Hydration and characteristics of metakaolin pozzolanic cement pastes

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Abstract
The industrial area produces lots of solid waste materials with CO2 emission. One of the most effective ways to solve these problems is the utilization of these waste materials. The production process of cements from its raw materials produces a lot of CO2. The most effective way to decrease CO2 emission of cement industry is the substitution of a proportion of cement with supplementary cementing materials. Cement blended with metakaolin (MK) is also required as a countermeasure to reduce the amount of CO2 generation. Metakaolin (MK), Al2Si2O7, is a highly amorphous dehydration product of kaolinite, Al2(OH)4Si2O5. The aim of our research was to investigate the effect of up to 20 wt% substitutions of OPC by MK on the hydration characteristics of MK-blended cement pastes. The physico-chemical properties of the hardened cement pastes were studied up to 90 days of hydration. The hydration products of some selected samples were investigated using XRD, DTA and DTG techniques. The results indicated that substitution of up to 20 wt% OPC by MK as pozzolanic materials resulted in an increase in the standard water of consistency, acceleration of the initial setting times, high compressive strength values at earlier ages and improvement of the mechanical and durability properties.

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Introduction

Cement industry produces the 7% of the global CO2 emission [1]. Researchers investigate the opportunities of how to decrease this level. The application of different supplementary materials can be the proper solution for this problem. With the development of industry, more and more by-products or wastes have been generated, causing serious environmental pollution problems. To solve this problem, a way must be found to consume or decrease such wastes. It has been discovered that...
many industrial wastes can be recycled as a substitute (replacement) for cement or aggregate in concrete [2].

Supplementary cementitious materials (SCMs) are now commonly used to reduce the clinker factor of cement. These materials can improve concrete properties such as compressive strength, durability and impermeability through hydraulic or pozzolanic activity. The main component of SCMs additive is usually an active amorphous SiO₂. The availability of common used industrial by-products such as fly ash, blast furnace slag, rice husk ash, silica fume, and metakaolin. Kaolinitic clays are widely available in the earth’s crust, and a heat treatment between 600 and 800 °C of such clays leads to the dehydroxylations of the crystalline structure of kaolinite to give metakaolin [3–5].

Metakaolin (MK), Al₂Si₂O₅(OH)₄, is a largely amorphous dehydration product of kaolinite, Al₄(Si₂O₅)₂(OH)₄, which exhibits strong pozzolanic activity [6–9]. MK is processed from kaolin clay by calcination at moderate temperature (650–800 °C). At higher temperatures (> 900 °C), the metakaolin undergoes further reactions to form crystalline compounds, the end-products being free silica and mullite. It contains silica and alumina in an active form which will react with CH. The principal reasons for the use of clay-based pozzolans in mortar and concrete have been materials availability and durability enhancement. In addition depending on the calcining temperature and clay type, it is also possible to obtain enhancement in strength, particularly during the early stages of curing. The very early strength enhancement is due to a combination of the filler effect and accelerated cement hydration [10]. Subsequently, these effects are enhanced by the pozzolanic reaction between MK and the CH produced by the hydration of the cement. The reactivity of MK has been linked to its content of pentacoordinated aluminum ions that are formed during the dehydration process [9,11]. The pozzolanic activation of MK by various activators (calcium hydroxide (CH), sulfates as well as alkali hydroxide) and the properties of these binders have been previously reported [2]. The principal reaction between MK and CH was derived from cement hydration, in the presence of water. This reaction forms additional cementitious C-S-H gel, together with crystalline products, which include calcium aluminate hydrate and alumino-silicate hydrates (C₃ASH₆, C₄AH₁₃ and C₅AH₁₆). The crystalline products depend principally on the MK/CH ratio and reaction temperature [4,13]. This reaction, which is even slower than the hydration of plain Portland cement improves the binding properties of blended cements [11].

Production of concrete with the incorporation of industrial waste not only provides an effective way to protect the environment, but also leads to better performance annually, and it is possible to completely consume most of the industrial waste in the world, provided that suitable techniques for individual waste incorporation are available [14]. Many researchers have shown a lot of interest in MK as it has been found to possess both pozzolanic and microfiller characteristics [6]. The replacement with 30 wt% of MK leads to substantial improvement in strength and transport properties of blended concrete when compared to that of unblended concrete [15]. Inclusion of MK as partial replacement of cement enhanced the compressive strength of concrete, but the optimum replacement level of OPC by MK was about 20 wt% [14]. Dinakar et al. [16] studied the effect of incorporating MK on the mechanical and durability properties of high strength concrete for a constant W/B ratio 0.3. MK mixture with cement replacement of 5, 10 and 15 wt% was prepared. The results showed that 10 wt% replacement level was the optimum level of MK content.

The objectives of this study were to investigate the substitution of OPC by MK up to 20 wt% on the hydration characteristics of MK-blended cement pastes. The physico-chemical properties of cement pastes were determined up to 90 days. The hydration products of some selected samples were investigated by using XRD, DTA and DTG techniques.

Materials and methods of investigation

The materials used in this study are ordinary Portland cement (OPC) and kaolinite clay. OPC was provided by Suez Cement Company, Suez plant, El-Ain El-Sokhna, and the kaolinite clay was derived from Ras Abu Zneima Zone, South of Sinai, Egypt.

Metakaolin (MK) is a product from dehydroxylation of a clay mineral, kaolinite, which is very fine powder prepared by firing in a muffle furnace from room temperature up to 800 °C for 2 h. The ground MK passed through 90 μm B.S. sieve. The chemical and physical properties of starting materials are shown in Table 1.

The mineralogical composition of MK is seen from XRD pattern in Fig. 1. It shows the presence of quartz as the main mineral and amorphous alumino-silicate phase, and the amorphous phase is formed as a result of reactions between SiO₂ and Al₂O₃ as well as fluxing oxides impurities oxides at high temperature. The mix composition of MK-pozzolanic cement is shown in Table 2.

Mixes were prepared by substitution of OPC with 5, 10, 15 and 20 wt% of MK. The dry constituents of each mix were mechanically mixed for one hour in a porcelain ball mill using four balls to attain complete homogeneity, then kept in airtight containers for further investigation. The standard water of consistency as well as initial and final setting times was determined.
according to ASTM methods using Vicat apparatus [17]. The mixing of OPC and blended cement dry mixtures was carried out with the required water of consistency and the fresh pastes were first cured with their molds at 100% relative humidity for 24 h as described in a previous work [18]. After 24 h, the specimens were demolded and cured under water until the desired curing times of 3, 7, 28 and 90 days. The hydration reaction of the pastes was stopped using an acetone–methanol mixture [19]. The powdered sample was dried at 70 °C for 2 h, and kept in airtight containers for further investigation. The rate of hydration was followed by the determination of free lime [20]. The combined water content was determined from the ignition loss of the dried paste at 900 °C for 20 min. The bulk density, compressive strength and the total porosity were determined as described elsewhere [21]. The hydration products of some selected pastes were characterized using XRD, DTA and DTG techniques.

**Results and discussion**

**Water of consistency and setting times**

The water of consistency, and initial and final setting times of the neat OPC and OPC–MK blended cement pastes are represented in Fig. 2. Water of consistency of the neat OPC cement paste was 30%, then increased with increasing MK content up to 10 wt% and decreased at 20 wt% MK. The substitution of 5 and 10 wt% of OPC by MK increases the water of consistency of MK-pozzolanic cement pastes up to 30% and 50% respectively. This is due to the high reactivity of MK, very high specific surface area and its amorphous structure. Therefore, it needs more water of consistency [22]. The increase of MK content up to 20 wt% decreases the water of consistency from 30.50% to 29.50%. This is due to the dilution effect of OPC by larger amounts of MK; the excessive amounts of MK act as a filler. OPC replacement by MK up to 20 wt% elongates the initial and final setting times of cement pastes due to coating effect of MK particles on the cement grains as well as the formation of ettringite and the dilution of OPC. As MK increases (15–20 wt%) the initial and final setting times are accelerated due to the slight decrease of water of consistency of cement pastes and filling effect of MK. Generally, setting of binary MK–OPC pastes does not show consistent changes with increase of MK content whereas 15–20 wt% of MK leads to shorten the setting times. So, the increase of MK levels was not proportional to replacement level [23].

**Chemically combined water content**

The combined water contents of OPC and OPC–MK pozzolanic cement pastes are graphically plotted as a function of curing time in Fig. 3. The combined water contents increase gradually with the increase of curing time for all cement pastes as a result of the progressive hydration of anhydrous cement phases as well as pozzolanic reaction and formation of increasing amounts of hydration products. It is clear that the chemically combined water content increases with increasing MK content up to 10%. This is mainly due the increase of water of consistency of cement pastes and very high specific surface area of MK [24] which reacts with CH liberated from hydration of OPC with the formation of additional hydration products.
products, mainly as calcium aluminosilicate hydrates (gehlenite hydrate $\beta$-C$_3$ASH$_x$, calcium aluminate hydrate ($C_4$AH$_x$) and calcium silicate hydrate (CSH)) in the pozzolanic cement pastes which have higher water contents than those of CSH in the neat OPC paste [25].

As the amount of MK increases to 15–20 wt% the combined water content decreases. This is mainly attributed to the dilution of OPC which has higher rate of hydration than MK as well as low water of consistency that decreases the rate of hydration. 10–15 wt% MK substitution acts as a nucleating agent which accelerates the rate of hydration of cement paste.

Free lime content

The free lime contents of OPC and OPC–MK pozzolanic cement pastes are graphically represented as a function of hydration age in Fig. 3. The free lime content of OPC paste increases with the increase of curing time up to 90 days; this is due to the continuous hydration of C$_3$S and $\beta$-C$_3$S which liberate free lime. On the other hand, the free lime contents of all MK-pozzolanic cement pastes increase with increasing hydration time up to 7 days, then decrease up to 90 days. The initial increase of free lime of pozzolanic cement pastes is mainly due to its liberation during the hydration of OPC and then the decrease after 7 days is due to its consumption by the MK.

There are two different processes, the first tending to increase and the other tending to decrease it. At early hydration the rate of liberation of CH by OPC cement pastes exceeds the rate of consumption by aluminosilicate materials of MK; therefore, the CH content increases up to 7 days. After 7 days up to 90 days the rate of liberation of CH by OPC cement pastes is less than the rate of CH consumption by MK and thereby, the CH content decreases. Also, the CH contents of all OPC–MK cement pastes are less than those of OPC at all hydration ages due to the decrease of the amounts of OPC minerals which are the source of CH. It is clear that, the residual CH content of OPC–MK pozzolanic cement pastes is mainly due to the pozzolanic activity of MK.

Fig. 3 Chemically combined water as well as free lime contents versus age of hydration of OPC and OPC–MK pozzolanic cement pastes.

XRD analysis

Fig. 4 shows the XRD-patterns of hydrated OPC paste after curing for 3, 28 and 90 days. The patterns show that the remaining parts of clinker minerals, namely $\beta$-C$_3$S and C$_3$S, are still existing up to 90 days of hydration. This is indicated by the decrease of the relative intensities of their peaks with increasing age of the hydration up to 90 days as a result of hydration of OPC phases. Also, the peaks of portlandite (CH) phase increase with the increase of curing time due to the hydration of the silicate phases of OPC clinker with the formation of CSH and liberation of CH. The carboaluminate hydrates can be formed and increase with time. Calcium carboaluminate is mainly formed by the reaction of atmospheric CO$_2$ with the CAH as a result of hydration of MK-pozzolanic cement [28].

XRD patterns of hydrated cement pastes of M1 (5 wt% MK) cured at 3, 28 and 90 days are shown in Fig. 5. The patterns show that anhydrous phases of clinker minerals $\beta$-C$_3$S and C$_3$S are still existing up to 90 days; their peak intensities decrease with curing time up to 90 days. Also, the intensities of the peaks of portlandite increase with increase of curing time due to the hydration of these silicate minerals with the formation of CSH and liberation of portlandite.

Fig. 6 illustrates the XRD-patterns of OPC and OPC–MK pastes containing 5, 15 and 20 wt% of MK (M1, M3 and M4) up to 28 days of hydration. The patterns show that the intensities of portlandite peaks of OPC paste are higher than those of set of Pozzolanic cement pastes due to the pozzolanic reaction of MK with CH. The intensity of calcite (CaCO$_3$) peak decreases with increasing MK contents; this is an indication for the consumption of CH by MK. The intensity of C$_3$S and $\beta$-C$_3$S minerals decreases with the increase of curing age due to the progress of hydration process. The peak characteristic for CaCO$_3$ is mainly overlapped with that of CSH gel. The quartz peaks are still present in OPC–MK blended cement pastes (M1, M3 and M4) due to its unhydraulic properties.

The peak intensity of CaCO$_3$ decreases with curing time due to the effect of CO$_2$ in the presence of H$_2$O to form Ca(HCO$_3$)$_2$.

Thermal analysis

The most widely used thermal method of analysis is differential thermal analysis (DTA). Fig. 7 illustrates the DTA/DTG thermograms of the hydrated OPC paste after curing up to 90 days. The DTA thermograms show the occurrence of four endothermic peaks at 100, 150, 420–450, 700–750 °C. The endothermic peaks located below 200 °C are mainly due to the dehydration of interlayer water of CSH and CAH or CASH, whereas the endothermic peak appeared at 420–450 °C is due to the decomposition of Ca(OH)$_2$ [26]. The last endothermic peak located at 700–750 °C is due to the decomposition of CaCO$_3$ [27]. It is clear that the intensities of the endothermic peaks characteristic for Ca(OH)$_2$ and CaCO$_3$ increase with the increase of curing time up to 90 days due to progress of hydration of OPC pastes. Also, the endothermic peaks of CSH and CASH increase with curing time due to progress of hydration.
Fig. 4  XRD-patterns of hardened OPC paste cured at 3, 28 and 90 days.

Fig. 5  XRD patterns of OPC–MK pozzolanic cement pastes of M1 cured at 3, 28 and 90 days.

Fig. 6  XRD-patterns of OPC and hardened OPC–MK pozzolanic cement pastes of M1, M3 and M4 cured at 28 days.
The hydration progress can be studied from thermal gravimetric analysis (TGA). The weight loss of the hydrated phases without Ca(OH)$_2$ and CaCO$_3$ increases with curing time. The weight loss increases with a slow rate up to 3 days, followed by a higher rate up to 90 days. The TG losses characteristic for the hydration products at low temperatures (up to 200 °C) are 7.796%, 9.668% and 11.78% after 3, 28 and 90 days, respectively. This means the degree of hydration increases with increasing time of curing. On the other hand, the TG losses characteristic for CH are 4.451%, 5.718% and 6.804% after 3, 28 and 90 days, respectively. The increase of TG loss of portlandite with curing time is due to the continuous liberation of CH as a result of hydration of OPC. The TG losses due to the decomposition of CaCO$_3$ are 4.994%, 6.883% and 5.678% after 3, 7 and 28 days, respectively. Also, the TG losses due to CaCO$_3$ decrease with curing time; this is attributed to the reaction of CO$_2$ and the moisture with CaCO$_3$ with the formation of Ca(HCO$_3$)$_2$.

The DTA/DTG thermograms of hydrated OPC–MK Pozzolanic cement paste made of mix M1 and cured up to 90 days are shown in Fig. 8. Evidently, there are four endothermic peaks. The first endothermic peak located below 100 °C is mainly due to the removal of free water and the decomposition of the amorphous part of calcium silicate hydrates (CSH). The second endothermic peak observed at about 150–160 °C represents the decomposition of crystalline part of CSH, CAH, CASH as well as the presence of carboaluminate and gehlenite hydrates [28]. The third endotherm located at about 450 °C represents the dehydration of calcium hydroxide (CH) [5,26]. The last endothermic peak located at 710–715 °C is due to decomposition of CaCO$_3$ [26,27]. It is clear that the second endothermic peak located at about 155 °C increases with curing time due to the formation of excessive amounts of CAH and CASH on the expense of CSH. These phases are formed as a result of the pozzolanic reaction of MK with CH. The main features of the thermograms are characterized by the relative increase of the peak areas characteristic for CH, CAH, CASH and CSH phases as the hydration time increases up to 90 days; this is due to that the small amount of MK acts as a nucleation agent which enhances the hydration process. The endothermic peak located at 709–713 °C is mainly due to the decomposition of CaCO$_3$.

The weight losses of hydrated phases up to 200 °C are 8.248%, 11.650%, 10.620% for OPC–MK blend of mix M1 hydrated for 3, 28 and 90 days, respectively. The TG losses of hydrated cement paste made of OPC–MK blend of composition of the amorphous part of calcium silicate hydrates (CSH). The second endothermic peak observed at about 150–160 °C represents the decomposition of crystalline part of CSH, CAH, CASH as well as the presence of carboaluminate and gehlenite hydrates [28]. The third endotherm located at about 450 °C represents the dehydration of calcium hydroxide (CH) [5,26]. The last endothermic peak located at 710–715 °C is due to decomposition of CaCO$_3$ [26,27]. It is clear that the second endothermic peak located at about 155 °C increases with curing time due to the formation of excessive amounts of CAH and CASH on the expense of CSH. These phases are formed as a result of the pozzolanic reaction of MK with CH. The main features of the thermograms are characterized by the relative increase of the peak areas characteristic for CH, CAH, CASH and CSH phases as the hydration time increases up to 90 days; this is due to that the small amount of MK acts as a nucleation agent which enhances the hydration process. The endothermic peak located at 709–713 °C is mainly due to the decomposition of CaCO$_3$.

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M1 are 4.846%, 5.884% and 7.165% for 3, 28 and 90 days, respectively; these are due to the dehydration of portlandite. This indicates that 5 wt% MK acts as a nucleating agent which accelerates the rate of hydration of OPC. The losses due to the decomposition of CaCO3 are 4.465%, 5.188% and 5.553% for cement pastes hydrated for 3, 28 and 90 days, respectively. The TG losses of CaCO3 increase with curing time, and this is due to the continuous carbonation of portlandite.

The DTA/DTG thermograms obtained for OPC and OPC–MK mixes having MK contents of 5, 15, 20 wt% (M1, M2 and M3) pozzolanic cement pastes cured for 28 days are seen in Fig. 9. This figure shows the same four endothermic peaks appeared in the thermograms obtained for the OPC–MK made of M1. The peak areas appeared in the thermograms obtained for OPC–MK pozzolanic cement pastes having MK contents of 5–15%, by weight, are nearly identical to those of the neat OPC pastes and then decrease at 20 wt% MK substitution due to the dilution of OPC as well as the pozzolanic reaction of MK with portlandite.

The TG losses of the CSH, CAH and CASH are 9.668%, 11.65%, 11.65% and 10.95%, respectively; this means that substitution of 5–15 wt% MK acts as a microfiller and nucleating agent which accelerates the rate of hydration and thereby the combined water increases. This is in agreement with the results of DTA. The weight loss of M1 cement paste due to the dehydration of CH is higher than that of OPC, M3 and M4. This indicates that 5 wt% MK acts as a nucleating agent. On the other hand, the weight loss decreases with increasing MK content due to the pozzolanic reaction of MK with CH.

The last step in the TG thermograms is the decomposition of CaCO3; the TG losses are 4.49%, 5.044%, 5.183% and 6.883% for OPC and OPC–MK pozzolanic cement pastes made with 5, 15 and 20 wt% MK. Therefore, the CaCO3 contents increase with increasing MK content in the OPC–MK pozzolanic cement pastes.

**Bulk density**

The bulk density of OPC and pozzolanic cement pastes made of OPC substituted with 5, 10, 15 and 20 wt% MK are graphically represented as a function of curing time in Fig. 10. The bulk density of OPC–MK pozzolanic cement pastes depends on the value of degree of hydration. As the hydration progresses, the hydration products fill a part of the pore volume because the volume of the hydration products is more than that of the anhydrous cement; this increases the bulk density of the hardened pastes [28]. The bulk density of all cement pastes increases with curing time. As the amount of MK increases the bulk density decreases. This is mainly due to the increase of the amount of water of consistency with MK content in addition to the decrease of specific gravity of MK (2.65 g/cm³) in comparison with 3.15 g/cm³ of OPC (Table 1); the initial water/cement ratio plays an important role in the values of bulk density. This is also due to that the rate of hydration of MK is lower than that of OPC especially at the early ages of hydration. The values of bulk density of pozzolanic cement pastes are lower than those of OPC pastes, at all curing times. In addition, the CSH formed from the pozzolana reaction has low density in comparison with that formed from the hydration of OPC. Therefore, the pozzolana cement pastes show lower values of bulk density [24].

**Total porosity**

The total porosity of OPC and OPC–MK pozzolanic cement pastes is also graphically represented as a function of curing time in Fig. 10. The porosity of the hardened pastes depends on many factors and typically increases with increasing W/C ratio and decreases with curing time; in addition, the type of cement plays a certain role [29]. The paste has the highest porosity immediately after mixing with water. As the hydration proceeds, the hydration products fill a part of the pore volume, and accordingly the porosity decreases [30]. The total porosity of OPC and OPC–MK pozzolanic cement pastes decreases with curing time due to the continuous precipitation of more hydration products within the pore system which leads to decrease the porosity. As the MK content of the OPC–MK mixture increases up to 20 wt% the total porosity values are relatively high due to the increase of water of consistency of OPC–MK blended cement pastes in addition to the relatively
low hydraulic character of MK in comparison with OPC. Therefore, the change in total porosity of OPC–MK blended pastes depends not only on curing age, but also on the MK content. The total porosity is sharply decreased up to 7 days and slightly decreased up to 90 days. This is due to the nucleating agent of MK which accelerates the hydration and then the amount of hydration products increases and fills excessive parts of the open pores at early ages of hydration [30,31].

It is clear that the OPC–MK paste containing 10 wt% MK gives apparent porosity values similar to those of OPC pastes.

Compressive strength

The compressive strength values of OPC and OPC–MK Pozzolanic cement pastes are graphically represented as a function of curing time in Fig. 11. The effect of pozzolana (MK) on the strength of OPC–MK pozzolanic cement pastes depends on a number of factors such as the pozzolana content of the cement, the type and surface area of pozzolana as well as the individual characteristics of the blending Portland cement [32]. It is clear that the compressive strength of all cement pastes increases with increasing time of hydration up to 90 days. This mainly due to the increase of the amount of hydration products such as CSH, CAH and CASH and their later accumulation within the available pores giving high strength [33]. It is clear also that pozzolanic cement paste having 5% MK gives the highest compressive strength values than those of OPC or the other pozzolanic cement pastes. This is also due to that 5 wt% MK acts as nucleating agent which accelerates the hydration of OPC. On the other hand, there is no real difference of compressive strength of OPC and the other blended cement pastes containing 10–20 wt% MK. As the MK increases up to 20 wt% the compressive strength is slightly decreased. This is due to the dilution of OPC, which decreases the compressive strength of pozzolanic cement pastes [34].

The increase of strength would be due to higher surface area of MK resulting in more nucleation sites to improve reactivity and improve packing as well as their pozzolanic reactivity [35].

Conclusion

From the above finding it may be concluded that:

(1) Metakaolin fired at 850 °C for two hours is mainly composed of quartz as a crystalline mineral in addition to the amorphous aluminosilicate glassy phase.
(2) Substitution of 10 wt% OPC by MK increases the water of consistency and then decreases up to 20 wt%. On the other hand, the initial and final setting times are elongated up to 10 wt% then shortened.
(3) The free lime contents of OPC–MK pozzolanic cement pastes increase up to 7 days then decrease up to 90 days due to the pozzolanic reaction of MK.
(4) The results of free lime of OPC–MK pozzolanic cement decrease with increasing time of hydration.
(5) The results of XRD are in agreement with those of DTA.
(6) The compressive strength values of OPC–MK pozzolanic cement pastes containing up to 20 wt% have small differences up to 90 days.

Fig. 10  Bulk density as well as total porosity of OPC and OPC–MK pozzolanic cement pastes up to 90 days.

Fig. 11  Compressive strength of OPC and MK pozzolanic cement pastes up to 90 days.
Conflict of interest

There is no conflict of interest.

References