The Metakaolin Waste Effect on the Physical and Mechanical Properties of High-Performance Concrete

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Abstract. This paper discusses the structure and properties of high-performance concrete (HPC) analysed by scanning electron microscopy, X-ray diffraction analysis, exothermic temperature, density, bending, and compressive strength. A certain amount of cement (5%, 10%, 20%) was replaced in the concrete mixes with metakaolin waste generated in the expanded glass manufacturing. This metakaolin waste consists of a high amount of $SiO_2 + Al_2O_3$ – 92.2% and has significant pozzolanic activity according to the Chapelle test – 1148mg/g. The results presented in the paper show that metakaolin waste is an active additive that accelerates the setting of HPC and makes its structure denser. HPC with up to 10% of cement CEM I 52,5 R substituted with metakaolin has approximately 28 day flexural and compressive strengths similar to control samples – 15 MPa and 135 MPa, respectively. The article also presents test results showing that metakaolin waste reduces the maximum temperature of the exothermic reaction in concrete and does not cause the formation of new compounds. Standard concrete minerals: portlandite, calcite, quartz, and alite were identified.

Keywords: High-performance concrete · Hydration · Metakaolin waste · Physical and mechanical properties

1 Introduction

Metakaolin (MK) is obtained from kaolinite heated at approx. 700 °C temperature and maintained at this temperature for 2–6 h. The appropriate amount of this additive can positively affect the properties of ordinary concrete [1–4]. Thermal treatment at 850 °C for 3 h is required to enhance the properties of MK with high alumina content [5]. The positive effect of MK on the properties of concrete and mortars depends on the type of this additive. High-quality MK containing more than 90% of $Al_2O_3{\cdot}SiO_2$ can substitute cement or SiO_2 fume to manufacture high-performance concrete (HPC).

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Researchers investigated the impact of metakaolin (93% Al_2O_3-SiO_2) on the properties of cement mortar where 0%–50% of cement was replaced with MK and found that the replacement of up to 20% of cement with MK increased compressive strength, density, and ultrasonic pulse velocity in the cement mortar samples [8–10]. The best results were obtained in the samples where 10% of cement was replaced with MK. These results can be explained by MK's accelerated cement hydration and reaction with $Ca(OH)_2$ (CH). It was suggested [11, 12] to increase the MK content in cementitious mixtures from 10% to 15% as higher strength, durability and chemical resistance of cementitious samples were observed in the tests. However, other researchers [4] argue that the 90-day compressive strength of the samples containing up to 20% of MK (89% $Al_2O_3 \cdot SiO_2$) used as the cement substitute was equivalent to those without MK.

Souri et al. [6] conducted comparative studies with different types of metakaolin (with kaolinite content varying at 56%, 88% and 98%). The calorimetric analysis showed that low-grade metakaolin did not affect the heat and rate of hydration. The commercial metakaolin containing 98% kaolinite caused a higher initial heat release and hydration rate, but the total heat released was practically the same. The early compressive strength values (at 1, 3, and 7 days) with all types of metakaolin additive were lower regarding the control sample. Still, the compressive strength increased at 28 days of curing and later. The highest 28-day strength (approx. 54 MPa) was obtained in the samples modified with MK of the highest grade. In contrast, the lower grade MK slightly reduced the sample strength to 49–52 MPa. The reaction of metakaolin with portlandite caused significant changes in the structure of hardened cement paste. The CSH gel absorbs a high amount of Al and a low amount of Ca, leading to the formation of CASH characterised by a low Ca/(Al + Si) ratio but a high Al/Ca ratio [13]. It was found [13] that high-grade MK accelerates cement setting but impairs the paste's workability. Therefore, it is advisable to use special polymer admixtures (styrene butadiene rubber latex, polyvinyl acetate emulsion and their mixtures) in cement mixes.

The analysis of the effect of low-grade MK (31–36%) on cement hydration showed [14] that MK used as a substitute for cement (at 10%, 20%, 40%) delayed cement setting time and slowed down cement hydration, i.e. the higher was MK content, the slower was cement hydration. From an economic and environmental viewpoint, using metakaolin waste (MKW) from the production of expanded glass rather than manufactured metakaolin is preferable. Such metakaolin was used in lightweight concrete with polystyrene and expanded glass aggregates [15, 16]. It was found that MKW was sufficiently active, reacted with CH intensively and promoted CSH formation. However, other authors [17] found that metakaolin waste can retard cement hydration, depending on the composition of the MKW and the composition of the mix where MKW is used. Several pozzolanic additives used together can increase the beneficial effect of the additives [18]. A mixed additive consisting of pure metakaolin and SiO_2 fume helps to control cement hydration [19] as MK accelerates and SiO_2 retards cement hydration. A mixed pozzolanic addition ensures the control of cement hydration time.

The research work described below was conducted to determine the effect of metakaolin waste and milled quartz sand (MQ) on the structure and physical and mechanical properties of HPC.

2 Materials and Methods

Aalborg white cement CEM-I 52.5 R (Denmark) was the primary binding material. Chemical compositions of cement, milled silica sand (MQ) (Anykščių kvarcas, Lithuania), and metakaolin waste (Stikloporas, Lithuania) are given in Table 1. The chemical analysis of the raw materials was done with an X-ray fluorescence spectrometer (XRF) Rigaku ZSX Primus IV using the wavelength dispersion method. The generator used 60 kV voltage and 150 mA current. Rh X-ray diffraction tube anode and 4 kW X-ray tube power were used. Powdered samples were formulated into small Ø40 × 3 mm cylinders. The cylinders were compressed with a hydraulic press Herzog TP20 (200 kN), holding the load for 5 min. The sample scanning diameter of 30 mm was used. The samples were tested under vacuum (~6 Pa) at 36.5 °C.

Table 1. Chemical composition of cement and pozzolanic additives.

Materials	SiO_2	CaO	Al_2O_3	Fe_2O_3	Na_2O	MgO	SO_3	$K O_2$	TiO_2	P_2O_5
Cement	22.8	70.4	2.18	0.29	0.07	0.65	2.67	0.20	0.06	0.28
MQ	99.2	0.07	0.57	0.05	0.03	0.02	0.02	0.02	0.05	-
MKW	52.4	1.27	39.8	1.03	3.39	0.37	0.08	0.93	0.54	0.12

Metakaolin waste (Table 1) has a relatively high content of $SiO_2 + Al_2O_3$ (92.2%). Such metakaolin is highly reactive and should accelerate cement hydration. Thus, the average particle size of MKW was as follows: 20.4 µm; d_{10}—2.6 µm; d_{50}—16.8 µm; d_{90}—44.5 µm.

The milled quartz sand used contained only 0.8% of impurities and was clean, judging by the chemical composition (Table 1). Therefore, the average particle size of milled quartz was as follows: 8.5µm; d_{10}—0.7 µm; d_{50}—5.8µm; d_{90}—20.5µm.

The 0/1 mm fraction quartz sand (QS) (Anykščių kvarcas, Lithuania) was used as fine aggregate in HPC.A superplasticiser (SP) Sika D190 (Sika Baltic SIA, Latvia) with a density of 1.08 g/cm^3 and pH 4.5 was used. To reduce the porosity of concrete, air-detraining admixture (AR), Vinapor DF 2941 F (BASF), was used. In addition, the same amount of steel micro-fibres with a 12 mm length and 0.8 mm diameter were added to the concrete. As a result, a constant W/(C + MKW) ratio of 0.3 was maintained in all HPC mixes. The compositions of concrete mixtures are presented in Table 2.

Table 2. Compositions of HPC, kg/m^3.

Denomination	CEM I 52 R	MQ	MKW	QS	Fibre	SP, kg	AR
G0	1000	400	0	900	30	15	2.3
GM5	950	400	50	900	30	15	2.3
GM10	900	400	100	900	30	15	2.3
GM20	800	400	200	900	30	15	2.3

The HPC sample preparation procedure: 1) Dry raw materials (cement, MQ, MKW, QS, AR) were mixed in a Hobart mixer for 2 min. 2) Water mixed with SP was added to the mixture and mixed for 7 min. 3) Metal microfibres were added, and the mixing continued for 3 more minutes.

After the mixing, 160 × 40 × 40 mm size samples were moulded. After 24 h, the samples were demoulded and kept in water at 20 ± 2 °C until the testing time (7 or 28 days).

To determine the hydration temperature (exothermic reaction temperature), the ready-mixed concrete (300 g) was poured into plastic moulds with a thermocouple inserted in the centre of each moulded sample to record the temperature rise. The moulds with the mixture were then placed in a container insulated with polystyrene foam (thickness 50 mm, thermal conductivity 0.043 W/[m·K]). The experiments were conducted at the ambient temperature of 20 ± 1 °C, continuously recording the heat release until it significantly reduced, but not longer than 48 h.

The density of the samples in the solid state was calculated from the sample's weight (0,01 g precision) and volume determined by the sample's dimensions (0.01 g precision). Three samples of each composition were tested for density and flexural strength, and six elements were tested for compressive strength.

The flexural and compressive strength values were obtained using a hydraulic press Tinius Olsen H200 KU according to the procedure laid down in the European Standard EN 196-1.

The mineral composition and microstructure of the samples were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM) after 28 days of curing. The hydration of the samples was terminated by soaking them in acetone for 72 h and then drying at 60 °C for 48 h. Scanning electron microscopy (SEM) analysis in the secondary electron mode was carried out using the JEOL JSM-7600F device. The images were obtained from the fracture surfaces of the gold-plated solidified samples. The following SEM analysis parameters were used: 10 kV voltage, 7-10 mm distance to the sample surface. Anatase was used as the internal standard for the samples prepared for XRD quantitative analysis at a ratio of 9:1 (binder/anatase). XRD analysis used a diffraction meter DRON-7 with Cu-Kα (λ = 0.154 nm) rays. The following test parameters were used: voltage of 30 kV, current of 12 mA, the diffraction angle range of 2θ from 4° to 60°, the step of 0.02°, and retention time of 0.5 s. The phases were compared to XRD patterns of the standard diffraction models the International Centre of Diffraction Data

(ICDD) provided. The peak heights in the diffraction patterns were converted using the same intensity of the significant anatase peak ($2\theta = 25{,}28°$) for all XRD patterns.

3 Results

The analysis of the impact of MKW on the properties of cementitious binder containing one pozzolanic additive MQ started by measuring the heat of hydration (Fig. 1, Table 3).

The results of the exothermic reaction tests showed that after approximately 6h of exposure to water, the temperature of the concrete mixtures starts to increase rapidly irrespective of the amount of MKW used and reaches 39 °C–47 °C after 13–14 h. Differences in temperature rise in the mixtures were fixed after approximately 6 h and then the control sample without MKW had the highest heat temperature of hydration; however, the temperature decreased with the replacement of cement with MKW. In the samples containing 20% of MKW, the temperature dropped by 7 °C compared to the control sample and reached the maximum temperature 1h earlier. Such behaviour can be attributed to the high pozzolanic activity of MKW (1148 mg/g according to the Chapelle test), which promotes the hydration of the cement mineral alite. Most of the heat and the highest temperature are generated during the hydration reaction of alite, during which CSH and $Ca(OH)_2$ are formed [20–22]. In the samples with a lower cement content, a decrease in the exothermic peak temperature was recorded due to the reduced alite content in the concrete mix. If an inert additive were used, the concrete hydration temperature should decrease proportionately to the additive content. Still, the pozzolanic properties of MKW result in a significantly smaller decrease in temperature and accelerated hydration.

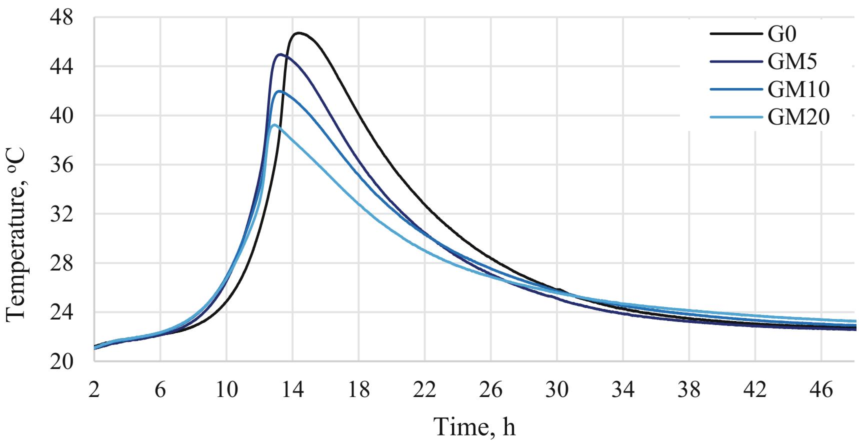

Fig. 1. Impact of MKW on the exothermic temperature of concrete.

Table 3. The maximum exothermic temperature and time to achieve it.

Characteristic	G0	GM5	GM10	GM20
Max temperature	46.7	45	42	39.3
Time, h	14.4	13.3	13.1	12.9

At 7 days, the density of the hardened concrete samples (Fig. 2) with MKW was lower and mainly depended on the amount of MKW additive used. A more significant positive effect of MKW on the density of concrete samples was seen after 28 days of curing. At that point, the samples containing 5% of MKW had the highest density, whereas the sample density when 10% of cement was replaced with MKW was similar to that of the control samples. With the increase of MKW content to 20% in the mix, concrete density decreased as a more compounds with a lower density were formed.

Figures 3 and 4 illustrate the relationship between HPC's flexural and compressive strength and MKW content.

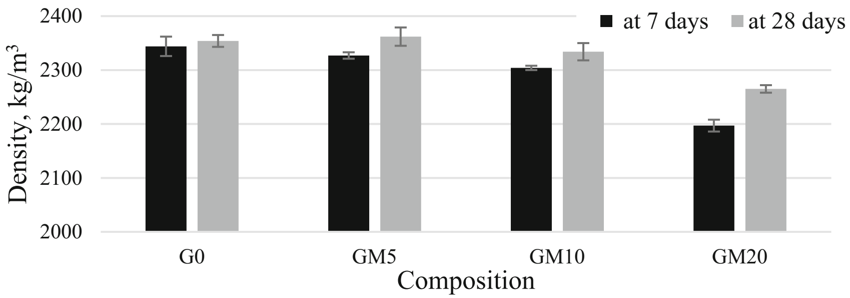

Fig. 2. The impact of MKW content on the density of HPC.

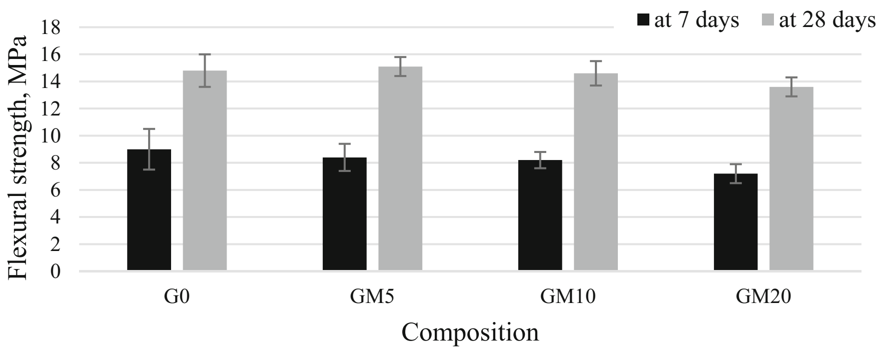

Fig. 3. Flexural strength results.

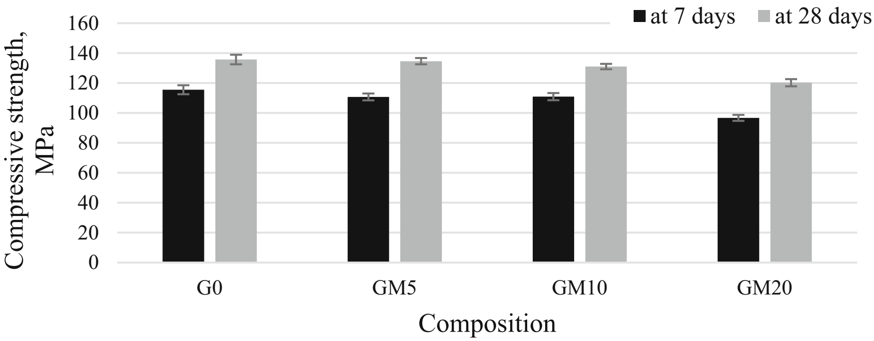

Fig. 4. Compressive strength results.

The flexural and compressive strengths of the samples where 5%–10% of cement was replaced with MKW were similar to the strength of control samples (15 MPa and 135 MPa, respectively (Figs. 3 and 4) event at the lower cement content in the mix. The literature suggests that pozzolans may influence the strength properties of cementitious materials for the following reasons: cement 'dilution effect', physical effect and pozzolanic activity [23, 24]. According to the literature: 1) the 'dilution effect' leads to a decrease in the compressive strength of cement-based materials in direct proportion to the volume of the cement replaced; 2) the physical effect is primarily related to the ability of fine additives to fill the pores, resulting in a denser cement matrix and consequent improvement in mechanical properties; 3) the pozzolanic activity of the additives improves mechanical properties due to the formation of additional strength phases, CSH and CASH [25–28]. In the case considered, MKW had a high physical and pozzolanic effect on HPC's flexural and compressive strength, due to which the dilution effect was minimized and only occurred with higher 20% MKW amount.

The physical effect is best illustrated by analysing the SEM images of characteristic microstructure of samples (Fig. 5), showing that control samples have approximately 100 μm diameter visible pores (Fig. 5a), while the samples with MKW do not demonstrate such pores (Fig. 5b). Presumably, the pores were filled with MKW additive and, during the pozzolanic reaction, MKW promoted the formation of CSH and CASH, which gradually filled the pores. MKW might have enhanced the pozzolanic efficiency of MQ because binary pozzolans generally have a more significant effect on the formation of increased amounts of CSH and CASH [29].

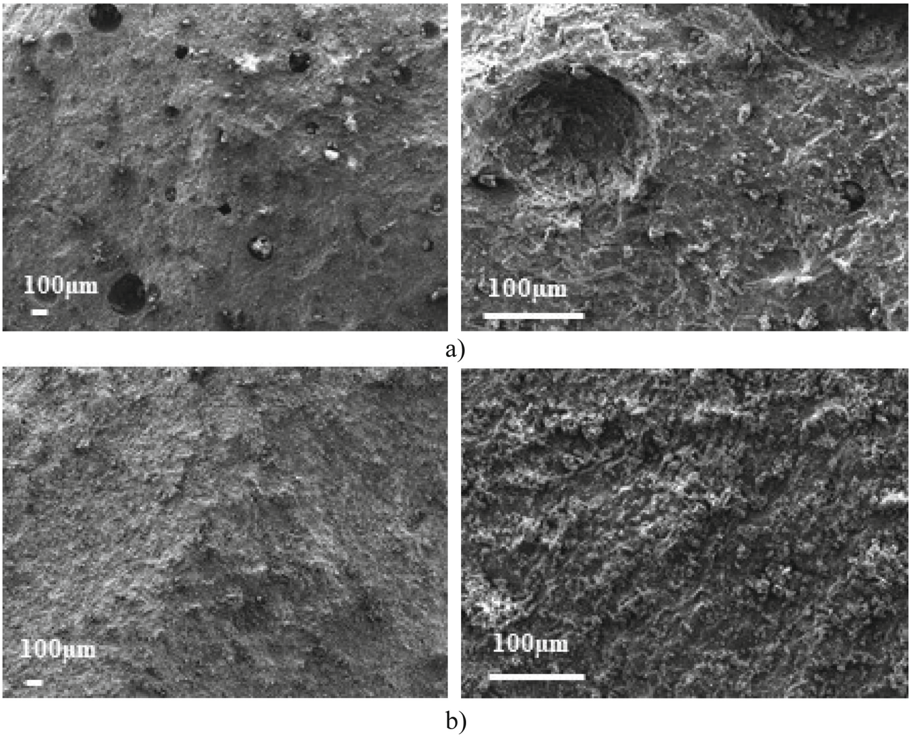

Fig. 5. The SEM images: a) control sample G0; b) G10.

The XRD analysis (Fig. 6) showed that after 28 days of curing, similar minerals were identified in all concrete compositions: portlandite (P), quartz (Q), calcite (C), and alite (S). Anatase (A) was used as a reference material to assess the quantitative change of minerals in concrete samples. Based on peak intensity, lower amounts of portlandite, calcite, and alite were identified in the samples with MKW additive (G5-G20). Therefore, the levels of these minerals could have been reduced only due to the lower cement content in the mix. However, analysis of other properties, particularly microstructure changes, Chapelle test results, etc., suggest that MKW is an active pozzolanic additive that accelerates cement hydration.

A denser concrete microstructure can explain the lower content of calcite and, consequently, the restricted penetration of CO_2 from the ambient air into the sample. Therefore, the carbonisation of portlandite occurs mainly on the surface of the sample.

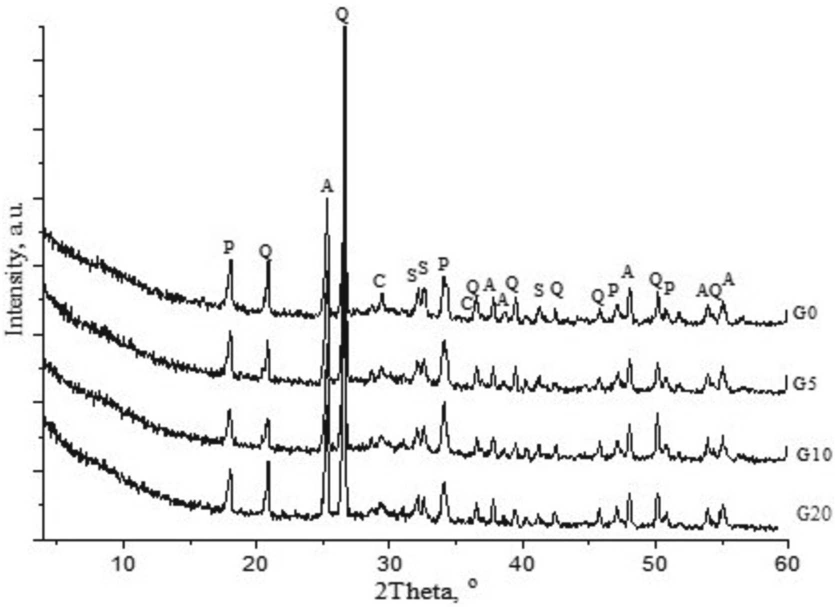

Fig. 6. X-ray diffraction patterns of concrete samples with a different MKW content: portlandite (P), quartz (Q), calcite (C), alite (S), anatase (A).

4 Conclusions

It was found that metakaolin waste (MKW) from expanded glass manufacturing can be used as an additive in high-performance concrete mixes. The pozzolanic activity of this additive and the fineness of the particles make the concrete microstructure denser. The flexural and compressive strengths of modified concrete mixes where up to 10% of CEM I 52,5R cement was replaced with MKW remain similar to those of the control samples: the flexural strength approximately 15 MPa and the compressive strength approximately 135 MPa.

The MKW accelerates cement hydration and reduces the maximum exothermic reaction temperature. The formation of new compounds was not affected by the MKW additive, but the appearance of different amounts of standard concrete minerals (portlandite, calcite) was observed.

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