30% kaolinite and after its treating at high temperatures highly pozzolanic product can be obtained [12]. Radonjanin et al has reported that replacement of ordinary Portland cement with metakaolin by 10 wt.% gives compressive strength increase by 13% at 28 days and 9% at 90 days [13].

Metakaolin greatly affects the pore structure of concrete reducing the permeability and diffusion rates of harmful ions [14]. This factor could increase the durability of concrete. In cement pastes blended with 10 and 20% metakaolin reduced Cl^- concentration in pore solution was detected [15]. The incorporation of metakaolin in concrete mixture composition reduces the expansion of concrete maintained in 5% sodium sulfate solution [16]. The freeze-thaw resistance of cement mortar can be increased more than two times for mortar containing waste paper sludge metakaolin from 10 to 20 wt.% of cement compared to reference sample [17]. Metakaolin also turns out to be an alternative pozzolanic additive in ultra high performance concrete effectively replacing silica fume [18].

There is a wide range of tests for concrete evaluation under freeze-thaw initiated damage. Some of them are used to measure scaling from the concrete surface during rapid freeze-thaw cycles (2 cycles per 24h) but does not give any evaluation of concrete compressive strength change or cracking [19]. Other test methods measures concrete strength change during freeze-thaw cycles by testing sample compressive strength, mass changes or ultrasonic pulse velocity

(LVS 156-1:2009, annex C). Also solutions, where concrete samples during freeze-thaw cycles are stored, could be different, beginning from deionized water and ending up to 5% NaCl solution. The freezing temperature of test methods could be starting from -18 °C and reach -50 °C. These conditions determine number of cycles necessary to obtain concrete freeze-thaw resistance at standard conditions [20].

The chloride penetration of concrete structures could be detected by various testing methods. The most popular among them are: Salt Ponding Test, Bulk Diffusion Test, Rapid Chloride Permeability Test, Electrical Migration Techniques, Rapid Migration Test, Resistivity Techniques, Pressure Penetration Techniques, Indirect Measurement Techniques, Sorptivity and others. The rapid testing method should be used for testing durability of high performance SCC in order to perform test in short term and provide reliable results. If long term testing methods usually applied for OC will be adapted for SCC then the test duration could increase to unacceptably long period of time or give inadequate results.

In the present research durability of the high strength SCC with metakaolin containing waste was tested. Compressive strength, chloride migration coefficient and freeze-thaw durability were obtained.

2. Materials and methods

Self-compacting concrete (SCC) mixture composition was designed from locally available cement, gravel and sand. Cement CEM I 42.5 N produced by Cemex Ltd (Latvia) with Blaine fineness of 3787 cm^2/g was used. Natural washed gravel with fraction 4/12 mm was used as coarse filler and natural sand with fraction 0/4 mm was used as fine filler. Quartz sand with fraction 0/0.3 mm was used as microfiller to improve workability of SCC and avoid segregation of fresh mixture.

In the present research metakaolin containing waste by-product (MKW) from foam glass granule production plant "JSC Stikloporas" Ltd. (Lithuania) with fraction <0.355 mm was studied as pozzolanic material in SCC partially replacing cement. The MKW comes from foam glass granule production process where kaolin clay is used as a substance for anti-agglutination in the final stage of granule production. During production MKW was calcined at 850 °C for about 40-50 minutes. The X-ray diffraction (XRD) analysis of MKW is given in Fig. 1. A halo of amorphous metakaolin was detected in 2θ region from 15 to 30° and quartz (Q) was detected in XRD as impurity present in MKW. Also unreacted kaolin (K) was detected in the structure of MKW and small illite (I) and microcline (M) peaks were detected.

SCC mixture series were created with different amount of MKW as partial cement replacement, and mixture compositions are given in Table 1. Reference (Ref) mixture composition with cement content 500 kg/m^3 was created. Then cement was replaced from 5 to 15 wt.% with MKW (5%MKW, 10%MKW and 15%MKW). The water to cement and pozzolan (MKW) ratio (W/(C+P) was constant for all mixture compositions being 0.38. The workability of SCC remained constant by changing the amount of superplasticizer and SCC with cone flow remained >600 mm by adding additional amount of superplasticizer.

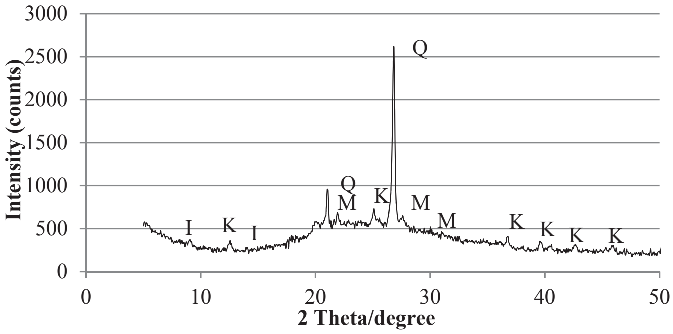

Figure 1. XRD pattern of metakaolin containing waste by-product (MKW). M – microcline, I – illite, K – kaolin, Q – quartz.

Table 1. Mixture composition of self-compacting concrete.

Compound	Amount (kg/m^3)			
	REF	5%MKW	10%MKW	15%MKW
Cement CEM I 42.5 N (Cemex)	500	475	450	425
Sand 0/4 mm	700	700	700	700
Quartz sand 0/0.3 mm	118	118	118	118
Gravel 4/12mm	908	908	908	908
Water	190	190	190	190
Superplasticizer Sikament 56	4.0	4.0	4.6	4.8
Metakaolin containing waste	0	25	50	75
W/C	0.38	0.40	0.42	0.45
W/(C+P)	0.38	0.38	0.38	0.38

The mixing procedure of SCC was carried out in a planetary drum mixer and included the following stages: all dry components were mixed together for 120 s to obtain homogenous mixture of dry components. Then half of the calculated amount water was added and mixing was continued for another 120 s. Then rest of water with superplasticizer was added and mixing was continued for additional120 s. Then density of fresh concrete was measured according to LVS EN 12350-6 and workability of SCC was tested according to LVS EN 12350-8. Samples were casted in 100x100x100 mm and 40x40x160 mm moulds for further investigations. Compressive strength was determined according to LVS EN 12390-3. Three specimens at every age were tested and average value with deviation calculated. Water absorption was tested by immersing the prismatic SCC specimens in water for 72h. The specimens were weighed and then dried in an oven at 80 °C to a constant weight for the following measurement of water absorption.
Durability of the chloride penetration for SCC was performed according to NT BUILD 492 (Fig. 2). Three specimens with Ø100 mm and height of 50 mm were created and tested.

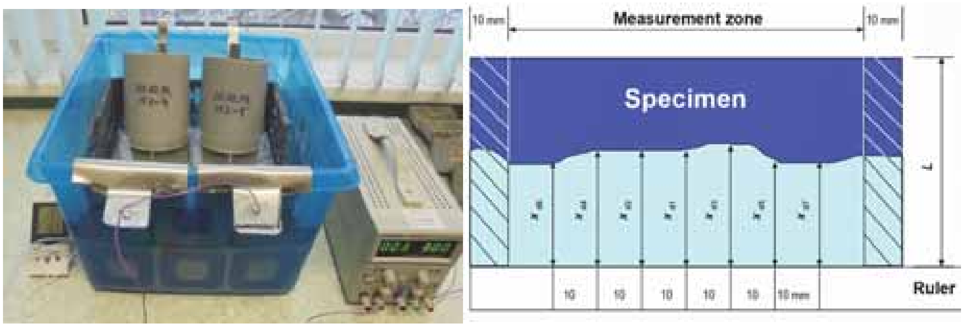

Figure 2. The experimental setup of the test to determine the depth of chloride migration coefficient and the illustration of measurement for chloride penetration depths.

The freeze-thaw test was performed according to Standard LVS 156-1:2009 annex C [20]. Six specimens of each series were tested. 5 % NaCl solution was used as deicing solution. All specimens were tested after 150 freeze-thaw cycles which is equal to 500 standard freeze-thaw cycles in deionized water. Strength reduction was calculated and the obtained result evaluated according to the Standard [20].

3. Results and Discussion

The properties of fresh SCC containing different amount of MKW as partial cement replacement are given in Table 2. The decrease of fresh SCC density was observed: from 2428 kg/m^3 for Ref to 2394 kg/m^3 for mixture composition with 15% of MKW as partial cement replacement (15%MKW). The partial cement substitution with MKW reduced workability to the level corresponding to data available in literature sources; therefore additional amount of superplasticizer should be used to retain the workability properties of SCC (see Table 1). Up to 20% more superplasticizer must be used to ensure workability >600 mm for SCC with 15% MKW as partial cement replacement. The flow time of fresh SCC increased from 25 to 34 seconds.

Table 2. Fresh self-compacting concrete properties.

Mixture design	Fresh concrete density, (kg/m^3)	Flow time, (s)	Cone flow diameter, (mm)
Ref	2430	25	630
5%MKW	2410	25	600
10%MKW	2400	23	680
15%MKW	2390	34	670

The compressive strength results of SCC are given in Fig. 3. The results indicate that SCC strength at 7 days was 56 MPa for Ref mixture and remained the same for 5% MKW and 10%

MKW (56 and 57 MPa) and reduced to 53 MPa for 15% MKW. The improvement of SCC particle packing provided by MKW and superplasticizer could retain the same strength at early age even replacing cement up to 10%, while the early age strength reduction is associated with slow rate of pozzolanic reactions and reduced amount of initial content of cement which lead to reduced compressive strength. At the age of 28 days compressive strength for Ref was 68 MPa while for mixture composition 15% MKW it increased to 70 MPa and for 5% MKW and 10% MKW it was 63 and 66 MPa respectively. Strength increase for SCC with MKW could be referred to the pozzolanic reactions. The increased amount of MKW provided higher compressive strength for SCC at the age of 28 days. The long term curing (180 days) lead to further strength increase. For Ref it was 79 MPa while for SCC with MKW it was from 71 to 74 MPa. The limitation of further strength increase was detected for SCC with MKW. This could be contributed to the reduced amount of cement in mixture composition and the pozzolanic reaction could be limited due to rapid strength increase at the age of 28 days.

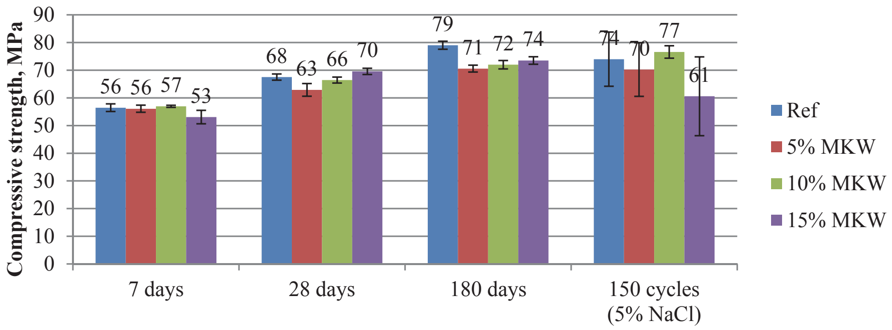

Figure 3. Compressive strength of self-compacting concrete with metakaolin containing waste as partial cement replacement at different ages and after 150 freeze-thaw cycles in 5% NaCl.

The durability of SCC was affected by the MKW content in the mixture composition. The freeze-thaw test indicates that 5% NaCl saturated SCC with 10% MKW can withstand up to 150 freeze-thaw cycles without mechanical or physical damage to the specimens. It was indicated that samples saturated with 5% NaCl after 150 freeze-thaw cycles reduced compressive strength for samples Ref, 5%MKW and 15%MKW (Fig. 3). The only series which retained the same strength and even gained strength was 10%MKW. The compressive strength increased to 77 MPa with acceptable standard deviation, while for other samples the strength deviation was not acceptable according to the Standard [20].
The chloride penetration test results are given in Table 3. Non-steady-state migration coefficient (D_{nssm}) indicates that incorporation of MKW in the mixture composition reduced D_{nssm} by 3.7 times compared to Ref. The test results indicate that SCC mixture composition 15%MKW could be evaluated as "very good" ($D_{nssm} < 2\cdot 10^{-12} m^2/s$) regarding to the resistance to chloride ingress while SCC with $D_{nssm} < 8\cdot 10^{-12} m^2/s$ has been evaluated as "good" resistance against chloride ingress [21]. The results for specimens Ref and 15%MKW after chloride penetration test are given in Fig. 4. The water absorption was from 3.3 to 3.5 wt.%

and open porosity from 7.6 to 8.2% and both slightly decreased by replacing cement with MKW, which could reduce the permeability of SCC and increase the durability.

Table 3. Chloride penetration test results of SCC (non-steady-state migration coefficient).

Mixture design	D_{nssm} [$10^{-12}m^2/s$]	Standard deviation
Ref	7.70	0.37
5%MKW	5.41	0.11
10%MKW	3.63	0.12
15%MKW	2.08	0.03

a) b)

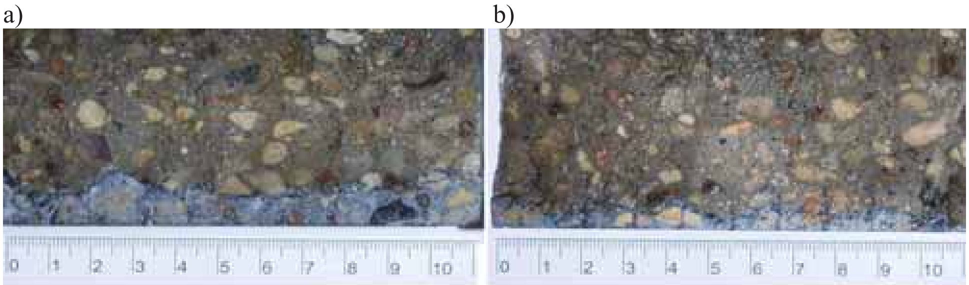

Figure 4. The depth of chloride migration according to NT BUILT 492 in reference (a) and SCC containing 15% metakaolin containing waste as partial cement replacement (b).

4. Conclusions

The reduction of workability should be taken into account if metakaolin containing waste products (MKW) are incorporated in self-compacting concrete (SCC) as partial cement replacement. By replacing cement with MKW from 5 to 15 wt.%, the amount of superplasticizer must be increased from 15 to 20% to ensure the proper mix flow. The strength index of SCC with MKW at the age of 28 days was from 93 to 103% compared to reference SCC (63 to 70 MPa). The durability against chloride penetration was increased more than 3.7 times which was detected by calculating non-steady-state migration coefficient (D_{nssm}7.70 $10^{-12}m^2/s$ for reference mix reduced to 2.08 for mixture with 15% MKW as partial cement replacement). Therefore NT BUILD 492 test method proved to be effective for testing and evaluating SCC chloride penetration durability. The freeze-thaw test results indicated that SCC durability up to 500 freeze-thaw cycles could be obtained by incorporating 10% of MKW as partial cement replacement. Using 5% NaCl solution as deicing fluid, according to Standard LVS 156:2009 annex C, the required number of freeze-thaw cycles could be reduced to 150 cycles which still takes a long period of time for performing this test due to capacity of 1 cycle per 24 h.

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