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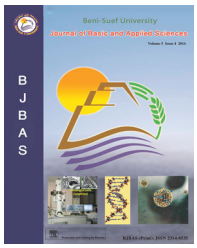

Full Length Article

Effect of hydrothermal curing on hydration characteristics of metakaolin–CKD pastes at different temperatures in a closed system

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ABSTRACT

Well sealed stainless steel capsule was used as a hydrothermal system to study the pozzolanic activity and hydration characteristics of metakaolin (MK)–cement kiln dust (CKD) at different temperatures (40, 80, 120 and 150 °C) up to 24 hours of hydrothermal curing. The physico-chemical properties of hydrothermally treated MK–CKD pastes were studied by measuring the compressive strength, porosity and bulk density of the hardened pastes as hydraulic properties. The hydration properties of the pastes were studied by measuring free lime and chemically-combined water contents. The phase composition and crystalline structure of the obtained hydrates were studied using X-ray diffraction (XRD) and differential thermal analysis (DTA). The results indicated that, the higher activity is shown at 80 °C especially at the later age of hydrothermal curing. Moreover, the mix containing 75% MK and 25% CKD by mass possessed the higher characteristics during the later age of hydrothermal curing and at all curing temperatures.

1. Introduction

Cement kiln dust (CKD) is a fine powdery material as a by-product of cement manufacturing. It is composed of very fine (micro-sized) particles obtained from electrostatic precipitators during the cement production process. Wet and dry kilns are the two types of cement kiln processes: where they take feed materials in slurry and dry forms, respectively. CKD that was produced from wet process has lower calcium content than that was produced from dry process. Free lime can be found in CKD with the highest concentration of the coarser particles collected close to the kiln. Fine particles tend to exhibit a high concentration of sulfates and alkalis. CKD has a similar chemical composition to that of the traditional Portland cement. The major constituents are compounds of lime, iron, silica, and

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alumina as well as some trace metals such as cadmium, lead, selenium, and radionuclides.

Metakaolinite (MK) could be produced by calcination of the crystalline kaolinite as a result of losing OH lattice water. MK offers good properties as mineral additive as it is more reactive than kaolin and has a highly disordered structure (Badogiannis et al., 2005). In addition, MK is considered a good synthetic pozzolana because it reacts with lime giving hydrated aluminum and calcium silicates (Wild et al., 1996). Pozzolanic property development in fired clays mainly depends on the nature and abundance of clay minerals, calcinations parameters and fineness of the final product. The calcination temperature in the range of 600–800 °C usually produces the reactive state. On continued heating, recrystallization and formation of mullite take place resulting in a decline of material reactivity (Badogiannis et al., 2005; Frías and Cabrera, 2000). C–S–H, C_2ASH_8 and C_4AH_{13} are the major and main phases formed during the pozzolanic reaction between MK and lime (Frías and Cabrera, 2000). Among the different factors which influence the reaction kinetics and the amounts of the hydrated phases produced, the curing temperature is the most effective because it influences on the stability and the transformation of the hydrates.

Hydrothermal treatment of cement materials gives building products with improved binding properties (Luke, 2004; Shatat et al., 2015). As a result of the hydrothermal interaction between the limes released from CKD with sludge, autoclaved CKD sludge pastes possess a considerable compressive strength (Amin and Hashem, 2011; Shatat et al., 2016).

The aim of this study is to investigate the physico-chemical properties of hydrothermally treated specimens made with MK and CKD as a function of time at different curing temperatures.

2. Materials and experimental techniques

Raw materials used in the present work are CKD from Assuit Cement Co., Egypt and kaolinite clay collected from Kalabsha, Aswan, Egypt. Kaolinite clay was calcined in an electrical muffle furnace with a heating rate 10 °C/min at 800 °C for 3 h, to give metakaolin (MK). The mixes' ratios and the chemical compositions of the starting materials are shown in Tables 1 and 2, respectively. Further sampling process and treatments are similar to those mentioned in our previous work (Shatat, 2014). The specimens were then demolded and cured at different temperatures (40, 80, 120 and 150 °C) and hydrothermal curing ages from 2 hours to 24 hours in well-sealed stainless steel capsule (shown in Fig. 1). The material characteristics such as; compressive strength, bulk density, total porosity, free lime and combined water contents were determined as described elsewhere (Shatat, 2013, 2014; Shatat et al., 2014, 2015). X-ray fluorescence (XRF, Philips X-ray PW1370) was used to verify the oxide content of the starting materials (CKD and MK). X-ray diffraction (XRD, a Philips PW1700 diffractometer system using Cu–Kα radiation) was used to identify the crystalline phases present in the samples. Differential thermal analysis (DTA, Schimaduz DTA-50 thermal analyzer Co – Kyoto, Japan) was used to study the thermal behavior of the samples.

Table 1 – Cement kiln dust and metakaolin weight ratios in pastes.

Sample code	Metakaolin	Cement kiln dust
M10	90	10
M20	80	20
M25	75	25
M40	60	40

Table 2 – Chemical composition of the paste materials, wt %.

Oxide contents	Metakaolin	Cement kiln dust
SiO_2	44.18	13.69
Al_2O_3	36.75	3.21
Fe_2O_3	1.36	2.41
CaO	0.26	46.09
SO_3	–	4.05
MgO	0.16	1.44
Na_2O	0.18	4.89
K_2O	0.25	4.94
TiO_2	2.94	–
L.O.I	13.55	12.06
Total	99.63	99.72

3. Results and discussion

3.1. *Compressive strength*

The compressive strength values obtained for the various hardened pastes made from MK and CKD for different hydrothermal curing time (2–24 hours) at different temperatures (40, 80, 120 and 150 °C) are shown in Fig. 2. The results indicated that, the compressive strength increases gradually from 2 to 24 hours under hydrothermal treatment for all mix compositions of pastes. This mainly attributed to the hydrothermal interaction between the lime released from CKD with metakaolin to give calcium silicate hydrates which contribute considerably to the compressive strength of these specimens. In addition, the presence of some alkali oxides in CKD (like Na_2O and K_2O) which increase the solubility of silica present in MK and so activates its hydrothermal reaction (Amin and Hashem, 2011). CKD represents effective alkaline activator for different aluminosilicate materials toward the hydrothermal reaction

Fig. 1 – Stainless steel capsule used in hydrothermal treatment.

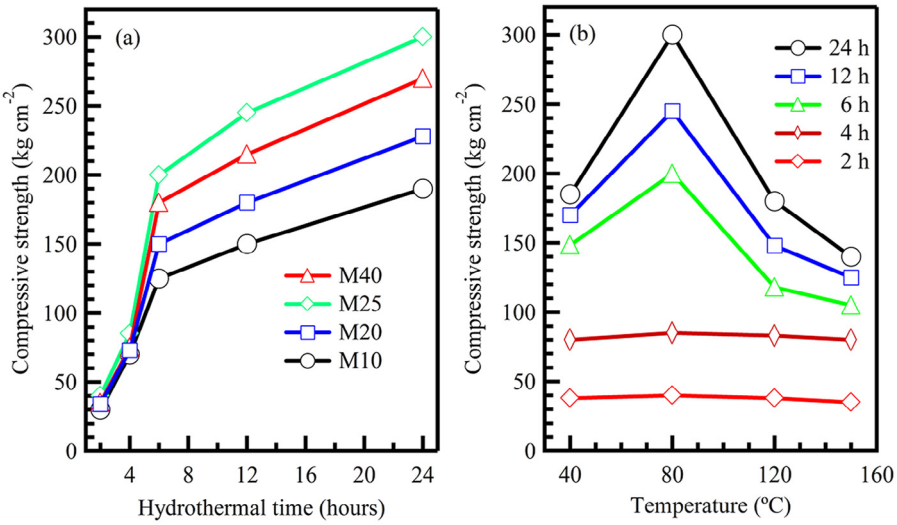

Fig. 2 – Compressive strength for all samples (a) at 80 °C as a function of hydrothermal curing age and for M25 (b) at different curing times as a function of curing temperature.

including quartz (Sarkar et al., 2006). Also, these results might be attributed to the increasing amounts of hydration products which act as binding centers in the cured specimens with increasing time of hydration. The low compressive strength value for some mixes in the early stage of hydration (3–6 hours) is mainly due to the interaction between the initially formed calcium silicate hydrates and the remaining parts of pozzolanic grains leading to a decrease of the lime content of theses hydrates (Massazza, 1993; Shatat, 2013). At later ages (12–24 hours), the hardened specimen possessed high strength values due to the accumulation and later stabilization of the hydration reaction products. Moreover, the strength values were higher for M25 which composed of MK (75%) with CKD contents (25%) as compared with the strength values of the other specimens (M10, M20 and M40) at all hydrothermal curing temperature. This result may be attributed to the increase in the formation of stabilized hydrates in presence of high lime contents. Mix M25 possessed the highest compressive strength values at all hydrothermal curing ages and all hydrothermal temperatures and the optimum value for this mix was at 80 °C after 24 hour curing. This indicates that these ratios of CKD to MK in these mixes possess the best hydrothermal reaction that led to the formation of hydration products having considerable hydraulic character. Mix M10 (90% MK: 10% CKD) possessed the lowest compressive strength values at all hydrothermal curing ages and all hydrothermal temperatures. On the other hand, mix M40 possessed the highest CKD contents, but it possessed compressive strength lower than mix M25 at all hydrothermal curing ages and all hydrothermal temperatures. This is mainly associated with two factors: (i) the good crystallization of the initially formed hydrates (mainly calcium silicate hydrates); the well crystallized CSH possesses low hydraulic characteristics with relatively low strength and/or (ii) the transformation of lime-rich CSH into low lime CSH with a metastable state leads to lower mechanical properties. The initially formed amorphous silicate gel (CSH) could be transformed into well-defined crystalline phases, the stability of which depends on the C/S ratio in $CaO–SiO_2–H_2O$ system and the hydrothermal conditions. Accordingly, mix M25 at hydrothermal temperature 80 °C was suitable for the production of building material containing MK and CKD (Maeda et al., 2011; Shatat et al., 2016). The compressive strength of the pastes was improved when the samples were subjected to hydrothermal reaction at 80 °C due to the formation of deposits, such as tobermorite, among the particles of starting materials that enhance the strength of the hydrothermal pastes and form a compact body. The compressive strength decreases with increasing hydrothermal temperature above 120 °C and this may be attributed to a compact body decomposed partially during the hydrothermal reaction at temperatures above 120 °C. It is proposed that during the hydrothermal process at a high temperature, the reactivity of kaolinite increases, because the aggregates are destroyed. Tobermorite $[Ca_5(Si_6O_{18}H_2) \cdot 4H_2O]$ and hydrogarnet $[Ca_3Al_2(SiO_4)(OH)_8]$ were the major phases formed after the reaction, which are responsible for strength development in the as-synthesized materials suitable for building (Sarkar et al., 2006).

3.2. *Bulk density and total porosity*

Bulk density and total porosity obtained for the various hardened pastes made from MK and CKD as a function of hydrothermal curing age at different temperatures (40, 80, 120 and 150 °C) were shown in Figs. 3 and 4, respectively. The density is an important factor in the determination of porosity, assessment of durability and strength and estimation of lattice constants for the CSH phase in hydrated Portland cement. As the hydration of cement progresses, the hydration products fill some of the pores because the volume of hydration products is twice than that of the anhydrous cement; this decreases the porosity and increases the bulk density of hardened cement paste. The bulk density increased while total porosity decreased with increasing hydrothermal curing age for all mixes at all hydrothermal temperatures. The paste containing mix M25 possessed the highest values of bulk density and the lowest values of porosity at all hydrothermal curing ages and all

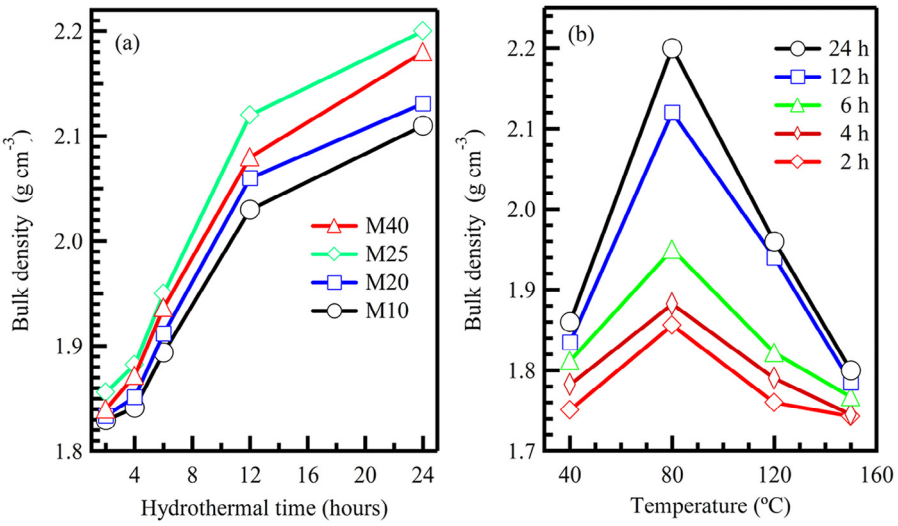

Fig. 3 – Bulk density for all samples (a) at 80 °C as a function of hydrothermal curing age and for M25 (b) at different curing times as a function of curing temperature.

hydrothermal temperatures, while pastes containing mix M10 give the lowest values of bulk density and the highest values of porosity. The increases in the bulk density with the increase of CKD content at all periods and all hydrothermal temperatures as well as the decrease in the porosity were mainly due to the consumption of lime with MK, which accelerates the rate of hydration process and increases the amount of hydration products that was deposited in the pore system of the cured specimens leading to an increase in the bulk density of these pastes. Although mixes M40 contain higher CKD contents than mixes M25, they possessed lower bulk density values at all hydrothermal curing stages and all temperatures. This is may be attributed to the formation of an inhibiting layer of reaction product on MK pastes and/or to the transformation from less dense C_2ASH_8 and C_4AH_{13} and dense hydrogarnet. Bulk density and porosity of the pastes were improved when the samples were subjected to hydrothermal reaction at 80 °C and this results in a good agreement with the previous studies.

3.3. *Free lime content*

The free lime content (CaO %) of hardened specimens obtained for the various hardened pastes made from MK and CKD as a function of hydrothermal curing age at different temperatures (40, 80, 120 and 150 °C) were shown in Fig. 5. The free lime was consumed gradually during the hydration process of all mixes under hydrothermal treatment and at all hydrothermal temperatures of pastes. Obviously, all of MK and CKD pastes possess extremely very low free lime content values at all stages, a result of the immediately complete reaction of liberated lime with active SiO_2 and Al_2O_3 of the decomposed MK.

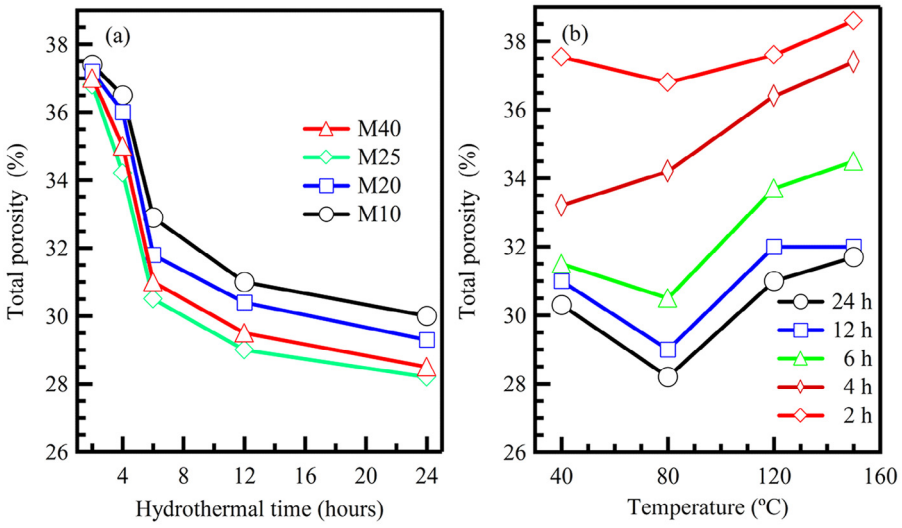

Fig. 4 – Total porosity for all samples (a) at 80 °C as a function of hydrothermal curing age and for M25 (b) at different curing times as a function of curing temperature.

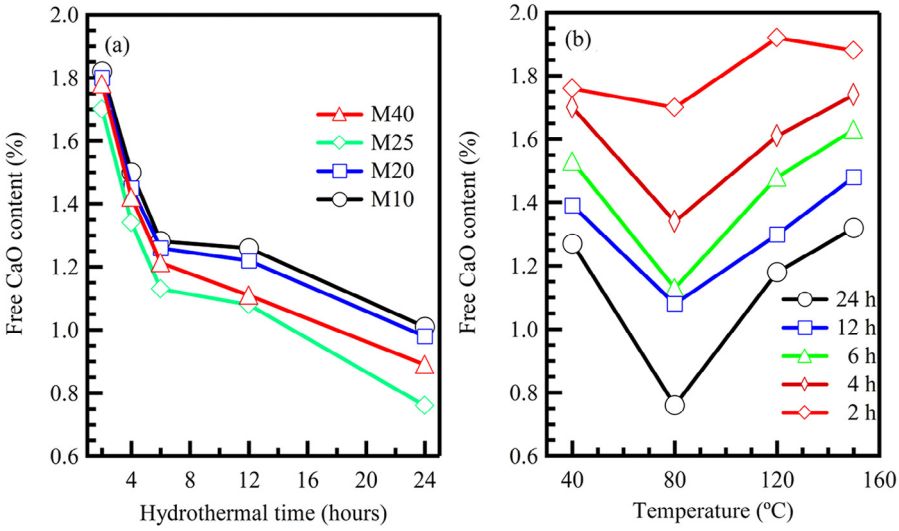

Fig. 5 – Free CaO content for all samples (a) at 80 °C as a function of hydrothermal curing age and for M25 (b) at different curing times as a function of curing temperature.

Generally, pastes containing mix M25 possessed low free lime contents; while those containing mix M10 possess the highest free lime contents at all hydrothermal curing ages and all hydrothermal temperatures. This is mainly attributed to the low liberated lime in mixes M25 which is completely consumed by decomposed MK. The free lime content of the pastes was the lowest when the samples were subjected to hydrothermal reaction at 80 °C. The free lime content increases with increasing hydrothermal temperature above 120 °C. It is clear that, the free lime content results are in a good agreement with the chemically-combined water content results.

3.4. *Chemically combined water content*

The results of chemically combined (non-evaporable) water content of hardened specimens obtained for the various hardened pastes made from MK and CKD as a function of hydrothermal curing time at different temperature (40, 80,120 and 150 °C) were shown in Fig. 6. Obviously, the combined water content values increase with increasing age of hydrothermal for all mixes up to 24 hours which indicates a progress of the hydrothermal reaction and formation of more hydrates. In other words, the combined water content increases with the increase of hydrothermal curing age for all pastes investigated in this study. This was due to the increase of the degree of hydration of the constituents of these pastes with increasing age of hydration. In addition to the pozzolanic activity of MK with released free lime (CH) of CKD which progresses with time, MK consumes higher amounts of CH liberated from the CKD to form additional amounts of hydration products. The present investigation illustrated that hardened specimens contain MK and CKD namely; mix M25 possessed the maximum values of

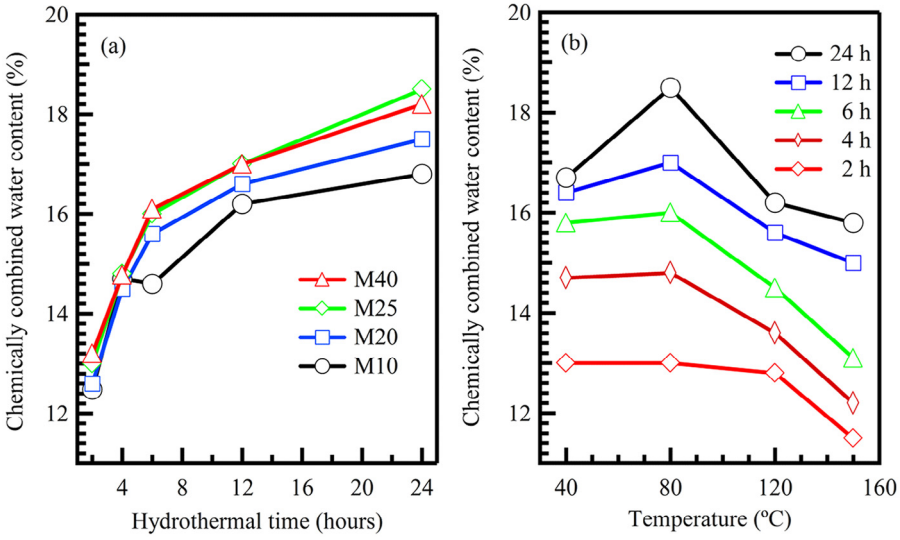

Fig. 6 – Chemically combined water content for all samples (a) at 80 °C as a function of hydrothermal curing age and for M25 (b) at different curing times as a function of curing temperature.

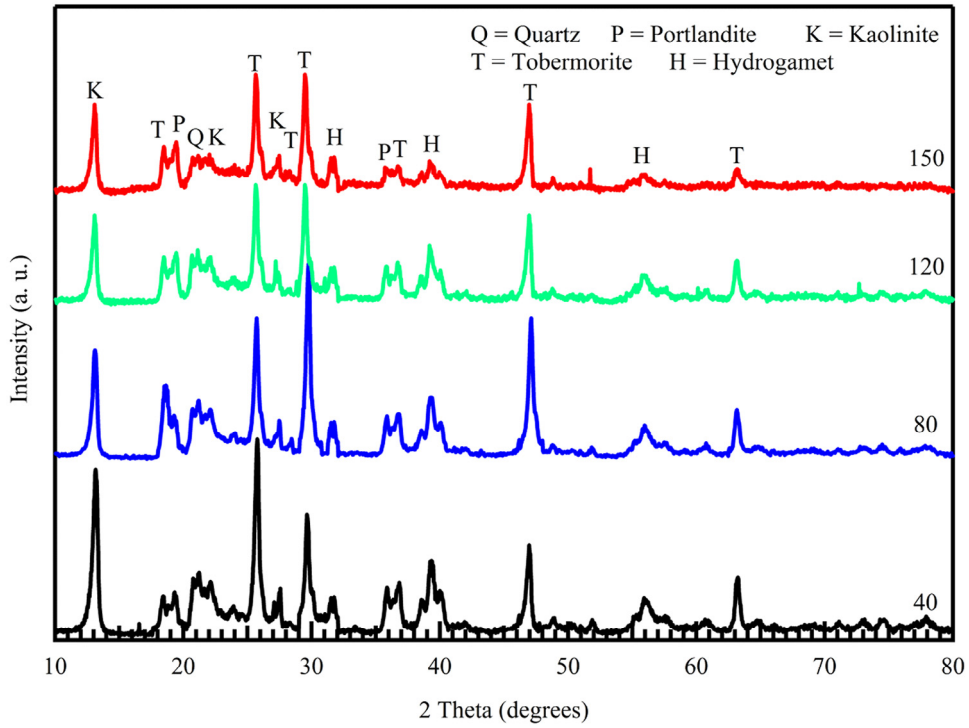

Fig. 7 – XRD of M25 at different curing temperatures.

chemically-combined water contents, the higher values of chemically combined water content indicate a formation of more hydrates. Also, mix M10 possessed the lowest chemically combined water content values at all hydrothermal curing ages and all hydrothermal temperatures. These results confirmed the compressive strength values. The chemically combined water contents of the pastes were improved when the samples were subjected to hydrothermal reaction at 80 °C. The chemically combined water contents decreased with increasing hydrothermal temperature above 120 °C. These results were in a good agreement with the previous results of compressive strength.

3.5. *Structure and phase analysis*

The main hydration products formed as a result of the hydrothermal reaction of the hardened specimens made from MK and CKD were identified by of X-ray diffraction (XRD) as shown in Fig. 7. At 40 °C hydrothermal curing temperature, the sample showed high intensity peaks for tobermorite ($Ca_5Si_6O_{17}{\cdot}5H_2O$) and hydrogarnet ($Ca_3Al_2$ (SiO_4) $(OH)_8$) phases as the calcium silicate hydrate products (Richardson, 2008). The intensity of these peaks decreased with increasing the curing temperature. The sample at 80 °C showed the high intensity peaks for this phase indicating higher hydration characteristics of the M25 at this temperature. The formation of this hydrated phase is the reason for the strength development in the hydrothermal hardened pastes (Sarkar et al., 2006). Kaolinite phase ($Al_2Si_2O_5(OH)_4$ is shown at all temperatures and the peaks intensity decreased with increase in curing temperature (Elimbi et al., 2014). On the other hand, the amount of portlandite produced from hydration reactions decreases at hydrothermal curing temperature 80 °C, this may be attributed to the high pozzolanic activity of metakaolin, which interacts rapidly with the free calcium hydroxide, liberated during the hydration process at 80 °C. These results were consistent with compressive strength and all previous findings.

3.6. *Differential thermal analysis*

The differential thermal analysis (DTA) is a useful technique to identify the phases coexisting during the hydration process. DTA curves for M25 paste under hydrothermal curing age of 24 hours at different curing temperatures (40, 80, 120 and 150 °C) were displayed in Fig. 8. The sample showed an endothermic peak at about 450 °C, indicating the existence of free portlandite (Gameiro et al., 2012). Where this peak is mainly due to the decomposition of calcium hydroxide, the intensity of the endothermic peak that is characteristic of CH decreases. This indicates that MK reacts with CH liberated from the hydration of CKD and forms additional calcium silicate. The broad peak at 200 °C was related to endothermic dehydration of pozzolanic hydrated products (tobermorite and hydrogarnet).

4. Conclusions

To sum up, metakaolin–cement kiln dust pastes possessed a considerably compressive strength at all different hydrothermal curing ages. This is mainly attributed to the hydrated phases produced from the hydrothermal interaction between the lime released from cement kiln dust with metakaolin. These phases include tobermorite and hydrogarnet as the major hydrated phases and are reasonable in the development of strength in

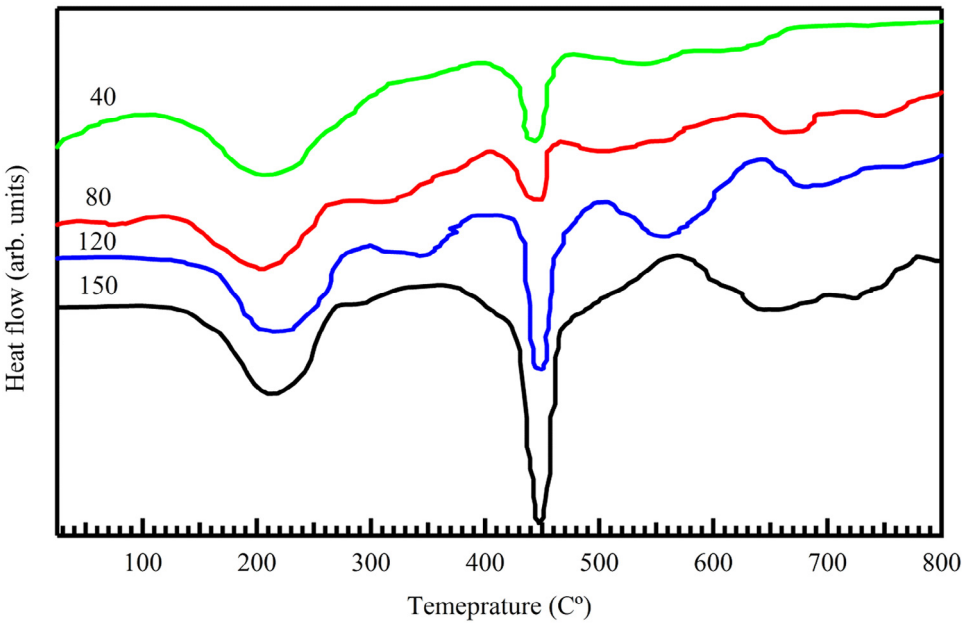

Fig. 8 – DTA curves of M25 at hydrothermal curing age 24 hours at different curing temperatures.

the samples. The replacement of metakaolin by 25 wt. % cement kiln dust resulted in a marked increase in the compressive strength and the combined water contents as well as the bulk density of the formed hydrates at a later age of hydrothermal curing ages. In addition the compressive strength and all other parameters showed that pastes hydrothermally treated at 80 °C possess the best characteristics. Accordingly it is recommended to use the mix containing 75 wt. % metakaolin and 25 wt. % cement kiln dust, hydrothermally treated at 80 °C for general construction purposes. In addition, the utilization of cement kiln dust in construction purposes solves the problem of its disposal thus keeping the environment free from pollution.

List of abbreviations

C	CaO
H	H_2O
CH	$Ca(OH)_2$
CSH	$3CaO.2SiO_2.xH_2O$

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