# Properties of Cement Pastes with Different Particle Size Fractions of Metakaolin

M. Boháč, R. Novotný, F. Frajkorová, R. S. Yadav, T. Opravil, M. Palou

*Abstract*—Properties of Portland cement mixtures with various fractions of metakaolin were studied. 10% of Portland cement CEM I 42.5 R was replaced by different fractions of high reactivity metakaolin with defined chemical and mineralogical properties. Various fractions of metakaolin were prepared by jet mill classifying system. There is a clear trend between fineness of metakaolin and hydration heat development. Due to metakaolin presence in mixtures the compressive strength development of mortars is rather slower for coarser fractions but 28-day flexural strengths are improved for all fractions of metakaoline used in mixtures compared to reference sample of pure Portland cement. Yield point, plastic viscosity and adhesion of fresh pastes are considerably influenced by fineness of metakaolin used in cement pastes.

*Keywords*—Calorimetry, cement, metakaolin fineness, rheology, strength.

## I. INTRODUCTION

METAKAOLIN (MK) is very promising supplementary cementitious material that still waits for wider implementation in cement industry production. It is produced by thermal activation of kaolinite as a main constituent of kaolin at approx. 700-800°C. As a result of burning, the crystal lattice of the kaolinite collapses into a quasi-amorphous matrix consisting predominantly of reactive alumina that influences early hydration and silica which provide the pozzolanic reaction at later ages. Its use in high-performance mortars and concrete [1]-[3] has been studied in last few decades. MK like other pozzolanic materials reacts with the portlandite (CH) to produce additional calcium silicate and calcium aluminate hydrates which has the added effect of pore blocking and permeability reduction [4], [5], thus further improving material durability. Micro-filler properties of MK similar to those described for silica fume was predicted by [6] and formulated by [7] considering the diffusion of chloride ions through cement mortars containing MK.

MK in Portland cement (PC) mixtures can act both as very fine filler and reactive micro-aggregate depending on its relative particle size. Implementation in cement production is often limited by the material price, which is more or less dependent on the MK composition and fineness. While on the one hand, considering the MK as cheaper substitution of silica fume in high-performance concrete on the other hand, there is the possibility of using even cheaper MK with coarser grain size distribution as micro-filler with reduced reactivity but as a material that usefully complements the particle size distribution of the PC, whether it is beneficial for cement paste, mortar or concrete.

The objectives of the paper are to find the possible applications for MK fractions of different fineness in cement mixtures. Relations between fractions of MK and its impact on strength development, hydration heat and rheology are discussed in the paper.

## II. EXPERIMENTAL

TABLE I
CHEMICAL AND PHYSICAL PROPERTIES OF PC AND MK

|  | PC | MK ref. |
|---|---|---|
| $SiO_2$ | 20 | 53 |
| $TiO_2$ | - | 0.3 |
| $Al_2O_3$ | 4 | 43 |
| $Fe_2O_3$ | 3 | 1 |
| MgO | 2 | 0.2 |
| CaO | 66 | 0.3 |
| $Na_2O$ | 0.12 | 0.04 |
| $K_2O$ | 0.78 | 0.9 |
| $SO_3$ | 3.0 | - |
| Cl- | 0.05 | - |
| LOI | 3.27 | 1.1 |
| Humidity | - | 0.5 |
| Density/kg.m$^{-3}$ | 3181 |  |
| Spec. surface/m$^2$.kg$^{-1}$ | 309 |  |

TABLE II
MATERIALS PARTICLE SIZE DISTRIBUTION

| sample | x (50%) | x (90%) | x (99%) |
|---|---|---|---|
|  | μm | | |
| PC | 10.84 | 42.62 | 75.57 |
| MK 2.06 | 2.06 | 4.86 | 8.11 |
| MK 2.64 | 2.64 | 6.57 | 10.20 |
| MK 3.12 | 3.12 | 8.86 | 14,41 |
| MK 3.27 | 3.27 | 9.80 | 15.15 |
| MK 4.97 | 4.92 | 11.08 | 15.90 |
| MK 7.85 | 7.85 | 13.80 | 17.16 |
| MK 12.20 | 12.20 | 30.82 | 53.55 |

Fractions of MK were prepared from commercial MK produced by Sedlecký kaolin, a.s. PC used was also commercial product CEM I 42.5 R from Českomoravský cement a.s., Heidelberg Cement group, plant Radotín. Chemical and physical properties of PC and MK are given in Table I. MK was classified in different granulometric fractions

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using Alpine classifier (system 50ATP, jet mill system 100AFG, classifier mill 50 ZPS). Granulometry of different fractions measured by laser particle size analyzer Sympatec Helos are shown in Table II. Samples were sorted accordingly to its mean particle size value of used MK fraction. PC was replaced by 10% of MK (reference MK and each classified fraction) in mixtures. Pure PC was taken as reference sample. Dry mixes were homogenized prior testing in three-dimensional rhythmically pulsing motion "Turbula" mixer for 30 minutes. Calorimetric measurements of cement pastes were conducted on TAM Air isothermal calorimeter. The mixtures of blended cements were placed in ampoules and lid. The water was injected in the ampoule using syringe. Four grams of sample with w/s=0.4 (water to solids) were used for all samples. The samples were gently stirred after adding of water and placed in the calorimeter. The measurement started few seconds after adding of the water. Heat flow was continuously measured for 48 hours.

Compressive and flexural strength were measured on mortar bars (1 part of cement, 3 parts of standard sand) after 1, 2, 7 and 28 days of hydration with w/s=0.5. Tests were following EN 197-1 only due to small amount of some fractions small prisms (2 x 2 x 10 cm) were measured.

Rheology tests were done by rotational rheometer Discovery HR 2 (TA Instruments). Geometries of parallel plates and outer cylinder with inner vane rotor were used in temperature controlled regime provided by Peltier system. All samples were mixed in small laboratory bowl by hand and the measurement started after 5 minutes from the time the water was added. With respect to higher water demand of fresh pastes containing MK the w/s was 0.45 for all analyses except flow measurement where w/s was 0.5 due to used geometry and its limits. All the geometries were calibrated for inertia, friction and rotational mapping prior to testing. Measuring gap thickness for parallel plate geometry tests was 2500 μm. Flow was measured using geometry of coaxial cylinders with inner vane rotor. This geometry was chosen to prevent slippage and sedimentation of particles during test. Samples were measured at temperature of 25 °C, shear rate 0.1 – 150 – 0.1 (1/s) – 120 sec., pre-shear 100 1/s for 30 seconds and sampling interval 1 s/pt. Adhesion was monitored by axial force development in tension regime by 20 mm parallel plates. Samples were tested without pre-shear at 25 °C, gap distance 0-400 μm with gap speed of 1 μm/s and sampling interval 1 s/pt starting from 0 axial force. Results of analyses were evaluated by TRIOS software that is provided by standard rheological models.

Nomenclature used for mixtures of PC and MK: PC – Portland cement CEM I 42.5 R, MK – metakaolin, value – mean particle size x (50%).

## III. RESULTS AND DISCUSSION

### A. Isothermal Calorimetry

Isothermal calorimetry is due to its sensitivity excellent instrumental technique for describing the role of MK and other supplementary materials in hydration process in cement based mixtures. The results of the measurement show clear trend

between fineness of MK fraction used in mixtures and heat flow (mW) development in time (Fig. 1). Calorimetric curves show three main peaks during 48 hours of hydration. The role of the fineness of MK can be evaluated from intensities and position of the peaks thereby heat flow maximum (HFmax) and time of the heat flow maximum (tmax) are described. The acceleration of hydration is present with increasing fineness of MK. This effect can be seen on the rate of exothermic reactions or more precisely from tmax for individual exotherms. The first peak that occurs in first minutes of hydration process is due to rapid hydration of $C_3A$. Dormant period that is closely related to the workability of the fresh cement paste is characterized by the throw between the first and the second peak. As the length of the dormant period or slow reaction period for the $C_3A$ and sulfate system has been reported to increase approximately as the square of the initial sulfate/aluminate ratio of the system [8], [9]. The finer and more reactive fractions of MK lower this ratio by contribution of reactive alumina into system and shorten this period. The acceleration period is characterized by second and third peak. The second peak, in terms of heat flow development the most significant one, is related to congruent dissolution of main cement clinker phase alite ($C_3S$) [10].
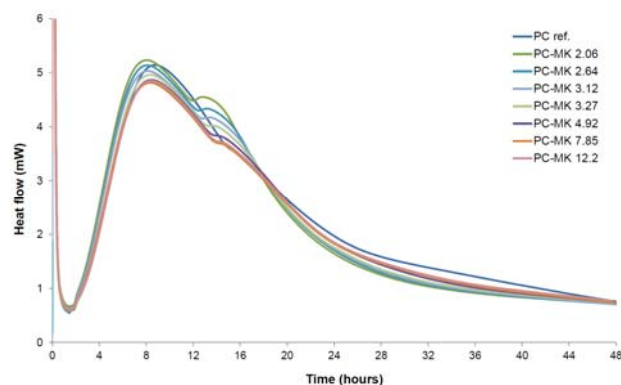


Fig. 1 The role of the fineness of MK on heat flow development of cement pastes

The third peak or it can be called shoulder of the second peak is related to renewed dissolution of $C_3A$. Some authors propose renewed formation of ettringite (second formation of ettringite) in system of pure PC [10], [11]. The analogy can be found between pure PC and mixtures with MK. MK as an additional source of reactive alumina strongly influences the third peak on calorimetric curve. There is clear trend between fineness of MK fraction and third peak intensity and position (time of reaching maximum – t-max.). Peaks gain in intensity and t-maxima move to earlier time with increasing fineness of MK used. In deceleration period the process is controlled by a diffusion process but also increasing size of reacting particles, lack of space or water are important factors [10].

Acceleration effect of MK on cement hydration [12], [13], [14] is closely related to its fineness. Development of total hydration heat is also influenced by fineness of MK. MK as less hydraulic active constituent lowers the values of total heat released during first 48 hours of hydration. There is rough

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trend of increase of total heat with increasing MK fineness. Values of total heat after 24 and 48 hours of hydration are given in Table III.

TABLE III
HYDRATION HEAT AFTER 24 AND 48 HOURS

| sample | Q total 24h | Q total 48h |
|---|---|---|
| | (J/g) | |
| PC | 270 | 370 |
| PC-MK ref. | 270 | 368 |
| PC-MK 2.06 | 280 | 366 |
| PC-MK 2.64 | 276 | 364 |
| PC-MK 3.12 | 272 | 361 |
| PC-MK 3.27 | 265 | 357 |
| PC-MK 4.92 | 263 | 358 |
| PC-MK 7.85 | 260 | 358 |
| PC-MK 12.2 | 261 | 359 |

*B. Strength Development*

The role of fineness of MK was monitored on compressive and flexural strength development after 1, 2, 7 and 28 days of hydration on mortar bars. Samples with different fineness of MK were compared to reference sample of pure PC.

Mixtures with MK have slower compressive strengths development compared to reference sample. As expected the best results were evaluated for the finest fraction of MK (CMK 2.06). The trend of decreasing compressive strengths is not clear considering sample CMK 7.85 that has considerably higher compressive strength in comparison with CMK 4.92 (Fig. 2). Previous study [12] proved that very early strength enhancement is due to a combination of the filler effect and accelerated cement hydration. As we dealing with role of filler effect we must consider the shape of MK particles that are not isometric but of a platy clay-like texture. Also relatively broad distribution of particles within one fraction of MK must be taken into account. Further studies supported by microstructural studies must be done for this topic.
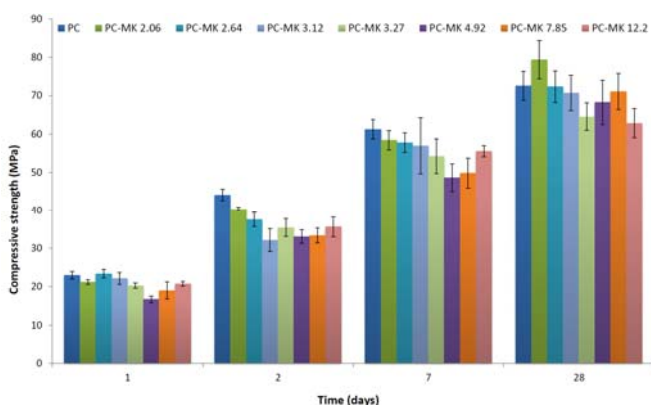


Fig. 2 The role of fineness of MK on compressive strengths development of samples

Qian and Li [15] reported that tensile strength of concrete increased systematically with increasing MK replacement finding the best results for 10 % and 15 % replacement. Courard et al. [16] determined the effect of MK additions on the bending strength of mortar. Cement was replaced on a mass basis by 5–20% of MK. Replacement of cement with MK very marginally decreased the bending strength after 3 days and almost attained equal strength after 7 days. In contrast, mortar containing MK attained higher strength after 14 and 28 days. Our results showed that all fractions of MK showed higher 28-day flexural strengths compared to reference sample (Fig. 3). The best flexural strengths were evaluated for CMK 2.64 especially after 1 day and 28 days of hydration.
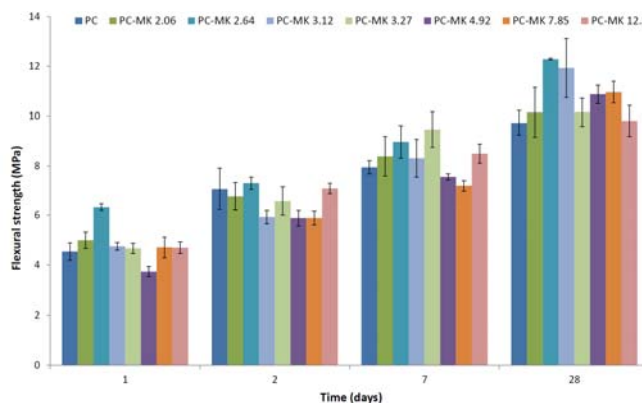


Fig. 3 The role of fineness of MK on flexural strengths development of samples

*C. Rheology*

Flow properties measured by dynamic test in range of shear rate of 0.1 – 150 – 0.1 (1/s) was performed to obtain hysteresis curves, calculate plastic viscosity and yield stress and to characterize shear and time dependent properties of viscoelastic materials. All the mixtures with different MK fractions show thixotropic behavior similar to that of reference PC. Thixotropy is characterized by the area of hysteresis curve of shear stress/shear rate dependency. Curve of viscosity/shear rate dependency show broad distribution of bonds in the studied materials and significant shear-thinning in tested range. Shear dependent properties of reference and MK mixtures are similar. Different models were used to calculate yield point and plastic viscosity with best fitting result for Bingham (1) and Herschel-Bulkley model (2):

$$\tau = \tau_0 + \eta\dot{\gamma} \qquad (1)$$

$$\tau = \tau_0 + K\dot{\gamma}^n \qquad (2)$$

where $\tau_0$ is the yield stress, $\dot{\gamma}$ is the shear rate, $\eta$ is the viscosity and K, n, are the parameters of flow equations. The selection of the models depends on the shape (linear or exponential growth) of the experimentally obtained flow curve. Calculated plastic viscosity and yield stress is strongly dependent on fineness of MK. There is decrease of both parameters with increase of MK median particle size. Previous study [17] proved that the influence of the size and shape of particles on viscosity is dependent on shear intensity. At low shear rates, the smallest particles remain preponderant. At

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higher shear rates, there is a predominance of particles larger or equal than 10 μm, provided that they are not diluted within the powder skeleton due to the increase in the replacement rate. The role of MK fineness on yield stress and plastic viscosity (Herschel-Bulkley model) is given in Fig. 4.
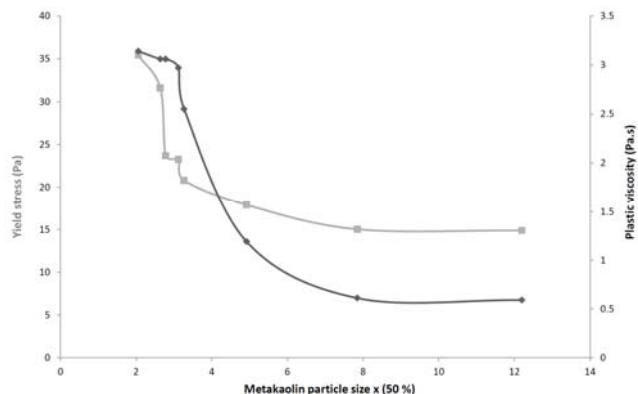


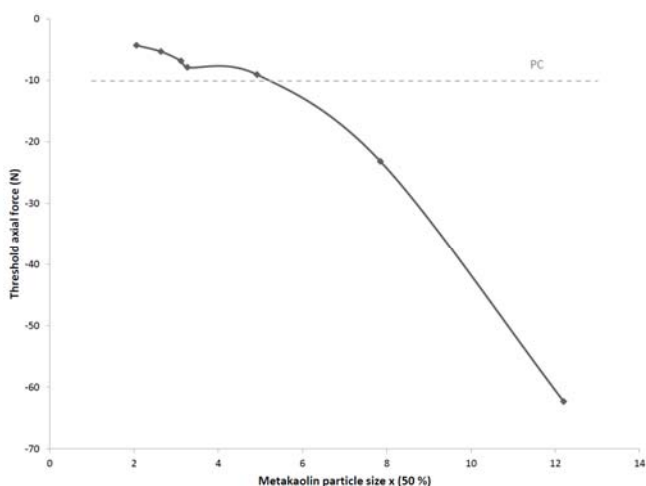Fig. 4 The role of MK fineness on plastic viscosity and yield stress of cement pastes



Fig. 5 The role of MK fineness on adhesion of cement pastes

Adhesion of fresh pastes is with respect of number of applications very important parameter. Adhesion is often modified using special additives that often undesirably influence other properties of the material like strength, workability etc. Results show that MK can significantly affect the adhesion with change of particle size. Simple push-out tests were carried out to evaluate adhesion of interface between cement paste and steel. Adhesion of samples was correlated using maximal axial force [N] as a threshold (tension regime – negative value) after which the material no longer sticks to measuring geometry. Adhesion increases with increasing median particle size of MK. The decisive for adhesion is probably the shape of the MK particles. Particles are platy aggregates of minerals that follow original sheet phillosilicate habitus of original mineral kaolinite. These sheet aggregates tend to orient parallel to measuring plates when pressed by the upper plate before the measurement. This orientation of sheet minerals under applied axial stress has

analogy in formation of metamorphic rocks. The adhesion then is the function of size of MK particles. Considering tension regime of test the higher are negative values of axial force the stronger is adhesion of the material (Fig. 5).

Fresh pastes with MK fractions with x (50 %) higher than 5 μm exhibit higher adhesiveness than pure PC paste (-10.12 N). Practical output of the measurement is that the coarser fraction of MK can be used for applications where enhanced adhesion is demanded and vice versa fractions with mean particle size below 5 microns hinder the adhesion.

## IV. Conclusions

The amount of released heat during hydration process increases and the main exothermic reactions are accelerated with increasing fineness of MK used in studied cement pastes. After depletion of sulfate metakaolin serves as additional source of very reactive alumina and thus contributes to renewed formation of ettringite characterized by third peak on calorimetric curve. Mixtures with MK show slower compressive strength development when only the sample with the finest fraction of MK show higher 28-day strength compared to reference sample. Improved 28-day flexural strengths show mixtures with all fractions of MK. Plastic viscosity and yield stress decrease with increasing MK median particle size. Adhesion increases with increase of median particle size of used MK in cement mixtures. The finest fraction of MK in mixtures with PC may find its application for high-performance concrete and possible partial replacement of considerably more expensive silica fume. Coarser fraction may find its applications for adhesive cementitious materials.

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