

# Microstructure of Portland cement mortar amended by burnt kaolin sand

L. Krajčí · S. C. Moujmdar · M. Kuliffayová ·  
I. Janotka

CTAS2009 Special Chapter  
© Akadémiai Kiadó, Budapest, Hungary 2010

**Abstract** Two types of raw materials, original kaolin sand OKS I and OKS II were used for experiment. They were transformed (1 h at 650 °C with 10 °C/min temperature increase) to burnt kaolin sand (BKS I and BKS II) with pozzolanic properties. Contents of decisive mineral—metakaolinite—in BKSs are as follows: BKS I (fraction below 0.06 mm) 20%; BKS II (fraction below 0.06 mm) 36% and BKS II (fraction below 0.1 mm) 31% by mass. Mortars with blends of Portland cement (PC) and BKS were prepared announced as: MK I (0.06) with 5 and 10% cement substitution by metakaolinite; MK II (0.06) with 5 and 10% cement substitution by metakaolinite and MK II (0.1) with 5, 10, 15 and 20% cement substitution by metakaolinite. The reference mortar with 100% of PC was made for comparison. All mortars were adjusted on the constant workability  $180 \pm 5$  mm flow. Besides significant increase in compressive strengths—the refinement of pore structure in mortars with BKS connected with decreases in permeability and  $\text{Ca}(\text{OH})_2$  content were revealed. The above facts confirm pozzolanic reaction of BKS in contact with hydrated PC and indicate perceptiveness of BKS for the use in cement-based systems as a pozzolanic addition.

**Keywords** Blended cements · Burnt kaolin sand · Pozzolana · Metakaolinite · Pore structure · Refinement

## Introduction

The properties of cement composite depend on the quantities and qualities of its components. Because cement is the most active component of composites and usually has the greatest unit cost, its selection and proper use are important in obtaining most economically the balance of properties desired for any particular composite mixture. Due to many disadvantages of Portland cement (PC) (cost, energetic and environmental problems, etc.); the prospective way is represented by formation of blended cements. Blended cement as defined in ASTM C 595 is a mixture of PC and second component, e.g., pozzolana. Many authors have investigated numerous blended cement systems with different origins and also studied their mechanical, microstructural and other properties [1–4].

World PC clinker production is responsible for about 7% of total  $\text{CO}_2$  emissions. The effective way for removing of this fact is associated just with incorporation of pozzolanic materials into PCs creating blended PCs. The use of pozzolanic materials as a blended component of Portland–pozzolan cements production is generally associated with significant saving in energy and reduction of the solid wastes [5]. Experts have widely agreed for decades that the use of pozzolana or supplementary cementitious materials can reduce concrete permeability by 7–10 times. In particular, the mechanism of pozzolana in this role can be viewed as having two principal aspects. First, the use of a quality pozzolana will result in a denser pore structure in the cement paste matrix. Second, the chemical reaction of lime crystals to form binders has a direct effect on

---

L. Krajčí · M. Kuliffayová · I. Janotka  
Institute of Construction and Architecture of Slovak Academy of Sciences, Dúbravská cesta 9, 845 03 Bratislava, Slovak Republic

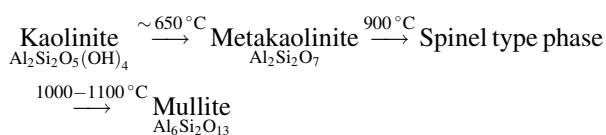
S. C. Moujmdar (✉)  
Department of Engineering, University of New Brunswick,  
Saint John, NB E2L 4L5, Canada  
e-mail: subhash.moujmdar@utoronto.ca;  
scmoujmdar@yahoo.com

I. Janotka  
Building Testing and Research Institute, Studená 3,  
Bratislava 821 04, Slovak Republic

increased paste density, reduced porosity over time and will enhance the matrix chemical resistance to many aggressive species.

The starting point for formation of often used pozzolana—metakaolin—is represented by kaolin [6–8]. Kaolin is fine clay mineral that has been traditionally used in the manufacture of porcelain. It is thought that the term kaolin is derived from the Chinese Kaoling which translates loosely to white hill and has been related to the name of a mountain in China that yielded the first kaolins that were sent to Europe. Kaolinite is the mineralogical term that is applicable to kaolin clays. It is defined as a common mineral, hydrated aluminium disilicate  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , the most common constituent of kaolin.

Kaolinite undergoes the following reaction on thermal treatment (calcination process):



Calcination at low temperatures is essentially dehydroxylation of the kaolinite mineral resulting in the formation of an X-ray amorphous material called metakaolinite. Further heating results in a spinel-type phase called primary mullite, which subsequently crystallizes into mullite [7]. In order to confirm the results of calcination process, thermal analysis can be performed. The comparisons between the results obtained before and after calcination for 60 min are presented in [9]. Thus, metakaolin is produced by calcination of clay material kaolin at 650–800 °C. It is a reactive pozzolana with a high specific surface, which makes it suitable as a cementing material in concrete. Metakaolin particles are nearly 10 times smaller than cement particles which results in a final effect in a denser structure of concrete. Metakaolin chemically reacts with  $\text{Ca}(\text{OH})_2$ , which is released by the hydration of PC to form compounds possessing cementitious properties. Metakaolin is available in a high state of purity (greater than 90%) and can react with more than its own mass of  $\text{Ca}(\text{OH})_2$  to give new cementitious compounds [10].

Generally, the use of calcined clay as pozzolanic admixture for cement has been known since the time of Romans. The study of metakaolin as pozzolanic additive for modern cement and concrete has become very popular in recent years [11–13].

Metakaolin exhibits strong pozzolanic activity. The pozzolanic activity is defined as the ability to react with portlandite  $\text{Ca}(\text{OH})_2$  in the presence of an excess of water. It depends on a number of factors, i.e., chemical and mineralogical composition of pozzolana, specific surface area and content of  $\text{Ca}(\text{OH})_2$  in cement paste [14].

According to Frias et al. [15] metakaolin exhibits lower pozzolanic activity than silica fume but significantly greater than fly ash. The evaluation of metakaolin pozzolanic activity in cement was studied by method of thermal analysis [16].

Recent works [17, 18] have shown that when metakaolin is used as partial cement replacement in mortar or concrete, it gives significantly enhanced early strength and increased long-term strength. It acts as filler which accelerates initial cement hydration and rapidly consumes the hydrated lime produced by cement hydration to produce additional cementitious reaction products. Respecting evolution of strengths Calderone et al. [13] produced concretes with 5 and 10% of metakaolin which showed enhanced strengths at ages up to 365 days. Similar influences of metakaolin on the strength of concrete have been reported by Wild et al. [17]. The authors identify three elementary factors which influence the contribution that metakaolin makes to concrete strength. These are the filler effect which is immediate, the acceleration of PC hydration which occurs within the first 24 h and the pozzolanic reaction which has its maximum effect within the first 7–14 days for all metakaolin levels between 5 and 30%.

The early strength enhancement is associated with substantial pore refinement [19]. To this effect, metakaolin is most efficiently utilized at small replacement levels (0–15%). Many authors deal with pore structure of cement composites with metakaolin blended cements [19–21]. It is well known that pore structure of metakaolin blended cement composites is finer than in plain composites. For example, it was found that the proportion of pores radii  $<0.02 \mu\text{m}$  within the pastes increased with the increase in metakaolin content and curing time [19].

Thermal analysis is very important to supplement the results of other methods [1]. The detailed explanation of differential thermal analysis (DTA) thermograms of hardened cement pastes containing 0, 10, 20 and 30% burnt kaolin clay connected with description of individual phases is given in Ref. [22]. The relations of thermal treatment and pozzolanic activity are presented by investigators as well [23, 24]. Because of the fact that the deleterious influence of various type of surrounding aggressiveness on cement-based materials is actually well known [25, 26], it is favourable that metakaolin blended composites have increased chemical resistance. Thus, using metakaolin in concrete increases the durability of concrete (resistance to chemical attacks, ASR expansion, free-thaw cycles). Like that it was found that mortars containing higher replacement level metakaolin exhibited a superior resistance against sulphate attack [27] because of significant consumption of calcium hydroxide and refinement of pore structure due to pozzolanic reaction of metakaolin. Thus, cement composites with metakaolin have presumptions for

application not only in sulphate but also in acid aggressive environment as well as in regions with chloride ions [4, 27, 28].

**Table 1** Chemical composition of the cement and burnt kaolin sand (BKS)

Component/ mass%	Cement CEM I 42.5R	BKS type		
		I (0.06/mm)	II (0.06/mm)	II (0.1/mm)
Humidity	0.38	0.22	0.24	0.17
Loss on ignition	1.45	1.05	1.52	0.68
Insoluble residue	0.83	74.60 <sup>a</sup>	62.91 <sup>a</sup>	80.24 <sup>a</sup>
SiO <sub>2</sub>	21.08			
CaO	61.02	0.85	1.02	0.73
Al <sub>2</sub> O <sub>3</sub>	5.76	18.86	28.92	14.91
Fe <sub>2</sub> O <sub>3</sub>	2.86	1.46	2.37	1.02
MgO	2.61	0.73	0.94	0.50
SO <sub>3</sub>	2.49	0.04	0.03	0.03

<sup>a</sup> Insoluble residue + SiO<sub>2</sub>

**Experimental**

**Materials**

These materials were used for mortars preparation: ordinary PC: CEM I 42.5R (fy Holcim, Rohožník Slovakia); burnt kaolin sand (BKS) of type I (fraction below 0.06 mm); of type II (fraction below 0.06 mm) and of type II (fraction below 0.1 mm); standard siliceous sand (0–0.5:0.5–1:1–2 mm = 1:1:1 by mass). The samples of BKS were gained by heating of original kaolin sands (OKSs) in an electric oven at the following experimental conditions:

- Rate of heating—10 °C/min
- Exposure time—650 °C/1 h dwell
- Rate of self-cooling—10 °C/min

OKSs were obtained from Vyšný Petrovec deposit, Slovakia. The amounts of metakaolinite (decisive mineral) in BKS are: metakaolinite in type I of BKS (0.06 mm) 20% by mass; metakaolinite in type II of BKS (0.06 mm) 36% by mass and metakaolinite in type II of BKS (0.1 mm) 31% by mass. RockJock program (specified in testing methods)

**Table 2** Basic physical properties of materials employed

Material	Specific gravity/g cm <sup>-3</sup>	Specific surface area/cm <sup>2</sup> g <sup>-1</sup> (Blaine)
Portland cement CEM I 42.5R	3.14 Initial setting: 3 h 50 min Setting time: 4 h 55 min Consistency/%: 29.5	4230 Mineralogical composition/% (Bogue) C <sub>3</sub> S: 45.37 C <sub>3</sub> A: 10.43 C <sub>2</sub> S: 26.22 C <sub>4</sub> AF: 8.70
BKS type		
I (0.06 mm)	2.67	3983
II (0.06 mm)	2.61	2718
II (0.1 mm)	2.63	2706

**Table 3** Water absorption capacity and specific gravity of the mortar specimens

Substitution of PC by metakaolinite/%	BKS type	Fraction/mm	Water absorption capacity/mass%		Specific gravity/g cm <sup>-3</sup>	
			28 days	90 days	28 days	90 days
5	BKS I	0.06	3.20	2.81	2.66	2.57
10	BKS I	0.06	3.00	2.61	2.62	2.55
5	BKS II	0.06	3.54	2.97	2.62	2.58
10	BKS II	0.06	3.03	2.55	2.58	2.53
5	BKS II	0.1	3.76	3.43	2.67	2.57
10	BKS II	0.1	3.74	3.07	2.60	2.56
15	BKS II	0.1	3.25	2.65	2.59	2.55
20	BKS II	0.1	3.04	2.67	2.56	2.51
Reference mortar with 100% PC			6.80	6.12	2.51	2.57

was applied for quantitative estimations of metakaolinite amounts in individual BKS samples.

#### Preparation of specimens

The mortar specimens were prepared from PC and BKS samples using also standard siliceous sand and water with superplasticizer Stachement based on polycarboxysilicates (fy Stachema, Rovinka Slovakia). The mortars were adjusted on the same consistency measured as  $180 \pm 5$  mm flow by Haegerman test according to EN 1015-3. This value was unit parameter in this experiment. The mixture composition and metakaolinite contents were selected as follows:

- (cement + metakaolinite in BKS): siliceous sand = 1:3 by mass
- type I of BKS with fraction below 0.06 mm: 5 and 10% of metakaolinite as percentage substitution of PC
- type II of BKS with fraction below 0.06 mm: 5 and 10% of metakaolinite as percentage substitution of PC

- type II of BKS with fraction below 0.1 mm: 5, 10, 15 and 20% of metakaolinite as percentage substitution of PC

The specimens with size of  $40 \times 40 \times 160$  mm were prepared according to EN 196-1. They were cured 24 h in steel moulds at 100% R.H. and 20 °C. After demoulding the mortars were stored in water at 20 °C until testing.

#### Testing methods

Quantitative analysis of BKS samples was performed applying the RockJock program [29]. The program fits the sum of stored X-ray diffraction (XRD) patterns of pure standard minerals (the calculated pattern) to the measured pattern by varying fraction of each mineral standard pattern, using the Solver function Microsoft Excel to minimize a degree of fit parameter between the calculated and measured pattern. Samples for analysis were prepared by adding 0.111 g ZnO (internal standard) to 1.000 g sample. The mixture was ground in a McCrone mill for 5 min with 4 mL of methanol then dried and sieved.

**Table 4** Strength development of the mortar specimens

Substitution of PC by metakaolinite/%	BKS type	Fraction/mm	Compressive strength/MPa		Flexural strength/MPa	
			28 days	90 days	28 days	90 days
5	BKS I	0.06	76.7	93.5	11.2	11.6
10	BKS I	0.06	69.9	84.0	10.5	12.3
5	BKS II	0.06	72.2	86.2	10.6	11.1
10	BKS II	0.06	68.6	83.6	9.4	10.1
5	BKS II	0.1	76.1	85.7	9.5	9.9
10	BKS II	0.1	63.1	84.0	9.2	11.3
15	BKS II	0.1	62.1	84.9	9.1	10.2
20	BKS II	0.1	62.3	81.2	8.7	9.9
Reference mortar with 100% PC			40.2	53.5	8.3	10.2

**Table 5** Pore structure parameters of the mortars after 90 days water curing

Mortar indication	SSA/m <sup>2</sup> g <sup>-1</sup>	V <sub>TP</sub> /mm <sup>3</sup> g <sup>-1</sup>	V <sub>MP</sub> /mm <sup>3</sup> g <sup>-1</sup>	Macro/%	M <sub>TP</sub> /nm	M <sub>MP</sub> /nm	BD/kg m <sup>-3</sup>	TP/vol%	K × 10 <sup>-10</sup> /m s <sup>-1</sup>
5 MKI (0.06)	4.23	40.46	25.66	36.58	29.96	14.46	2150	8.69	0.4
10 MKI (0.06)	10.55	51.07	44.71	12.45	14.24	10.35	2190	11.18	0.2
5 MKII (0.06)	3.74	31.29	24.90	20.43	27.84	21.03	2210	6.91	0.5
10 MKII (0.06)	5.34	45.51	39.04	14.21	21.28	18.50	2160	9.82	0.3
5 MKII (0.1)	2.16	31.58	24.98	20.90	37.07	28.69	2420	7.64	0.8
10 MKII (0.1)	6.23	43.61	35.18	19.34	20.08	15.07	2160	9.42	0.2
15 MKII (0.1)	5.04	37.42	30.99	17.18	20.46	16.79	2290	8.56	0.4
Reference mortar	8.33	65.55	56.40	13.96	39.19	29.10	2180	14.28	1.2

SSA specific surface area of pores, V<sub>TP</sub> total pore volume (3.7 nm–0.06 mm), V<sub>MP</sub> micropore volume (3.7–7500 nm), Macro portion of macropores (above  $r = 7500$  nm), M<sub>TP</sub> total pore median radius (3.7 nm–0.06 mm), M<sub>MP</sub> micropore median radius (3.7–7500 nm), BD bulk density, TP total porosity (3.7 nm–0.06 mm), K permeability coefficient

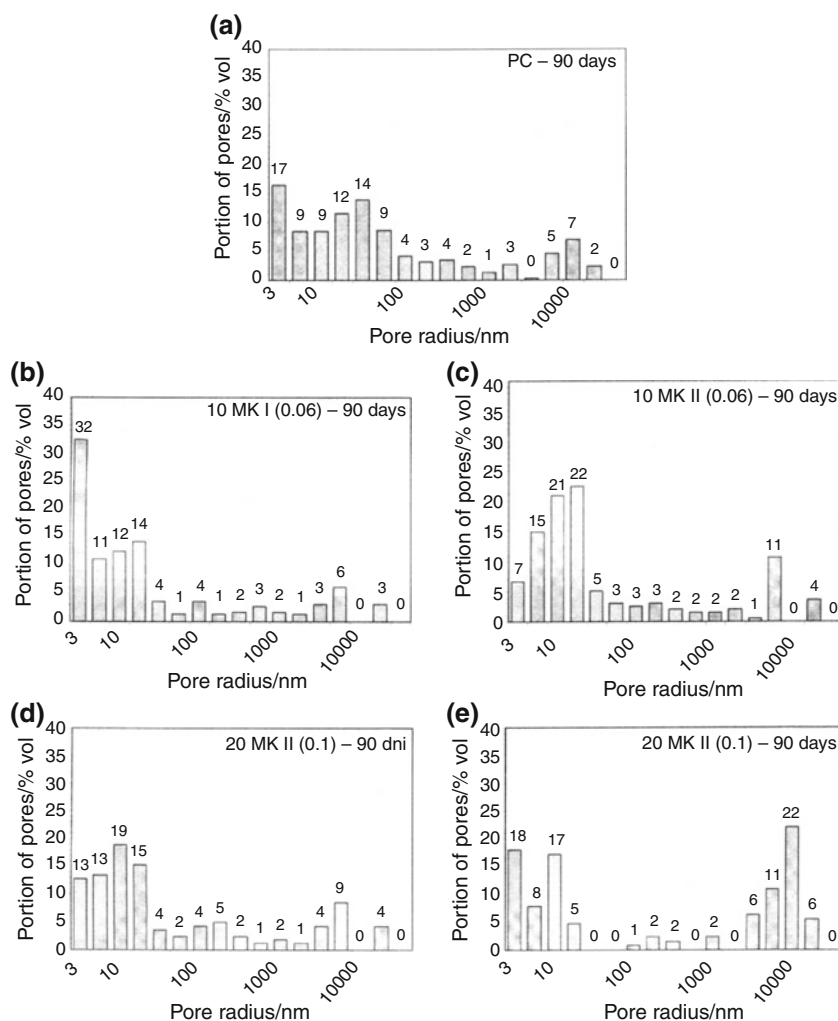
Chemical analysis was done by standard wet analytical methods using procedures for estimation of individual oxide contents and ignition loss values according to EN 196-2. Powder XRD patterns were recorded in the  $2\theta$  range from  $12^\circ$  to  $19^\circ$  on a Philips diffractometer coupled with an automatic data recording system.  $\text{CuK}_\alpha$  radiation and Ni-filter were used. Thermogravimetry (TG) and DTA were simultaneously conducted from 20 to 1000 °C using a Derivatograph Q instrument (1500 MOM Budapest, Hungary). In general, 200 mg of sample mass was heated at the heating rate of 20 °C/min in flowing air. The pore structure was studied by mercury intrusion porosimetry (MIP) using the high-pressure porosimeter mod. 2000 and macro porosimeter mod. 120 (Carlo Erba Science Milan, Italy). From the measured data (volume of micropores up to 7500 nm, average micropore and pore median radius, total porosity and pore size distribution) permeability coefficients were calculated [30].

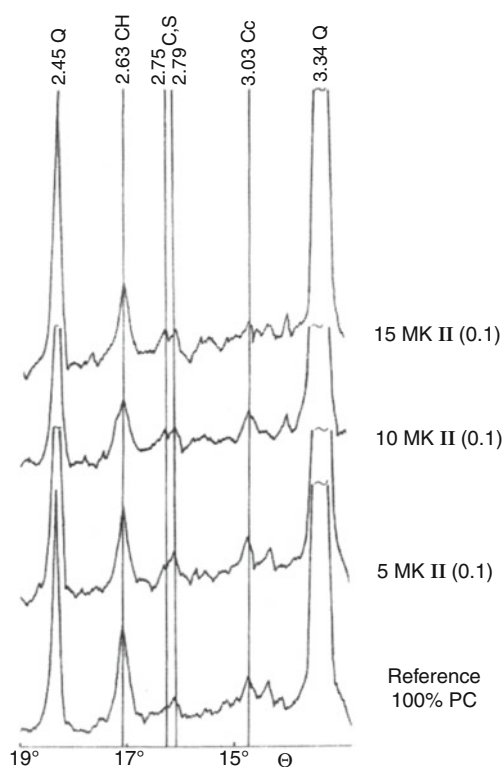
**Results and discussion**

The chemical composition of PC and BKS samples is presented in Table 1.  $\text{Al}_2\text{O}_3$  content in BKS of type II is increased in comparison with that of BKS of type I at the same fraction of 0.06 mm. On the other hand,  $\text{Al}_2\text{O}_3$  content is decreased on half in type II of BKS with the coarser fraction of sand (0.1 mm). The basic physical properties of materials used in the experiment are reported in Table 2. Specific gravity and specific surface area of all BKS samples are lower opposite to PC.

The results of water absorption capacity and specific gravity of BKS-amended mortars are presented in Table 3. Water absorption capacities of mortars made with BKS are lower relative to that of the PC mortar. This decrease is greater at later age of 90 days and more pronounced when PC is substituted by higher metakaolinite contents. Similar tendencies are observed for changes in specific gravity values.

**Fig. 1** Pore size distribution of mortars with BKS of type I and II (0.06 mm fraction with 10% of metakaolinite) and type II (0.1 mm fraction with 15 and 20% of metakaolinite) kept for 90 days in water

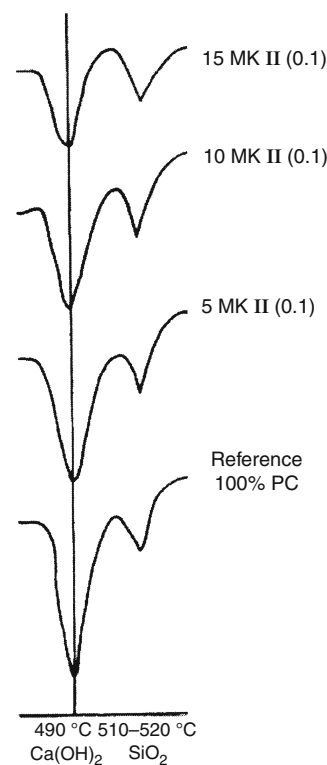




**Fig. 2** XRD patterns of the mortars kept for 90 days in water. Abbreviations: *Q* –SiO<sub>2</sub>, *CH* Ca(OH)<sub>2</sub>, *C<sub>3</sub>S* tricalciumsilicate and *Cc* calcite CaCO<sub>3</sub>

Strength development (compressive, flexural) of the mortar specimens is presented in Table 4. Compressive strengths of mortars made with BKS after 28- and 90-day water cures are increased compared to those found in the reference PC mortar. Strength increases (especially 90-day) are not dependent on the fineness of BKS samples; the coarser fraction (0.1 mm) gives strength increment similar to that of finer (0.06 mm). The similar tendencies are valid for flexural strengths as well.

Pore structure characteristics and calculated permeability coefficients of the specimens are summarized in Table 5.

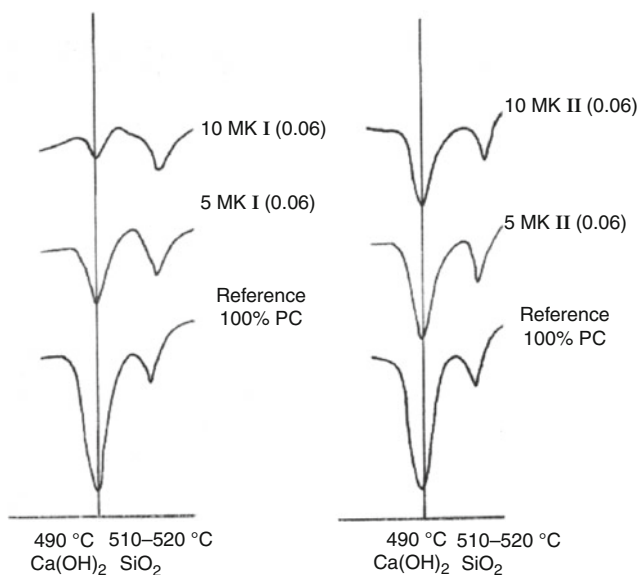


**Fig. 3** DTA curves of the mortars made from BKS of type II 0.1 mm fraction with 5, 10 and 15% of metakaolinite kept for 90 days in water

The results reveal that average micropore ( $M_{MP}$ ), total pore ( $M_{TP}$ ) median radii and permeability coefficient ( $K$ ) are decreased for all mortars made from BKS relative to the PC mortar. Contrary, the highest total porosity (TP) of the reference mortar indicates the large volume of air voids occurring in this specimen. Gradual increase in very fine pores, mainly those under radius of 40 nm (Fig. 1) is caused by incorporation of BKS into the mortars when metakaolinite substitutes 5–20 wt% portion of PC. The portion of micropores in reference PC mortar is 47% (Fig. 1a); whereas those in 10 MK I (0.06) and 10 MK II (0.06) mortars

**Table 6** Results of thermal analysis based on TG calculations after 90 days water curing

Substitution of PC by metakaolinite/%	BKS type	Fraction/mm	Surface bound water/%	Water bound in C–S–H, C–A–H/%	Ca(OH) <sub>2</sub> /%	Ca CO <sub>3</sub> /%	Total ignition loss/%
5	BKS I	0.06	0.69	2.88	2.1	4.6	6.19
10	BKS I	0.06	0.56	3.44	1.3	3.8	6.50
5	BKS II	0.06	0.50	3.13	2.6	2.3	5.63
10	BKS II	0.06	0.56	3.38	1.8	2.6	5.88
5	BKS II	0.1	0.50	2.81	2.3	2.3	5.19
10	BKS II	0.1	0.56	3.31	2.1	2.7	5.88
15	BKS II	0.1	0.69	3.13	1.8	3.7	6.19
20	BKS II	0.1	0.38	3.56	1.5	2.6	5.75
Reference mortar with 100% PC			0.63	3.44	3.3	4.0	7.00



**Fig. 4** DTA curves of the mortars made from BKS of type I and II 0.06 mm fraction with 5 and 10% of metakaolinite kept for 90 days in water

(Figs. 1b, c) are 69 and 65%, respectively. The above findings evidently prove the pore structure refinement resulting in lower permeability of the mortars incorporated by BKS of I and II type with fractions below 0.06 mm. Similar results confirming the pore structure refinement gives mutual comparison of micropores portions ( $r < 40$  nm) and large pore portions ( $r > 7500$  nm) occurring in the specimens. The reference PC mortar contains 47% of micropores and 14% of large pores. The finer in fraction 10 MK II (0.06) mortar is characterized by 65 and 16% of micropores and large pores, respectively. No evident differences in micropore and large pore portions are found in the coarser fraction 15 and 20 MK II (0.1) (Figs. 1d, e) mortars relative to MK II (0.06) mortar. Both 15 and 20 MK II (0.1) mortars contain 60 and 48% of micropores, and 13 and 39% of larger pores,

respectively. High levels of pore structure refinement for all mortars made with BKS independently on the type of sand—I and II, and fraction—below 0.06 and 0.1 mm except that of 20 MK II (0.1) mortar (Fig. 1e) is confirmed. The latter contains 48% of micropores and 39% of large pores. Higher volume of large pores is attributed to starting symptoms of the loss in workability at the 20 MK II (0.1) mortar preparation.

Pore structure refinement results in evident decrease in absorption capacity (Table 3) and increase in compressive strength (Table 4) of the mortars made with BKSs when compared to the reference PC mortar. The substitution of 20 wt% of PC by metakaolinite in MK II (0.1) is not suitable for the mortar use because of negative impact of such BKS-type addition on the workability of fresh mortar.

The diffraction line at 2.63 Å (0.263 nm) clearly proves the presence of Ca(OH)<sub>2</sub> abbr.: (CH) in the mortars (Fig. 2); that at 2.45 and 3.34 Å (0.245 and 0.334 nm) belongs to SiO<sub>2</sub> coming from the used standard siliceous sand. The content of Ca(OH)<sub>2</sub> gradually decreases with percentage replacement of PC by BKS. The (5, 10 and 15) MK II (0.1) mortars differ from the reference mortar by higher CH consumptions. The presence of unreacted cement clinker mineral C<sub>3</sub>S is proved by diffraction lines at 2.79 and 2.76 Å (0.279 and 0.276 nm). Calcite (Cc) detected at 3.03 Å (0.303 nm) is the carbonation product accomplished with the cement hydration. The higher consumptions of Ca(OH)<sub>2</sub> compared to the reference PC mortar is also distinguished by TG–DTA analysis. The results of TG analysis show these trends towards releasing bound water from the hydration products and Ca(OH)<sub>2</sub> (Table 6): the mortars made with BKSs contain higher volume of gel-like hydration products towards lower volume of Ca(OH)<sub>2</sub> crystals relative to the reference PC mortar. By contrast, the content of water bound in hydration products in the BKS-amended mortars gradually increases with percentage PC replacements. Changes in

**Table 7** Mortars comparison study based on different method outputs

Mortar indication	MIP $M_{TP}/nm$	MIP $M_{MP}/nm$	MIP $K \times 10^{-10}/m s^{-1}$	TG Ca(OH) <sub>2</sub> /%	EN 196-1 compressive strength/MPa
5 MKI (0.06)	29.96	14.46	0.4	2.1	93.5
10 MKI (0.06)	14.24	10.35	0.2	1.3	84.0
5 MKII (0.06)	27.84	21.03	0.5	2.6	86.2
10 MKII (0.06)	21.28	18.50	0.3	1.8	83.6
5 MKII (0.1)	37.07	28.69	0.8	2.3	85.7
10 MKII (0.1)	20.08	15.07	0.2	2.1	84.0
15 MKII (0.1)	20.46	16.79	0.4	1.8	84.9
Reference mortar	39.14	29.10	1.2	3.3	53.5

MIP Mercury intrusion porosimetry, TG thermogravimetry

Other abbreviations according to Table 5

total ignition loss of the mortars made with BKS are mainly contributed to bound water contents increases. DTA plots related to CH dehydroxylation at 490 °C indicate more intense CH consumption in the BKS-amended mortars compared to the PC mortar (Figs. 3 and 4).

The mortars with the PC replacement by BKS create very similar structure to that of the reference PC mortar. Both structures are characterized by the homogenous skeleton of the formed hydration products with comparable densities and compactness. The substantial difference is in the markedly higher CH consumption found in the mortars made with BKS indicating pozzolanic reaction of metakaolinite occurring in the used BKS samples [31, 32].

Evident correlation among pore structure results, those of XRD, TG and DTA analyses and strength are found. The lower is the loss in water content bound in  $\text{Ca}(\text{OH})_2$  (TG calculations confirmed by XRD patterns and DTA plots), the more intense is the pore structure refinement (micropore and pore median radii reductions), and more evident is the decrease in permeability in the mortars with BKS on the one hand and the increase in compressive strength of the mortars on the other hand (Table 7) compared to the reference PC mortar.

## Conclusions

The effort was given into investigation of three types of BKSs poor on metakaolinite content. These results are applicable from the test results obtained:

1. BKS samples differ in metakaolinite amounts varying between 20 and 36% by mass.
2. Mortars up to 10 and 15% by mass PC substitution by metakaolinite (BKS in fractions below 0.06 and 0.1 mm) are specified with the workability suitable for application use. The larger percentage PC substitutions as above stated result in workability losses.
3. Pore structure of BKS-amended mortars is markedly refined compared to the reference PC mortar; the higher level of the pore structure refinement corresponds to higher replacement rate of PC by BKS in the mortars whereas finer BKS fraction gives better refinement than the coarser one.
4.  $\text{Ca}(\text{OH})_2$  content and permeability of all mortars made with BKS are decreased and compressive strength is evidently increased compared to the reference PC mortar; this gives clear evidence on positive effect of BKS on the microstructure development and mortars utility properties.
5. BKS is the addition showing pozzolanic activity when contacting PC at hydration and it therefore seems to be perspective for the future use in building practice.

**Acknowledgements** The authors are thankful to the Slovak Grant Agency (project No. 2/0053/09) for the financial support of this work.

## References

1. Mojumdar SC. Processing-moisture resistance and thermal analysis of macro-defect-free materials. *J Therm Anal Calorim.* 2001;64:1133–9.
2. Drábik M, Gáliková L, Hanic F, Sharp JH. MDF-related compositions based on novel low-energy clinker. *Chem Pap.* 1997;51:363–6.
3. Palou MT, Majling J, Dovál M, Kozánková J, Mojumdar SC. Formation and stability of crystallohydrates in the non-equilibrium system during hydration of sab cements. *CERAMICS-Silikáty.* 2005;49:230–6.
4. Janotka I, Krajčí L'. Sulphate resistance and passivation ability of the mortar made from pozzolan cement with zeolite. *J Therm Anal Calorim.* 2008;94:7–14.
5. Heikal M, El-Didamony H, Morsy MS. Limestone-filled pozzolanic cement. *Cem Concr Res.* 2000;30:1827–34.
6. Moulin E, Blanc P, Sorrentino D. Influence of key cement chemical parameters on the properties of metakaolin blended cements. *Cem Concr Comp.* 2001;23:463–9.
7. Chandrasekhar S, Ramaswamy S. Influence of mineral impurities on the properties of kaolin and its thermally treated products. *Appl Clay Sci.* 2002;21:133–42.
8. Vavro M, Martinec P. Durability properties of concrete with admixtures of thermally activated kaolins and shales. International science conference on quality and reliability in building industry, Levoča; 2006 pp. 399–404. [Vavro M, Martinec P. Durability properties of concrete with admixtures of thermally-activated kaolins and shales. *Sborník mezinárodní konference Quality and Reliability in Building Industry*, ISBN 80-8073-594-8, FAST TU v Košiciach, s. 399–404, Levoča, Slovensko].
9. Souza PSL, Dal Molin DCC. Viability of using calcined clays. From industrial by-products, as pozzolans of high reactivity. *Cem Concr Res.* 2005;35:1993–8.
10. Kostuch JA, Walters GV, Jones TR. High performance concretes incorporating metakaolin: a review. In: Dhir RK, Jones MR, Sporn FN, editors. *Concrete 2000*, vol 2; 1993. pp. 1799–1811.
11. Schvarzman A, Kovler K, Groder GS, Shter GE. The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite. *Cem Concr Res.* 2003;33:405–16.
12. Sabir S, Wild S, Baj J. Metakaolin and calcined clays as pozzolans for concrete: a review. *Cem Concr Comp.* 2001;23:441–54.
13. Caldarone MA, Gruber KA, Burg RG. High reactivity metakaolin (HRM): a new generation mineral admixture for high performance concrete. *Concr Int.* 1994;37–41.
14. Schvarzman A, Kovler K, Schamban I, Grader G, Shter G. Influence of chemical, phase composition of mineral admixtures on their pozzolanic activity. *Adv Cem Res.* 2002;14:35–41.
15. Frias M, Sánchez de Rojas MI, Cabrera J. The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin-cement mortars. *Cem Concr Res.* 2000;30:209–16.
16. Moropoulou A, Bakolas A, Aggelakopoulou E. Evaluation of pozzolanic activity of natural and artificial pozzolans by thermal analysis. *Therm Acta.* 2004;420:135–40.
17. Wild S, Khatib JM, Jones A. Relative strength, pozzolanic activity and cement hydration in superplasticised metakaolin concrete. *Cem Concr Res.* 1996;26:1537–44.
18. Zhang MH, Malhotra VM. Characteristics of a thermally activated alumino-silicate pozzolanic material and its use in concrete. *Cem Concr Res.* 1995;25:1713–25.



19. Khatib JM, Wild S. Pore size distribution of metakaolin paste. *Cem Concr Res.* 1996;26:1545–53.
20. Frias M, Rojas MIS. Influence of the MK on porosity of matrixes based in MK/cement. *Mater Constr.* 2000;50(259):57–67
21. Rojas MF, Rojas MIS. Influence of metastable hydrated phases on the pore size distribution and degree of hydration of MK-blended cements cured at 60 C. *Cem Concr Res.* 2005;35:1292–8.
22. Morsy MS, El-Enein A, Hanna B. Microstructure and hydration characteristics of artificial pozzolana-cement pastes containing burnt kaolinite clay. *Cem Concr Res.* 1997;27:1307–12.
23. Oriol M, Pera J. Pozzolanic activity of metakaolin under microwave treatment. *Cem Concr Res.* 1995;25:265–70.
24. Kakali G, Perraki T, Tsvivilis S, Badogiannis E. Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity. *Appl Clay Sci.* 2001;20:73–80.
25. Jerga J, Halas P. Ingress of chloride into the prestressed concrete structure. In: *Proceedings of the 5th international conference on concrete*, Prague, Czech Republic; 1990, pp. 400–404
26. Jerga J. Physico-mechanical properties of carbonated concrete. *Constr Build Mater.* 2004;18:645–52.
27. Khatib JM, Wild S. Sulphate resistance of metakaolin mortar. *Cem Concr Res.* 1998;28:83–92.
28. Asbridge AH, Jones TR, Osborne GJ. High performance metakaolin concrete: results of large scale trials in aggressive environments. In: Dhir RK, Hewlett PC, editors. *Proceedings of the international conference on concrete in the service of mankind*, Radical Concrete Technology. Dundee, Scotland; 1996. pp. 13–24.
29. Eberl DD. U.S. geological survey, Open-File Report 03-78; 2003, 40 pp.
30. Bágel Ľ, Živica V. Relationship between pore structure and permeability of hardened cement mortars: On the choice of effective pore structure parameter. *Cem Concr Res.* 1997;27:1225–35.
31. Frias M. The effect of metakaolin on the reaction products and microporosity in blended cement pastes submitted to long hydration time and high curing temperature. *Adv Cem Res.* 2006;18:1–6.
32. Torres J, de Gutiérrez RM, de Puertas F. Effect of kaolin treatment temperature on mortar chloride permeability. *Mater Constr.* 2007;57:61–9.