LONG – TERM PROPERTIES OF CEMENT COMPOSITES WITH VARIOUS METAKAOLINITE CONTENT

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The optimal temperature transformation of kaolin sand to metakaolin sand (MKS) resulting in complete conversion of kaolinite to pozzolanic active metakaolinite (MK) is 650°C in the time of 1 hour. To obtain information on mechanism of pozzolanic reaction in studied binary system, the cement pastes with two MKS at substitution level of Ordinary Portland cement (OPC) with MKS by 10, 20 and 40 wt. % corresponding to 3.6 - 16.0 % MK content in pastes, were tested. Pozzolanic reaction of MK with hydrating OPC was clearly confirmed mainly by XRD and thermal analyses. This process accompanied with gradual reduction of $Ca(OH)_2$ content was the most intense in pastes with the highest MK contents (14.4 and 16.0 %). The decrease of micropore and total pore volume until MK content in paste of 7.2 % is measure of pore structure improvement specified as pore structure refinement. Until MK content of 8.0 % in paste, micropores portion with pore radius less than 10 nm rises and pore radius in the range between 10 and 100 nm declines. Resulted compressive strengths of related cement pastes with various MK content were comparable with strengths of pastes without MK. The obtained results confirmed that MKS can be used as promising additive in OPC to form prospective blended cements.

INTRODUCTION

Generally, the development of construction materials offering the desirable benefits is the main challenge in this millennium. Though the manufacture and utilization of Ordinary Portland cement (OPC) remains considerable, the disadvantages begin to be predominant. Some problems are connected with energetical, ecological and costly aspects. The global cement production rate is approximately 1.2 billion tons per year and it is expected to grow exponentially to about 3.5 billion tons by the year 2015 [1]. About 4.2 GJ energy is required to produce 1 tonne of OPC, resulting in approximately 0.8 - 1.0 tonne of carbon dioxide release into the atmosphere [2]. Cement production involves less CO_2 emission and energy consumption than other building materials such as steel. However, due to the high amount of cement that every year is produced, global annual production of cement accounts for about 8 - 10 % of the global anthropogenic CO_2 emission [3]. It is not surprising that in recent times there has been a lot of interest in the development of less energy intensive and more ecological cements. To this respect, artificially-made materials, industrial by-products or natural materials (such as limestone) can be used as supplementary cementitious materials (SCMs) substituting OPC in composites [4-7]. Thus, cement plants produce blended cements, comprised materials such as silica fume, fly ash and metakaolin. These materials are specified as pozzolans.

When pozzolana particles are dispersed in the cement paste, they react according to the pozzolanic reaction but additionally they also generate a large number of nucleation sites from the precipitation of the hydration products. Therefore, this mechanism makes the paste more homogeneous and dense as for the distribution of the fine pores [8]. This is due to the pozzolanic reaction. In general, the pozzolanic effect depends not only on the own pozzolanic reaction, but also on the physical or filler effect of the smaller particles in the mixture.

Because of presented pozzolanic effect and resulting properties, metakaolin has been studied in recent years [9, 10]. The raw material input in the metakaolin manufacture is kaolin. Kaolin is formed as a result of the alteration of aluminosilicates (feldspar, feldspathoid, spodumene, sillimanite) and volcanic glasses, sometimes altered by acidic hydrothermal solutions [11]. It is usually white, but also grey and yellow. Kaolin is applied in the construction industry as a raw material in the production of white cement (e.g. in Turkey) and as a pozzolanic material for cement composites (in the calcined form of metakaolin). Kaolinite is related common mineral and its crystals are usually arranged in pseudohexagonal plates forming flaky aggregates and it has the same chemistry as its polymorphs [11].

Thermally treated kaolin at high specific temperatures gives „calcined kaolin" or metakaolin with characteristic properties such as high brightness, hydrophobicity, abrasive nature and improved electrical properties. The temperature transformation of kaolin into metakaolin is expressed in simplified form as follows [12]:

$$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O \xrightarrow{650\text{-}800°C} 2SiO_2 \cdot Al_2O_3 + 2H_2O \quad (1)$$
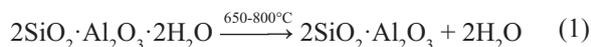
When heated kaolin becomes calcined, losing up to 14 % hydroxyl water is characteristic [13]. The resulted metakaolin is a reactive aluminosilicate pozzolan that is grinding to a high fineness. Chemically, the main components are SiO_2 and Al_2O_3 and in smaller quantities Fe_2O_3, CaO, MgO, SO_3. The efficiency of metakaolin as a pozzolan in cement composites is mainly governed by high content of SiO_2 and Al_2O_3.

Metakaolin on reaction with $Ca(OH)_2$ in the presence of water in cement composites produces C–S–H gel at ambient temperature and reacts with $Ca(OH)_2$ to produce alumina containing phases [14]. It was shown that calcium hydroxide can be virtually eliminated from the cement matrix by using sufficient adapted metakaolin concentrations. It is necessary to notice that metakaolin particles are nearly 10 times smaller than cement particles, which results in a final effect in a denser structure of concrete composite. Considering the fact that great surface structure and specific surface area of metakaolin are its main properties, the microstructure of high quality in cement paste is expected [15].

Thus, metakaolin as a typical pozzolan exhibits pozzolanic activity. This term is defined as the measure of its ability to react with $Ca(OH)_2$ in the presence of an excess of water. According to Frias et al [16], metakaolin exhibits lower pozzolanic activity than silica fume but significantly greater than fly ash.

Metakaolin is used in construction industry as substitution of cement since 1960´s and the interest in this material has considerably increased in recent years. Pure commercial metakaolin has been successfully used as a supplementary cementitious material in composites since 1990 [12, 17, 18]. Overall strengths and durability of the metakaolin cement composites are greatly affected by the physical and chemical properties of metakaolin [19, 20]. Many works have shown that metakaolin used as a partial substitution in cement composites, gives significantly enhanced early strength and increased long-term strength [22]. 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. Calderone et al [13] have produced concretes with 5 and 10 % of metakaolin which showed enhanced strengths at age up to 365 days.

The use of metakaolin has received considerable interest in recent years and is well documented in cement and concrete industry [23-28]. The presence of metakaolin affects the pore structure of cement composites towards the pore structure refinement [9, 29, 30] increasing the total pore volume and decreasing the pore median radius [9, 16, 17]. It was found that the proportion of pores radii less than 0.22 μm within the pastes increased with the increase in metakaolin content and curing time [31]. These processes lead to permeability reduction [32]. Alkali activation of metakaolin produces a cementitious material - a zeolitic precursor with excellent cementing properties in terms of mechanical strength [33]. Cement-based materials are often subjected to action of aggressive environment [34, 35] and therefore it is important that composites with metakaolin exhibit high chemical resistance against sulphate and chloride attack [36-39].

Kaolinite content in kaolin clays varies giving information on kaolin quality. The kaolinite content in the range 75 to 94 % is typical for kaolin of high quality [40]. Kaolins with kaolinite content of 40 - 65 % may be classified as a medium-quality raw material which is sufficiently suitable for use [11, 12]. Schwartzman [12] demonstrated that useful properties of metakaolin are preserved even at reduced (ca 30 %) kaolinite content in the raw material. Thus, the worthy properties of composites with metakaolin (especially strengths) were observed in the kaolin of low-quality in Korea [41]. Alike kaolins with decreased kaolinite content (38 - 52 %) occurs in Greece. However, their utility properties are very similar than commercial metakaolin with very high content of metakaolinite (96 %) [42, 43]. This fact is related especially to setting times and hydration, strength development as well as durability. These raw materials are often marked as poor Greek kaolins.

Natural kaolins with low kaolinite content are in Slovakia known as kaolin sand [44-47]. These kaolin sands are not suitable for glass and ceramic industry as input raw material after laboratory-made treatment [48]. However, the utilization of this material in cement composites seems to be beneficial. Therefore, in this paper the long-term properties of cement systems containing metakaolin sands with various metakaolinite content in composites (3.6 - 16 %) have been studied.

EXPERIMENTAL

Materials

Kaolin in the form of kaolin sands with various kaolinite contents has represented primary material-origin for subsequent conversion in the experiment. Two kaolinite sands from Vyšný Petrovec deposit (Slovakia) containing 36.0 % and 40.0 % of kaolinite were ground and sieved under 63 μm. These specimens were subjected to the temperature alteration to metakaolin sands (MKS) at the heating rate 10°C/min; exposure time 1 hour at 650°C; the self-acting cooling rate 10°C/min. Temperature transformation at 650°C has induced

the total conversion of kaolin sands to MKS. Thus, metakaolinite (MK) contents in resulted MKS have represented the same values – 36 % in MKS 1 and 40 % in MKS 2 – as original kaolinite contents in kaolin sand.

Ordinary Portland cement CEM I 42.5 R (OPC) – manufactured in Holcim Rohožník (Slovakia) cement plant in accordance with STN EN 197-1 [49] was used for preparation of tested cement pastes. Blended OPC – MKS systems were prepared through substitution of OPC with MKS by 10, 20 and 40 wt. % of individual MKS. Subsequently as resultant, the MK content in the prepared cement pastes was calculated. Tested paste specimens – cubes with edge of 20 mm – were made with water/solid ratio of 0.5. The cement paste with 100 % OPC by weight (without MKS) was prepared as reference with the same water/cement ratio of 0.5. For long-term evaluation of cement systems with MKS, the water curing was used. Tested cubes were kept in water at 20 ± 1°C until 365-day testing. Water was monthly changed to be re-fresh.

Chemical composition of metakaolin sands (MKS1 and MKS2) used in the experiment is presented in Table 1. Results of chemical analysis of OPC and its standard strengths are shown as well. Mineralogical composition of MKS given by contents of clay and nonclay minerals is introduced in Table 2. The content of most substantial mineral-active metakaolinite (MK) differs each other in

MKS1 and MKS2 only by 4 %. Other minerals represent practically inert (non-reactive) components which are inconsiderable in the process of pozzolanic reaction in cement composites. However, because of overall relatively low content of MK – unlike commercially made MKS with 90 % of MK – the Slovak MKS are indicated as poor MKS.

On the basis of MK content in MKS and substitution of OPC by MKS for related cement paste specimens, the MK content in individual cement paste was calculated (Table 3), Thus, defined MK content varies from 3.6 % to 16 %. Consequently, the properties of cement paste with listed range of MK contents was proved including physical-mechanical characteristics, phase composition as well as parameters of the formed pore structure.

Table 3. Metakaolinite (MK) contents in metakaolin sand (MKS), substitution levels of Ordinary Portland cement (OPC) by MKS and contents of MK in prepared cement pastes.

Meta-kaolin sand	Metakaolinite content in metakaolin sand (%)	Substitution of PC by metakaolin sand (%)	Metakaolinite content in cement pastes (%)
MKS 1	36.0	10	3.6
MKS 2	40.0	10	4.0
MKS 1	36.0	20	7.2
MKS 2	40.0	20	8.0
MKS 1	36.0	40	14.4
MKS 2	40.0	40	16.0

Test methodologies and methods

Chemical composition of input materials (MKS 1, MKS 2 and OPC) was assessed by standard analytical methods. Quantitative X-ray analysis was accomplished by the Rock Jock program [50]. This program fits the sum of stored XRD patterns of pure standard minerals (the calculated patterns) to the measured pattern by varying fraction of each mineral standard pattern, using a 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 (interval standard) to 1.000 g of each MKS sample. The mixture was ground in a McCrone mill for 5 minutes with 4 ml of methanol that dried and sieved.

The X-ray diffraction tests were made on the Philips diffractometer (The Netherlands) and run in a θ range of 8 - 18° and 22 - 24°. Cu K_α radiation and Ni-filter was used. Thermal studies were performed on OD-102 Derivatograph MOM Budapest (Hungary) in air at the heating range 20 - 1 000°C and heating rate 10 K/min. The pore structure was studied using a mercury intrusion porosimetry (MIP) by high-pressure porosimeter mod. 2000 and macro-porosimetry unit mod. 120 (both Carlo Erba, Italy).

Table 1. Chemical composition of reference Ordinary Portland cement (OPC) and metakaolin sand (MKS).

Component (wt. %)	Portland cement	Metakaolin sand	
		MKS 1	MKS 2
Humidity	0.26	0.24	0.26
LOI *	1.93	1.52	1.07
SiO_2	20.87	-	-
I.R.*	1.48*	62.91**	71.77**
Fe_2O_3	2.72	2.73	1.71
Al_2O_3	5.58	28.92	21.40
CaO	61.33	1.02	0.72
MgO	2.58	0.94	0.85
SO_3	2.43	0.03	0.07

* Loss on ignition; I.R.; ** Insoluble residue + SiO_2

Standard strength of Ordinary Portland cement (MPa)	
1-day	14.2
3-day	36.0
7-day	43.1
28-day	56.2

Table 2. Mineralogical composition of metakaolin sand (MKS) identified by RockJock program in XRD diffraction analysis.

Meta-kaolin sand	Composition (%)				
	Clay minerals			Non clay minerals	
	Metakaolinite	Illite	Muscovite	Quartz	Feldspar
MKS1	36.0	6.9	31.0	21.9	4.2
MKS2	40.0	6.2	31.9	18.1	3.8

RESULTS AND DISCUSSION

The long-term 365-day compressive strengths of studied cement paste with MKS are illustrated in Figure 1. It is clear that with the increase of MK content, the related strengths are slightly decreased. This fact is valid until MK content of 14.4 %. However, slight rise of strength in the paste with 16.0 % MK content was observed. The reduction of strengths in the tested pastes based on MK content ranged between 5.2 - 21.5 % in comparison with the reference cement paste without MKS. This is mainly caused by the pozzolanic reaction of MK with hydrated cement, which is connected with $Ca(OH)_2$ consumption, formation of gel-like hydration products of CSH and CAH type and the pore structure refinement as shown later in this section.

The results of thermal analysis are evaluated in Figures 2-4 and Table 4. Pozzolanic activity of MK (Figures 2 and 3) is confirmed by the DTA plots. The increase in MK content results in gradual $Ca(OH)_2$ consumption in the cement paste (Figure 4). This process is the most intense in the pastes with the highest cement dilution by MK (14.4 and 16.0 %). In contrast, $CaCO_3$ and bound water contents represented by the presence of CSH and CAH gels remain approximately unchanged (Table 4). Thermal analysis results show, as also stated previously [45], that the pozzolanic effect is present at any dilution of OPC by MK. The patterns obtained by XRD analysis are shown in Figures 5 and 6. The results proves evident $Ca(OH)_2$ consummation, mainly at higher dilution of the cement by MK.

The results obtained from mercury intrusion porosimetry (MIP) are summarized in Tables 5 and 6 and Figures 7-10. Volume of micropores is estimated between median radii 3.7 nm and 7 500 nm and total pores between 3.7 nm and 0.6 mm. Pore structure is evidently refined until 7.2 % cement substitution by MK (Table 5) when compared to that of the reference OPC paste. Cement dilution by 3.6 to 7.2 % of MK results in the pore structure improvement but, contrary, not in the strength uptakes (Figure 1). The MK content of 7.2 % in the paste causes ca 10 % strength reduction relative to the reference paste. Pore volumes measured in the pastes with 8.0 to 16.0 % of MK start to growing up together with total porosity increase. Though permeability coefficients – as the measure of density and compactness - at 14.4 % and 16.0 % dilution of the cement by MK show slight increase, however the resulting impermeability of studied OPC-MK systems is still enough appropriate to supply sufficient impermeability of the studied OPC-MK systems.

Figure 7 illustrates dependence of total pore radius on MK content in studied pastes. The MK content in

Table 4. Evaluation of some parameters of thermal analysis in dependence on metakaolinite (MK) content.

Metakaolinite content (%)	Bound water content (%)	CaCO$_3$ content (%)	Total ignition loss (%)
0	12	10	24
3.6	12	8	23
4.0	13	10	24
7.2	13	8	22
8.0	13	9	22
14.4	13	8	18
16.0	14	9	23
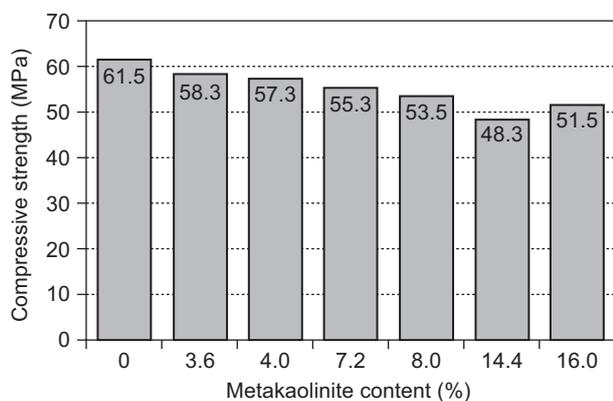
Figure 1. Dependence of 365-day compressive strengths on metakaolinite content.
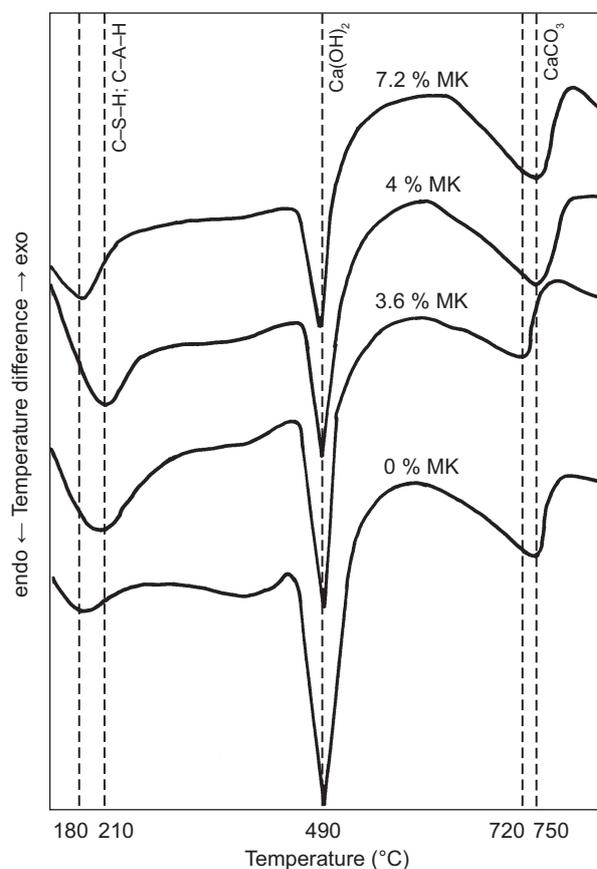
Figure 2. DTA curves of cement pastes with 3.6 - 7.2 % of metakaolinite content kept 365 days in water.

paste until 8 % favourably affects the values of this factor. These values were gradually decreased opposite to reference paste. This contributes to pore structure refinement as well. However, pore radius rises in the structure of pastes with the highest MK contents (14.4 and 16.0 %). Apart from MK content in paste, the values of micropore radius are approximately at the similar level (Figure 8). By contrast with these facts, the pore size distribution represents portion of individual pore

Table 5. Parameters of pore structure in dependence on metakaolinite (MK) content.

Metakaolinite content (%)	Total pore volume (mm³/g)	Micropore volume (mm³/g)	Total porosity (%)	Permeability coefficient K×10⁻¹⁰ (m.s⁻¹)
0	121.7	116.5	20.7	0.1
3.6	108.2	105.6	18.6	0.1
4.0	105.8	100.7	18.2	0.1
7.2	97.3	94.4	16.3	0.1
8.0	101.8	96.7	16.6	0.1
14.4	114.2	109.1	19.0	0.2
16.0	154.7	144.5	23.8	0.2

Table 6. Pore size distribution obtained by Hg-porosimetry in dependence on metakaolinite (MK) content.

Metakaolinite content (%)	Pore radius portion (%)			
	< 10 and 10-100 nm	10²-10³ nm	10³-10⁴ nm	>10⁴ nm
0	95	1	2	2
3.6	98	0	0	2
4.0	94	2	2	2
7.2	93	4	0	3
8.0	95	1	2	2
14.4	91	3	5	1
16.0	90	2	6	2

Figure 3. DTA curves of cement pastes with 8.0 - 16.0 % of metakaolinite content kept 365 days in water.
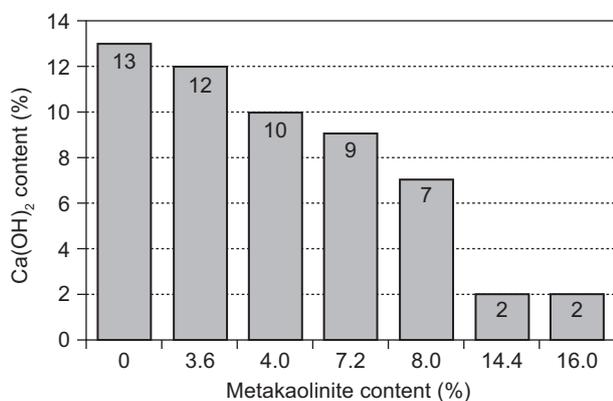
Figure 4. Reduction of Ca(OH)₂ content at increasing metakaolinite content.
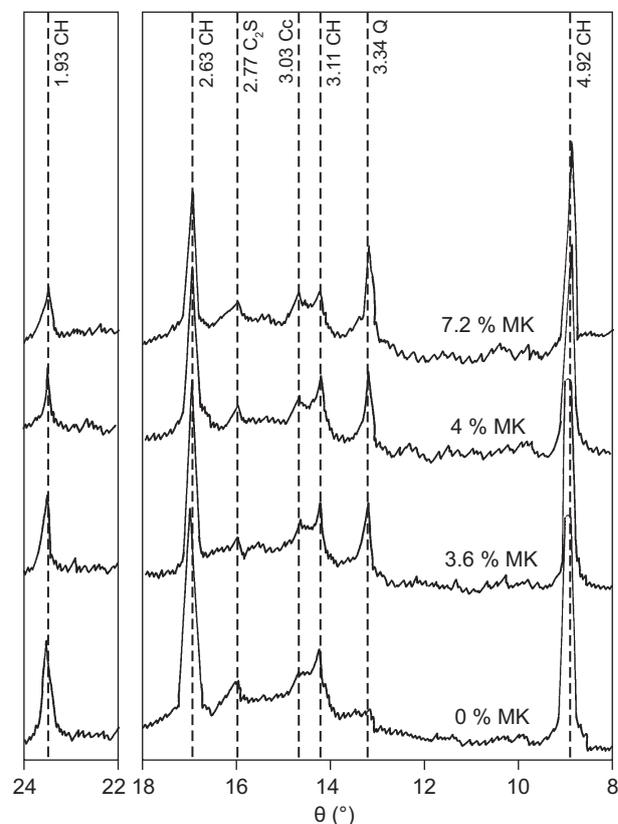
Figure 5. XRD patterns of cement pastes with 3.6 - 7.2 % of metakaolinite content kept 365 days in water.

radius sizes in the paste and provides more specific information mainly on occurrence of fine pores (< 10 nm and 10 - 100 nm). These dependences are presented in Table 6 and Figures 9 and 10. Until MK content of 8 % in paste, the portion of micropores with pore radius less than 10 nm rises and micropores with radius between 10 and 100 nm declines (Figures 9 and 10). However, the highest MK content (14.4 and 16.0 %) in the paste contributes to light anomalies. This fact is mainly caused by the increase in portion of pore radius with 1 000 - 10 000 nm (5 and 6 %) in the relevated pastes.

Table 6 obviously indicates this actuality. This results in a sudden but temperate enhancement in total pore and micropore radii (Figures 7 and 8) as well as slight reduction of compressive strengths (Figure 1).

The observed slight pore structure coarsening is attributed to insufficient water supply necessary for achieving satisfactory plasticity to avoid the larger pore occurrence in the pastes. It is therefore thought that water to solid ratio of 0.5 is not suitable for preparation
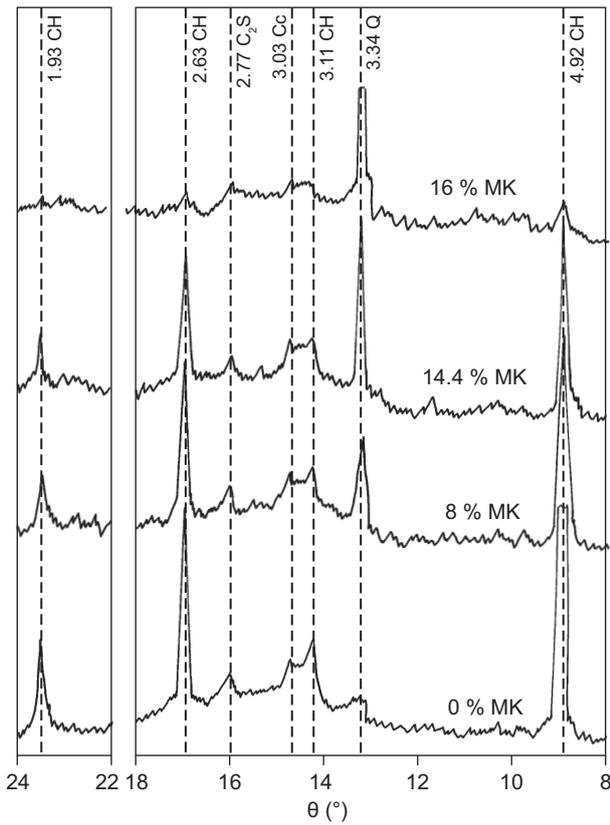
Figure 6. XRD patterns of cement pastes with 8.0 - 16.0 % of metakaolinite content kept 365 days in water.
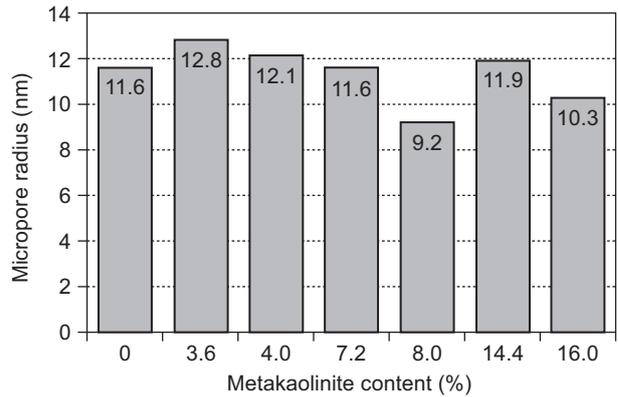
Figure 8. Relation between micropore radius and metakaolinite content.
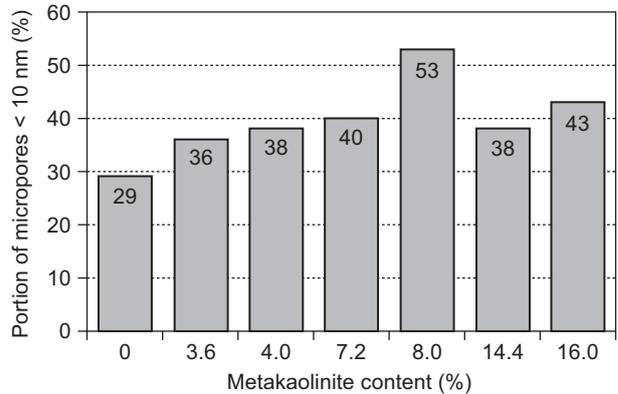
Figure 9. Dependence of micropores with pore radius < 10 nm on metakaolinite content.
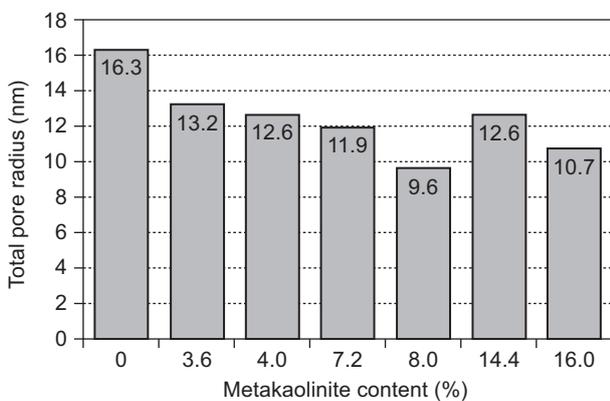
Figure 7. Relation between total pore radius and metakaolinite content.
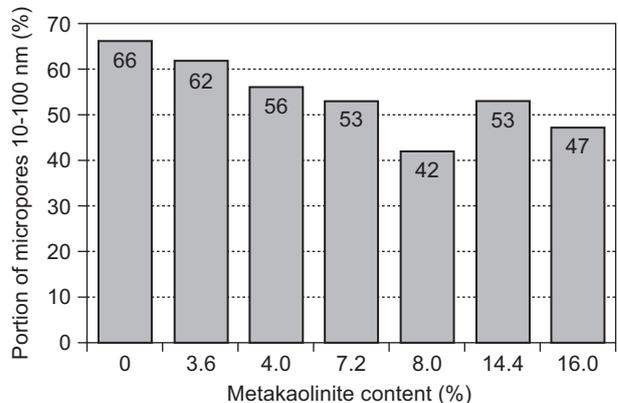
Figure 10. Dependence of micropores with pore radius in the range 10 - 100 nm on metakaolinite content.

of the cement pastes with the substitution of cement by MK higher than 14.4 % by weight.

All the obtained results confirmed that MKS can be used as promising mineral addition to OPC to form prospective new blended cements.

CONCLUSIONS

Based on the performed tests, the following conclusions are drawn after one-year water curing:

1. Compressive strengths of the pastes with 3.6 to 16.0 % substitution of the cement by metakaolinite vary within 58.3 to 48.3 MPa opposite to 61.5 MPa of the reference Portland cement paste. The higher strength losses are related to the higher cement dilution by MK. Also a positive effect of pozzolanic activity of metakaolinite reduces a higher lost of compressive strengths.
2. $Ca(OH)_2$ is evidently consumed by pozzolanic activity of metakaolinite. Opposite to time-relevant strength reductions, the lower $Ca(OH)_2$ content is present in the pastes containing higher metakaolinite. This effect is dominant at 14.4 and 16.0 % substitution of the cement by metakaolinite.
3. Pore structure refinement in the cement paste having 3.6 % and 8.0 % MK contents is confirmed opposite to the slight coarsening at 14.4 - 16.0 % cement dilution by MK. Pore structure coarsening is caused by the 5 - 6 % portion of larger pores with radii between 1 000 and 10 000 nm. The observed larger pores increment is thought to be caused by a starting batch water lack over 14.4 % metakaolinite content in cement pastes.
4. Reduction of the Ordinary Portland cement through the use of metakaolin sand in amounts of 10 % up to 40 % by weight, which is proportional to 3.6 % up to 16.0 % of metakaolinite content in cement pastes, is found perspective for near future applications.
5. These findings seem to be of great importance because metakaolin sands were found not suitable for glass and ceramic industry as input raw material as exhibited previously [48]. The only interesting opportunity for metakaolin sands application in building practice remains the cement industry.

Acknowledgement

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