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Thermal behaviour and characterization of cement composites with burnt kaolin sand

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Abstract The kaolin sand containing 36 wt% of kaolinite was thermally transformed at 650 °C/L h to the burnt kaolin sand (BKS) with relevant content of metakaolinite. Thermal behaviour of composites with substitution of Portland cement (PC) by the BKS containing 0, 5, 10 and 15 wt% of metakaolinite and water-to-solid ratio of 0.5 kept for 90 days in 20 ± 1 °C water was studied by thermal analysis. TG/DTA/DTG studies concerned calciumsilicate hydrate and calciumaluminate hydrate formation, portlandite dehydroxylation and calcite decarbonation. The influence of curing time and metakaolinite content were estimated. The reduction in portlandite content was observed in PC–BKS composites opposite to that found in the reference PC system. Compressive strength uptakes were observed in PC–BKS composites relative to that of reference PC system. BKS is characterized as effective pozzolanic material giving cement composites of high performance. The above findings were confirmed by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) results.

Keywords Burnt kaolin sand · Metakaolinite · Pozzolana · Cement composite · Thermal behaviour

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Introduction

Concrete structures are mostly manufactured with Portland cement. Beside other materials, each tonne of Portland cement requires ~1.5 tons of limestone, a considerable amount of fossil fuels and electrical energy. Thus, the cement industry is highly energy intensive and the emissions of CO_2 during cement manufacturing have created enormous environmental concerns. Globally, cement companies are producing nearly two billion tonnes/year of their product and emitting nearly two billion tonnes of CO_2 (or around 6–7% of planet's total CO_2 emissions) in the process. At this pace, by 2025 the cement industry will be emitting CO_2 at a rate of 3.5 billion tonnes/year [1]. This forms pressures to reduce cement consumption through the use of artificial-made materials, industrial by-products as well as supplementary cementing materials substituting the Portland cement in concrete [2–6].

The most common cementitious materials that are used as constituents in composites with Portland cement (as substitution) are mainly silica fume, fly ash and blast furnace slag [7–9]. The utilization of calcined clay in the form of metakaolin has received considerable interest in recent years and is well documented [10–12]. The metakaolin use in cement industry seems to be intense [13–15].

Metakaolin is a highly active aluminosilicate material which is formed by the dehydroxylation of kaolin ($Al_2(OH)_4Si_2O_5$) precursor upon heating in the ca 650–800 °C temperature range [14, 16, 17]. This process is often well-known as calcination and can be in simplified form expressed as follows:

$$\underset{\text{kaolin}}{Al_2Si_2O_5(OH)_4} \rightarrow \underset{\text{metakaolin}}{Al_2O_3 \cdot 2\,SiO_2} + 2\,H_2O.$$

During heating, it is essential to convert unreactive kaolin to reactive metakaolin. Formed metakaolin contains usually ca 50–55% SiO_2 and 40–45% Al_2O_3 and is naturally highly reactive [18]. The hydration reaction of cement with metakaolin depends on cement kind, substitution rate of cement by metakaolin, water-to-binder ratio as well as the relevant calcination temperature [19, 20].

The prime objective of a couple of presented works is the characterization of the compounds formed when metakaolin reacts with $Ca(OH)_2$ in the process of pozzolanic reaction. The $Ca(OH)_2$ is gradually removed in a similar way than in composites with other pozzolana, e.g., silica fume. However, the pozzolanic reaction increases the content of calciumsilicate hydrates (CSH gel) and calciumaluminate hydrates (CAH gel) in the hydrated matrix. Thermal analysis provides information on processes and phenomena in matrix composition. The main endothermic peaks were observed in the following temperature ranges [16, 21]: 120–145 °C dehydration of CSH; 180–200 °C dehydration of C_2ASH_8 gehlenite; 350–400 °C dehydration of C_3AH_6 hydrogarnet; 490–525 °C dehydroxylation of $Ca(OH)_2$; 720–760 °C decarbonation of $CaCO_3$ and 940–970 °C "precursors" of mullite and cristobalite.

Thus, the incorporation of metakaolin leads to the enhancement of utility properties of cement-based composites and consequently to the expansion in possibilities of their using in practice [22]. It has been reported that the substitution of Portland cement by 5–20% metakaolin results in significant increases in compressive strength for high-performance concretes and mortars up to 28 days [18, 23].

The critical factor affecting the performance of concrete structure is pore structure development—pore size distribution rather than the total porosity. The pore size distribution has been studied in metakaolin—Portland cement pastes [24, 25]. Partial substitution of metakaolin by the weight of cement (5–20%) affects pore size and consequently reduces permeability [26] due to the pore structure refinement [24, 27]. SEM microstructures indicate a good improvement for the matrix structure of the composites where a more dense structure is observed [28]. Since cement-based materials are often subjected to action of aggressive environment [29, 30], it is important the fact that composites with metakaolin exhibit high chemical resistance against sulphate attack and chloride diffusion [22, 28].

Kaolin from natural sources may be notably impure, even after beneficiation [18]. Poor Greek kaolins with a low kaolinite content (often ca 52%) exhibited similar properties than commercial metakaolin with 96% of metakaolinite [31]. The metakaolins derived from poor Greek kaolins when combined with Portland cement to produce blended cements, impart similar behaviour to that of commercial metakaolin especially with respect to cement strength development, setting times and hydration as well as durability [32]. The similar kaolins with relatively poor kaolinite content are in Slovakia denoted as kaolin sands [33–36].

Table 1 Chemical composition, mineralogical composition and physical properties of Portland cement (PC) and burnt kaolin sand (BKS)

Component/ Mass%	PC	BKS	Mineralogical composition of PC/% (Bogue)
Humidity	0.38	0.24	C_3S: 45.37
Loss on Ignition	1.45	1.52	C_2S: 26.22
Insoluble residue	0.83	62.91*	C_3A: 10.43
SiO_2	21.08		C_4AF: 8.70
CaO	61.02	1.02	Physical properties of PC
Al_2O_3	5.76	28.92	Initial setting: 3 h 50 min
Fe_2O_3	2.86	2.37	Setting time: 4 h 55 min
MgO	2.61	0.94	Consistency/%: 29.5
SO_3	2.49	0.03	

*Insoluble residue + SiO_2

The effect of cement substitution by burnt kaolin sand (with 36% of metakaolinite) on hydrated phases, pore structure development and mechanical properties in cement composites was evaluated and relevant results are presented in the paper.

Experimental

Materials

The materials used in this study include CEM I42.5R Portland cement (PC) in accordance with STN EN 197-1 [37] supplied by Holcim Rohožník (Slovakia) and burnt kaolin sand (BKS) prepared by heating raw material—kaolin sand mined at the Vyšný Petrovec deposit (Slovakia) for 1 h at 650 °C. The content of kaolinite (metakaolinite) in kaolin sand (burnt kaolin sand) was 36 wt% according to quantitative X-ray analysis realized by the Rock Jock program [38]. The PC was substituted with BKS including 0, 5, 10 and 15 wt% of metakaolinite for making the cement composites (CC). The CC was prepared with water-to-solids ratio of 0.5. The reference cement paste with 100% PC by weight (without BKS) was also prepared. The properties of the materials determined according to STN EN standards [39–41] are presented in Table 1.

Methods

The CC were cast into the 20 × 20 × 20 mm cubes. The moulds were stored at an atmosphere with 95% relative humidity at 20 ± 1 °C for the first 24 h and then the cubes were kept in water at 20 ± 1 °C until testing. The CC were studied on their 28- and 90-day compressive strengths and characterized by X-ray diffractometry (XRD), thermal analysis (TG/DTA/DTG), mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) techniques.

The X-ray diffraction tests were made on the Philips diffractometer (Eindhoven, The Netherlands) and run in a Θ range of 8°–18°. CuK$_\alpha$ radiation and Ni filter was used. Thermal studies were performed on OD-102 Derivatograph MOM (Budapest, Hungary) in air; the heating range: 20–1,000 °C, heating rate 10 K/min, sample mass 400 mg and TG range 200 mg; the reference material was Al_2O_3. The pore structure was studied using a mercury intrusion porosimetry (MIP) by the high-pressure porosimeter mod. 2000 and macro-porosimeter unit mod. 120 (both Carlo Erba, Milan, Italy). The measured data give volume of micropores up to 7,500 nm, average micropore and pore median radius, total porosity and pore size distribution. Permeability coefficient of the matured CC composites and PC paste were calculated according to computation described in [42]. The calculated permeability coefficient is, however, not fully coincident with the actual and absolute value of permeability coefficient but serves as new pore structure indicator, which can be related to strength developments and bound water contents of the concretes, respectively [43]. The SEM studies were performed on SEM instrument Quanta 3D 200i (FEI Company, Hillsboro, USA). Small pieces of CC were appropriately treated and prepared for scanning electron mode of the microscope.

In order to investigate the effect of BKS, a deeper study of its use in CC with 5, 10 and 15 wt% substitution of PC by metakaolinite was carried out. The CC without BKS was applied as reference cement paste.

Results and discussion

Table 2 Compressive strengths of cement composites with burnt kaolin sand

Composite indication	Compressive strength/MPa	
	28 days	90 days
0MKCC	40.6	44.6
5MKCC	38.6	60.8
10MKCC	45.3	65.2
15MKCC	50.2	54.6

Compressive strengths of the metakaolinite cement composites (MKCC) prepared at different substitution levels of PC by BKS cured in 20 ± 1 °C water are listed in Table 2. The highest 28-day strength enhancement opposite to the reference cement paste occurs in specimens with 15 wt% substitution of PC by metakaolinite in MKCC. By increasing curing time to 90 days, the maximum compressive strength belongs to the composite with 10 wt% substitution of PC by metakaolinite in MKCC. These results indicate that at shorter curing time of 28 days, the highest portion of $Ca(OH)_2$ can be released from hydration products that could be consumed by BKS in MKCC with 15 wt% substitution of PC by metakaolinite. This results in the improvement in the formed microstructure and compressive strength of MKCC with 15 wt% substitution of PC by metakaolinite due to effective pozzolanic reaction. As curing time increases and more calcium hydroxide is produced within 90-day hydration process period, additional amounts of gel-like hydration products appear in the cement composite, which contribute to strength increase at

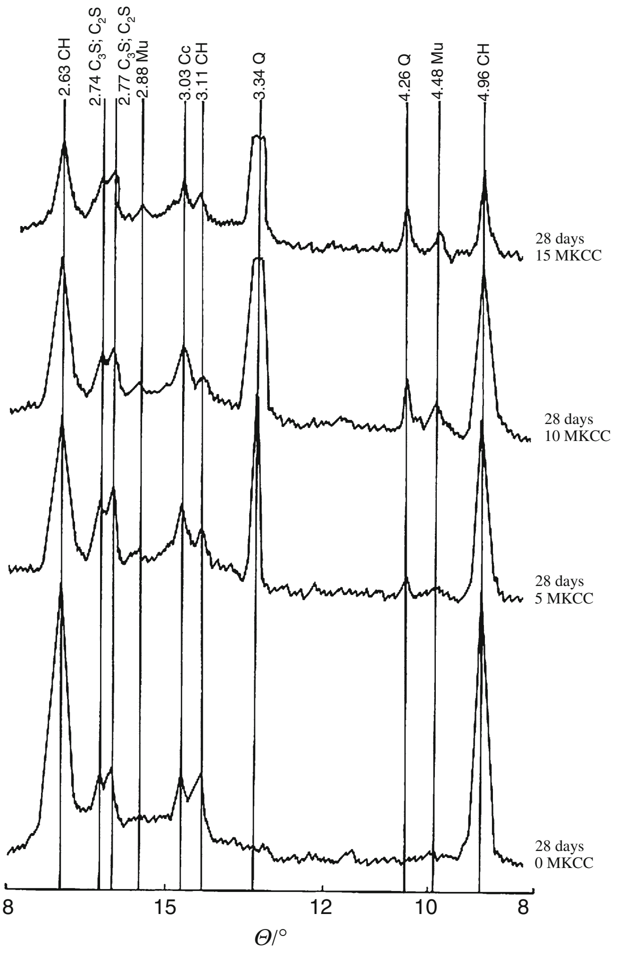

Fig. 1 XRD patterns of cement composites (CC) with burnt kaolin sand cured 28 days in water. 0MKCC—0% of metakaolinite (MK) in CC CH—portlandite $Ca(OH)_2$·5MKCC—5% of MK in CC Cc—calcite $CaCO_3$·10MKCC—10% of MK in CC Q—quartz SiO_2·15MKCC—15% of MK in CC Mu—muscovite

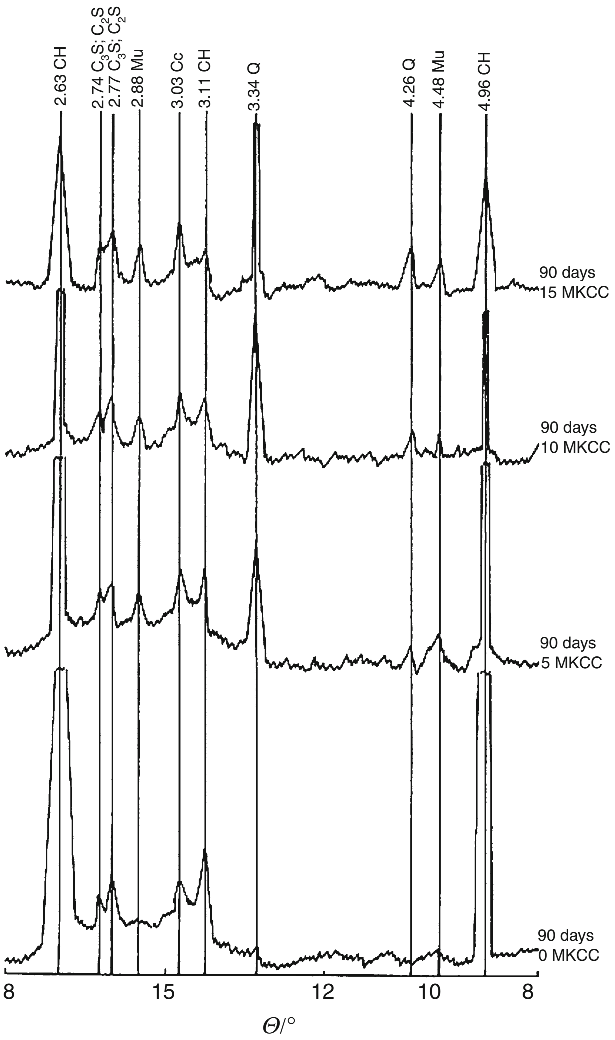

Fig. 2 XRD patterns of cement composites (CC) with burnt kaolin sand cured 90 days in water. 0MKCC—0% of metakaolinite (MK) in CC CH—portlandite $Ca(OH)_2$·5MKCC—5% of MK in CC Cc—calcite $CaCO_3$·10MKCC—10% of MK in CC Q—quartz SiO_2·15MKCC—15% of MK in CC Mu—muscovite

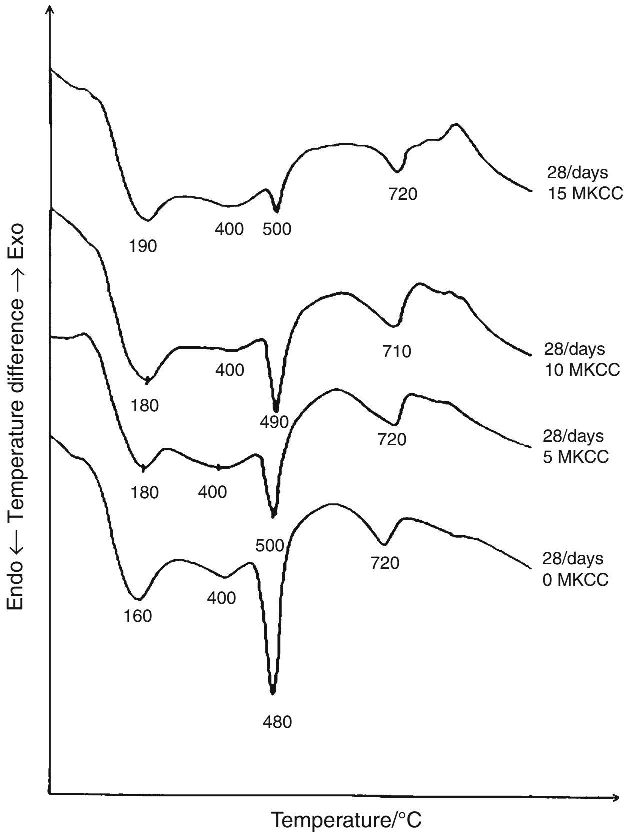

Fig. 3 DTA curves of cement composites (CC) with burnt kaolin sand cured 28 days in water (120–260) °C: CSH gel and C_2ASH_8 (gehlenite), (300–440) °C: C_3AH_6(hydrogarnet), (440–530) °C: CH (portlandite), (530–900) °C: Cc (calcite)

later curing time. This is the expected reason for which the substitution of PC by 10 wt% of metakaolinite in MKCC gives the highest compressive strength after 90-day cure. The observed strength enhancements in the compressive strength of MKCC composites are attributed to the pozzolanic activity of BKS.

Table 3 Results of thermal analysis of cement composites with burnt kaolin sand

Composite indication	Surface bound water/%	Water bound in C–S–H, C–A–H/%	$Ca(OH)_2$/%	$CaCO_3$/%	Total ignition loss/%
28 days					
0 MKCC	2.8	10.3	14.4	10.2	21.0
5 MKCC	2.5	10.5	10.3	9.1	19.5
10 MKCC	2.5	10.5	8.2	8.5	18.8
15 MKCC	2.5	10.5	4.1	9.1	18.0
90 days					
0 MKCC	3.0	12.5	14.4	9.7	23.3
5 MKCC	3.0	12.5	11.3	8.5	22.0
10 MKCC	3.0	12.5	8.2	8.0	21.3
15 MKCC	3.0	12.0	6.2	6.8	19.5

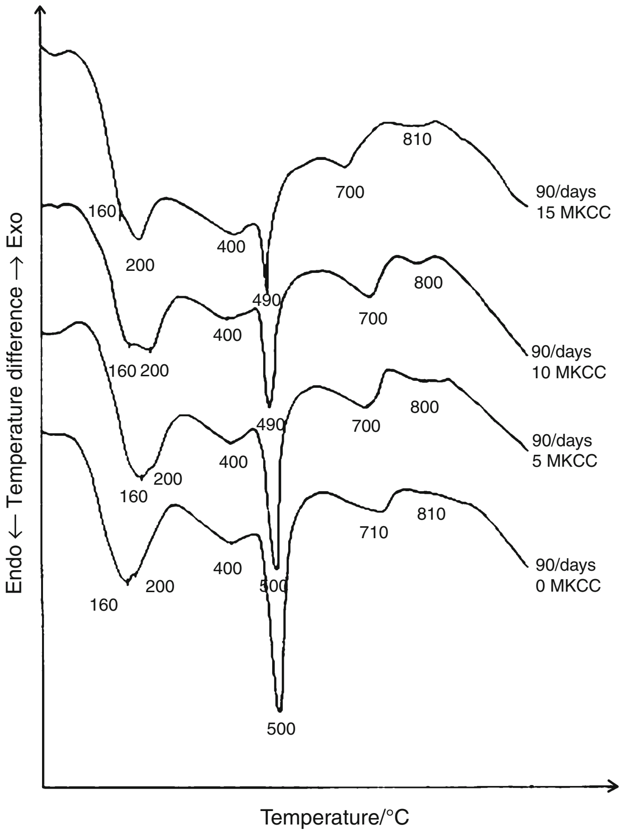

Fig. 4 DTA curves of cement composites (CC) with burnt kaolin sand cured 90 days in water (120–260) °C: CSH gel and C_2ASH_8 (gehlenite), (300–440) °C: C_3AH_6(hydrogarnet), (440–530) °C: CH (portlandite), (530–900) °C: Cc (calcite)

The pozzolanic activity of BKS is confirmed by XRD analyses (Figs. 1, 2). According to these diffractograms, less calcium hydroxide—$Ca(OH)_2$ was detected in MKCC relative to the reference cement paste without BKS. The XRD study clearly indicates that BKS exhibits pozzolanic activity. The $Ca(OH)_2$ is mostly consumed in the composite with 15 wt% substitution of PC by metakaolinite that is present in BKS.

The results of TG/DTA/DTG analysis are evaluated in Table 3 and Figs. 3 and 4. The lowest temperature range between 120 and 260 °C is connected with decomposition of CSH gel and C_2ASH_8 (gehlenite). The presence of CSH gel and gehlenite is more significant with the increased curing time (90 days). The amount of $Ca(OH)_2$ is decreased with the elevated substitution of PC by metakaolinite because of portlandite consumption in the pozzolanic reaction of BKS. The decarbonation process is accompanied with the gradual reduction of calcite $CaCO_3$ amount with the increased content of metakaolinite in CC. This statement is valid for evolution of total ignition values too.

The MIP findings for the studied cement composites are summarized in Table 4. The results show that for 28- and 90-day composites the average micropore and pore radii, total porosity and permeability coefficients are lower than in the reference cement paste without BKS. Moreover, the average pore radii, total porosity and permeability coefficient values are reduced with curing time. The observed pore structure refinement of MKCC relative to those in reference cement paste is contributed to the reduced $Ca(OH)_2$ contents after 28- and 90-day cure in 20 ± 1 °C water. The reason of this fact lies in pozzolanic reaction of metakaolinite with the cement. The MIP results are also consistent with strength developments (Table 2). Thus, the cement composites with BKS are characterized by lower total porosity, smaller mean micropore and pore radius as well as lower permeability on the one hand, but by higher compressive strength on the other hand than the reference cement paste. This result represents valuable indication that PC substitutions by 5–15 wt% metakaolinite in MKCC effectively refine the formed pore structures.

Table 4 Pore structure parameters of cement composites with burnt kaolin sand

Composite indication	SSA/m^2 g^{-1}	V_{TP}/mm^3 g^{-1}	V_{MP}/mm^3 g^{-1}	M_{TP}/nm	M_{MP}/nm	BD/kg m^{-3}	TP/vol%	Kx10^{-10}/m s^{-1}
28 days								
0 MKCC	10.42	112.20	112.20	38.36	38.36	1 700	19.07	0.961
5 MKCC	12.77	106.85	106.85	27.24	27.24	1 700	18.16	0.439
10 MKCC	18.05	108.91	108.91	17.11	17.11	1 700	18.51	0.080
15 MKCC	17.90	94.40	94.40	14.72	14.72	1 720	16.23	0.093
90 days								
0 MKCC	13.26	85.86	85.86	21.53	21.53	1 720	14.76	0.106
5 MKCC	15.58	82.38	82.38	12.55	12.55	1 800	15.40	0.059
10 MKCC	17.30	79.48	79.48	10.15	10.15	1 730	13.75	0.042
15 MKCC	17.38	75.82	75.82	9.64	9.64	1 790	13.57	0.041

SSA specific surface area of pores; V_{TP} total pore volume (3.7–0.06 mm); V_{MP} micropore volume (3.7–7,500 nm); M_{TP} total pore median radius (3.7–0.06 mm); M_{MP} micropore median radius (3.7–7,500 nm); *BD* bulk density; *TP* total porosity (3.7–0.06 mm); *K* permeability coefficient

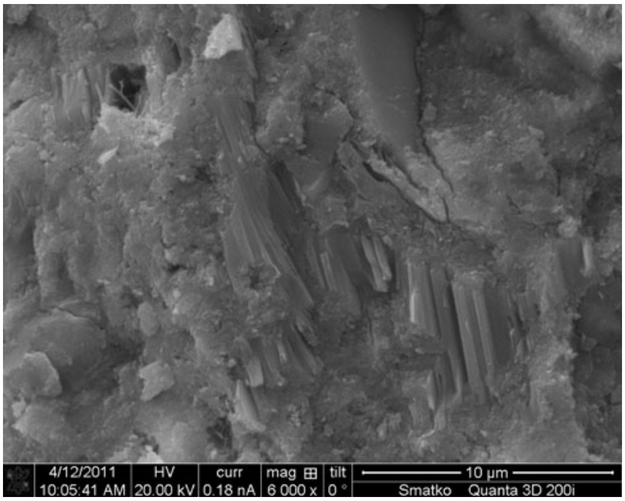

Fig. 5 SEM micrograph of reference cement paste without burnt kaolin sand—0MKCC—0% of metakaolinite (MK) in CC after 28 days curing in water

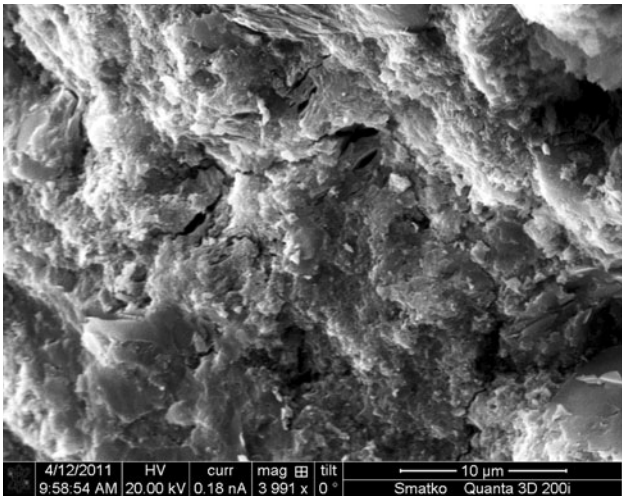

Fig. 6 SEM micrograph of cement composite with burnt kaolin sand corresponding to 15 wt% substitution of PC by metakaolinite—15MKCC after 28 days curing in water

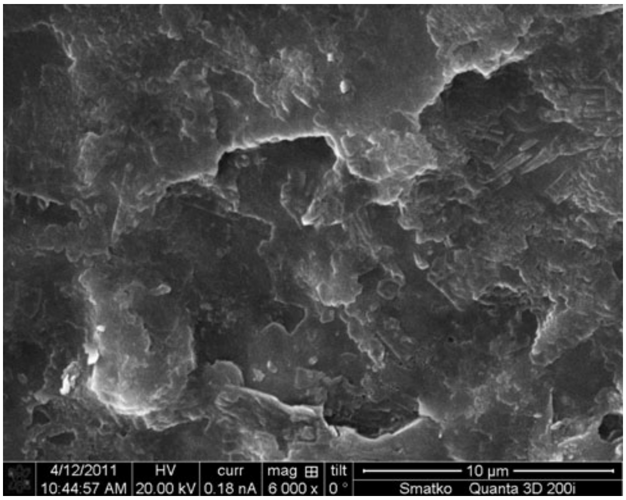

Fig. 7 SEM micrograph of cement composite with burnt kaolin sand corresponding to 15 wt% substitution of PC by metakaolinite—15MKCC after 90 days curing in water

Figures 5, 6, 7 show SEM images of MKCC with 15 wt% substitution of PC by metakaolinite and reference cement paste without BKS prepared at different magnifications after 28- and 90-day water curing. Microstructure of cement composite appears to be more uniform considering the content of crystalline constituents than that of reference cement paste. The MKCC with 15 wt% substitution of PC by metakaolinite is characterized by lower content of platy and needle-like calcium hydroxide—$Ca(OH)_2$ crystals of smaller size opposite to the reference cement paste. Careful observations in the case of MKCC reveal a composite microstructure consisting of a dense matrix, whose surface is covered by extremely small nanoparticles of honeycomb-like CSH gel of different sizes and shapes. This confirms the pozzolanic reaction of BKS by the effective consumption of $Ca(OH)_2$, which results in the higher compressive strengths of MKCC relative to the reference cement paste on the one hand and lower mean pore median radii, total porosities and permeability coefficients values relative to those in the reference cement paste on the other hand.

Conclusions

Based on the performed tests, the following conclusions were drawn:

1. Substitution of Portland cement by burnt kaolin sand containing 36 wt% of metakaolinite in cement composites corresponding to 5–15 wt% substitution of Portland cement by metakaolinite shows 24% for 28-day and 46% for 90-day compressive strength increase compared to the reference cement paste.
2. Burnt kaolin sand with the metakaolinite content of 36 wt% exhibits a strong pozzolanic activity by consuming $Ca(OH)_2$ and represents an efficient pozzolana.
3. Substitution of Portland cement by burnt kaolin sand containing 5–15 wt% of metakaolinite in cement composites results in following changes happening in the formed microstructure and pore structure: (a) significant positive effect on compressive strength due to reduction in $Ca(OH)_2$ content and (b) pore structure refinement presented by decreased mean pore radii,

total porosity and permeability coefficient opposite to reference cement paste without burnt kaolin sand.

4. The micropore and total pore radii, total porosities and permeability coefficients are decreasing with curing time.

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