EFFECT OF TEMPERATURE ON HYDRATION KINETICS AND STABILITY OF HYDRATION PHASES OF METAKAOLIN–LIME SLUDGE–SILICA FUME SYSTEM

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This paper presents experimental study to determine the effect of temperature on the hydration kinetics of metakaolin (MK)–lime sludge–silica fume mixture. The kaolin was activated at 800°C for 2 hours. The metakaolin and lime sludge were mixed in a ratio of 1:1. To this mixture, 5 wt.% of silica fume was added to form the final blended composition. The water/binder ratio is 0.93 by weight. The specimens were cured at temperature 20 and 60°C at 100% relative humidity (RH). The phase composition of the formed hydrates was determined by X-ray diffraction and from the thermal analysis (TG and DSC) data. The results showed that the compressive strength of sample cured at 60°C was greater than that cured at 20°C. It is also demonstrated that, the sequence of appearance of hydrated phases at 20°C was CSH, C_2ASH_8 and C_4AH_{13}; while the formed hydrates at 60°C were CSH, C_2ASH_8, C_4AH_{13} and hydrogarnet (C_3ASH_6).

INTRODUCTION

The use of pozzolanic materials as a blended component of Portland-pozzolan cements production is generally associated with significant savings in energy and reducing the solid wastes [1]. Although cost saving was probably the original reason for the development of blended Portland cements, force to rapid growth in the production of blended cements in many countries of Europe and Asia came as a result of their energy-saving potential [2]. Also, during the production of Portland cement clinker a significant amount of CO_2 is released into the atmosphere. The estimations carried out show that, the production of every ton of Portland cement releases about 1 ton of CO_2, a major greenhouse gas that is implicated in the global warming [3]. World's Portland cement clinker production is responsible for about 7 % of total CO_2 emissions, therefore topical is a reduction in the portland cement clinker production without decreasing the needed amount of cement for the construction industry. This can be achieved by incorporating larger than customary proportions of pozzolanic materials into blended Portland cements. The high-performance concrete mixtures containing high-volume of fly ash (>50% fly ash by weight of the blended Portland-fly ash cement) can be produced with the help of superplasticizing admixtures [4-5]. Nowadays, pozzolanic materials have been used for construction, mainly because of their influence on the microstructure and durability of the blended concrete [6-8]. One such

pozzolan is metakaolin (MK), material obtained under a carefully controlled process of thermal activation of kaolinite clay [9-11]. The kaolinite is dehydrated at 600-850°C, which causes major structural disorganization and significant increase in pozzolanic activity. In the previous works [12,13], the positive effect of MK on the properties of blended cements has been shown. MK improves workability, microstructure, mechanical strength as well as less permeability, higher durability that the equivalent OPC matrix. These advantages allow its use in new application fields, for example, consumption of wastes.

Metakaolin exhibits lower pozzolanic activity than silica fume, but significantly greater pozzolanic activity than fly ash [14]. This fact is related to chemical and mineralogical composition, pozzolanic activity, fineness, etc. It is well documented that the main phases that form during the pozzolanic reaction between MK and lime at ambient temperature are C-S-H, C_2ASH_8 and C_4AH_{13}. various factors can influence the reaction kinetics and the amounts of the hydrated phases produced [14-16]. Among them, curing temperature is the most important factor because it influences on the stability and the transformation of the hydrates.

A significant changes occur in the phase development pattern of MK mixed with $Ca(OH)_2$ with curing temperature (20 and 55°C) after 3 days of hydration. C_2ASH_8 and C_4AH_{13} phases are not stable and normally convert into hydrogarnet at elevated temperature [17]. It was reported that C_2ASH_8 and C_4AH_{13} were stable under

the conditions of the study, and there was no evidence of a possible conversion reaction from these phases to hydrogarnet [18,19].

The aim of the present work is focused on the reuse of an industrial by-product, namely the lime sludge produced as a by-product from the manufacture of acetylene gas. Acetylene produced from the hydrolysis of calcium carbide CaC_2, as a result of this lime sludge is lifted. It also focuses on the influence of curing temperature on the mechanism of reaction in MK-lime sludge-silica fume systems. This investigation reports the behavior of the MK-lime sludge-silica fume at 20°C and 60°C, in the period between 3 and 28 days.

EXPERIMENTAL

The starting materials used in this study were metakaolin (MK) of Blaine surface area ≈3000 cm²/g, lime sludge of Blaine surface area ≈3100 cm²/g, and silica fume of Blaine surface area ≈20 m²/g. The oxide composition was (wt.%): CaO 0.67; SiO_2 53.03; Al_2O_3 33.47; Fe_2O_3 1.86; MgO 2.0; SO_3 0.21; Cl- 0.05 and ignition loss 8.39. The chemical composition of silica fume was (wt.%): CaO 0.21; SiO_2 96.10; Al_2O_3 0.58; Fe_2O_3 0.70; MgO 0.48; SO_3 0.10; Na_2O 0.31; K_2O 0.49 and ignition loss 1.14. The oxide composition of lime sludge was (wt.%): CaO 67.01; SiO_2 1.21; Al_2O_3 2.25; Fe_2O_3 0.08; MgO 0.29; SO_3 0.19; Cl- 0.01; K_2O 0.16 and ignition loss 27.53. The lime sludge was composed mainly of $Ca(OH)_2$. In this investigation; the blended composition consists of the metakaolin and lime sludge mixed in a ratio of 1:1 by weight and silica fume added as 5 wt.% of blended weight. The mixes were made from metakaolin–lime sludge–silica fume using ethanol to attain ascertain homogeneity. The water/binder ratio is 0.93 by weight. The pastes were cast in steel molded

of 2 cm cubs, cured in a humidity chamber at room temperature for 24 hours, then demolded and cured at 20°C; 60°C as well as 100 % relative humidity until the time of testing. After the predetermined curing time; the hydration of the paste were stopped by grinding in aceton-methanol mixture as described elsewhere [20]. For each test the average results of the two close values were reported. The compressive strength of the hydrated pastes was determined after 3, 7, 14 and 28 days. The kinetics of hydration was followed by determination of chemically combined water contents at the corresponding ages using a thermogravimetric analysis (TGA). During the TGA test, the sample was heated at a constant rate, 20°C/minute, in a nitrogen atmosphere. The weight was automatically and continuously recorded. Differential thermal analysis runs were conducted using a Shimadzu DSC 50 thermal analyzer at a heating rate of 20°C/min. The samples chamber was purged with nitrogen at a flow of 30 cc/min. The crystalline phases present in the hydrated product were identified using the X-ray diffraction technique. Nickle-filtered Cu-Kα radiation at 40 KV and 20 mA were used throughout in a Philips PW 1390 diffractometer. scanning speed of 2°/min. were used. The CH content was calculated using the following equation:

$$W_{CH}=4.11\times(W_{440}-W_{580})+1.68\times(W_{580}-W_{1007})/W_{1007}\times100 \ (\%),$$

where W_{CH} is the weight ratio of $Ca(OH)_2$ in the paste. W_{440}, W_{580} and W_{1007} are the weights of the specimens at 440, 580 and 1007°C respectively [21].

RESULTS AND DISCUSSION

The variations of the DSC thermograms of metakaolin–lime sludge–silica fume system hydrated at 20 and 60°C are shown in figures 1 and 2. Evidently, there
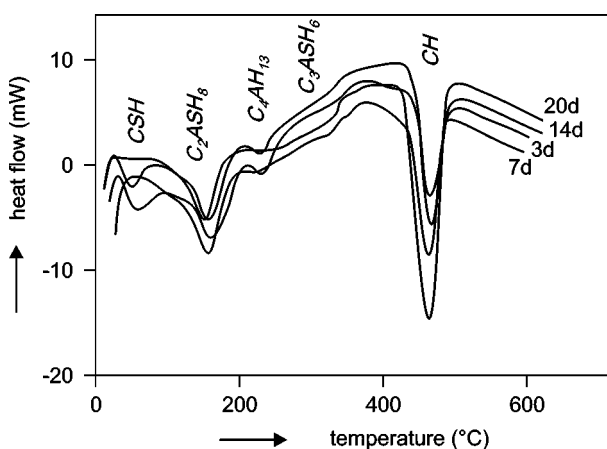
Figure 1. DSC thermograms of metakaolin-lime sludge-silica fume system hydrated at 20°C for 3 to 28 days.
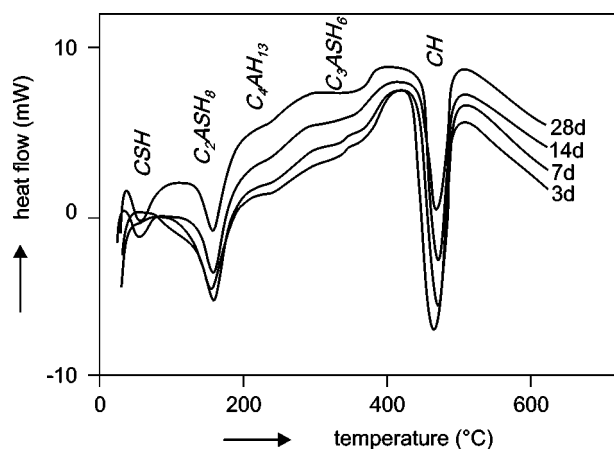
Figure 2. DSC thermograms of metakaolin-lime sludge-silica fume system hydrated at 60°C for 3 to 28 days.

were almost five endothermic peaks. The first peak located at about 110-120°C, which is mainly due to the decomposition of calcium silicate hydrates; mainly as CSH. The second endothermic peak observed at about 160°C represents the decomposition of the gelhenite hydrate (C_2ASH_8). The third endothermic peak located at about 210°C represents the decomposition of C_4AH_{13}. The forth endothermic peak located at about 310°C represents the decomposition of hydrogarnet (C_3ASH_6). The last endothermic peaks are appearing at about 470°C represents the decomposition of calcium hydroxide (CH). The mean features of the thermograms are characterized by a decrease of the peak area of CH and increase of the peak areas of C_2ASH_8, C_4AH_{13} and CSH phase as the hydration time increased up to 28 days. It is clear that, the thermograms at the first days of reaction (up to 7 days) show a very weak endothermic peak at about 110-120°C but well crystalline CSH phase were formed at hydration age 14 and 28 days.

Evidently, this may be due to further reaction between metakaolin, silica fume and lime sludge at latter ages. It is also clear that, the hydration at 60°C accelerate the rate of hydration as well as formation of proud peak from hydrogarnet (C_3ASH_6) at 310°C and wide band of the C_4AH_{13} phase. This may be due to the fact that the metastable phases (C_2ASH_8 and C_4AH_{13}) experience a slight change, forming a wide band with a maximum situated at about 210°C. This phenomenon might indicate an evolution of hydrogarnet from C_2ASH_8 to C_4AH_{13}.

XRD analyses of the phases present in the metakaolin-lime sludge-silica fume system hydrated at 20 and 60°C after 3 and 28 days are shown in figure 3. Obviously, the main hydration products are to be calcium silicate hydrate gel, gehlenite, C_4AH_{13} and hydrogarnet phases. It is clear that, the intensity of CH phases decreases as the hydration temperature and hydration time increases. This may be due to further reaction
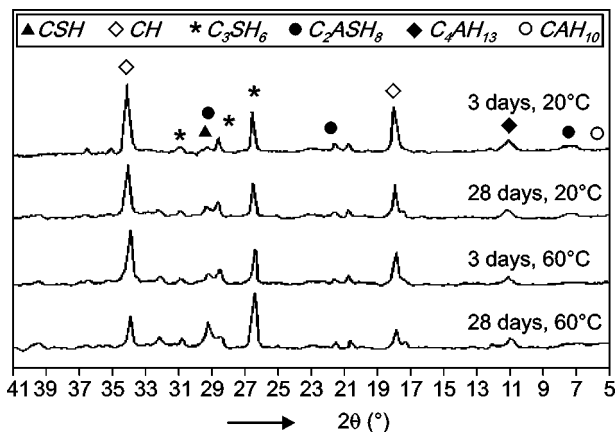
between CH and alumino-silicate. The formed phases of C_2ASH_8 and C_4AH_{13} are probably present as metastable phases that after 28 days of curing at 60°C which convert to hydrogarnet. They also belived that the appearance of C_4AH_{13} at early ages of hydration is a metastable phenomenon caused by super saturation of the aqueous phase with respect to CH. High concentrations of Ca^{2+} and OH^- in the pore solution maintained a pore fluid composition that allowed C_4AH_{13} to precipitate.

The amount of the various phases present in the hardened paste can be monitored through the measurement of the enthalpy under the corresponding peaks. The change in crystallization enthalpy of the formed hydrates during hydration of metakaolin–lime sludge–silica fume system is illustrated in figures 4 and 5. The general trends may be used to monitor the hydration progress. It is clear that the enthalpy of calcium hydroxide hydrated at 20°C decreases as the hydration time increases but the enthalpy of C_4AH_{13} and CSH increases as the hydration time increases. On the other hand the
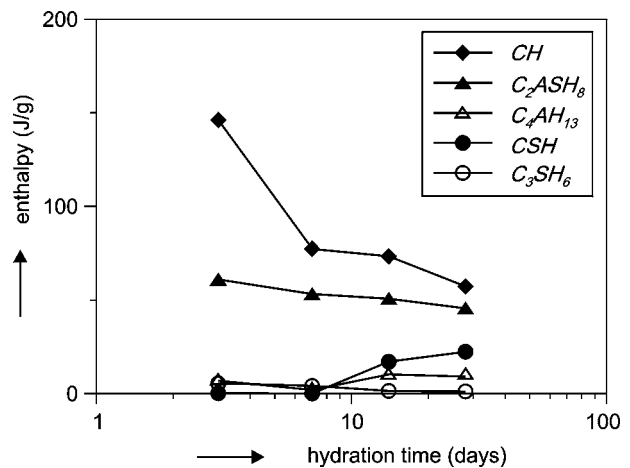

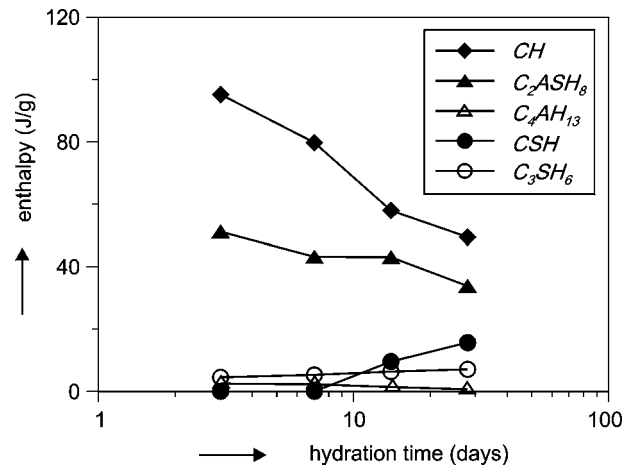Figure 4. DSC peak enthalpy of formed hydrates at 20°C.

Figure 3. XRD patterns of metakaolin-lime sludge-silica fume system hydrated at 60°C for 3 to 28 days.

Figure 5. DSC peak enthalpy of formed hydrates at 60°C.

enthalpy of gelhenite hydrate (C₂ASH₈) and hydrogarnet (C₃ASH₆) decreases gradually as hydration time increases. This may be due to the conversion of C₂ASH₈ to C₄AH₁₃ at latter ages (14 and 28 days). It is also illustrated that, the enthalpy of calcium hydroxide, C₄AH₁₃ and gelhenite hydrated at 60°C decrease as the hydration time increases but the enthalpy of hydrogarnet and CSH increase as the hydration time increases up to 28 days. This may be due to; the hydration at higher temperature leads to further reaction, and its conversion of gelhenite and C₄AH₁₃ to hydrogarnet. The Al₂O₃ and SiO₂ present in metakaolin and silica fume react with Ca(OH)₂ at significantly different rates and extents with different mechanisms and the preferentially retained Al₂O₃ or SiO₂ may crystallise at the slightly different temperature.

Figure 6 illustrates the variation of reacted lime in metakaoline-lime sludge-silica fume system with hydration time at 20 and 60°C. The amount of total calcium hydroxide present in the mixture was calculated from the weight loss TGA data (table 1) due to the dehydroxilation of Ca(OH)₂ and decarbonation of CaCO₃. It is clear that, the reacted lime increased as the hydration time and hydration temperature increases. Different trend of decreasing lime content as the temperature increases is shown in figure 6. In the sample cured at

60°C, lime is rapidly consumed during the first 3 days. Evidently, the curve corresponding to the samples cured at 20°C shows that lime is consumed at a slower rate than that at 60°C.

Figure 7 shows the variation of compressive strength values of the hardened metakaolin–lime sludge–silica fume system pastes with hydration time. Evidently, the compressive strength of hardened pastes increased with increasing curing time and hydration temperature. It is clear that, the sample cured at 60°C possesses higher values of compressive strength than that cured at 20°C. This may be due to that the pozzolana has a maximum activity at higher curing temperature, which leads to more lime consumption. The principal reaction is that between the AS₂ and the calcium hydroxide in the presence of water. This reaction forms cementitious aluminium containing CSH gel, together with crystalline products, which include calcium aluminate hydrates and alumino-silicate hydrates (i.e., C₂ASH₈, C₄AH₁₃ and C₃ASH₆). The crystalline products formed depend principally on the AS₂/CH ratio and reaction temperature. Therefore, the increase in compressive strength of metakaolin–lime sludge–silica fume paste hydrated at 60°C; may be due to pozzolanic reaction and transformation of C₂ASH₈ and C₄AH₁₃ in to C₃ASH₆ as shown earlier in this paper.
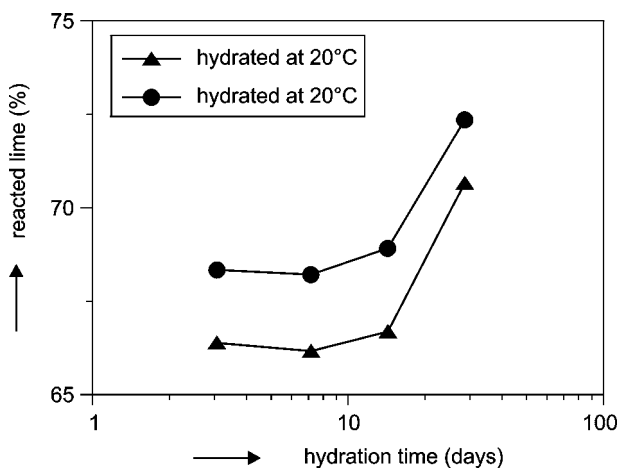

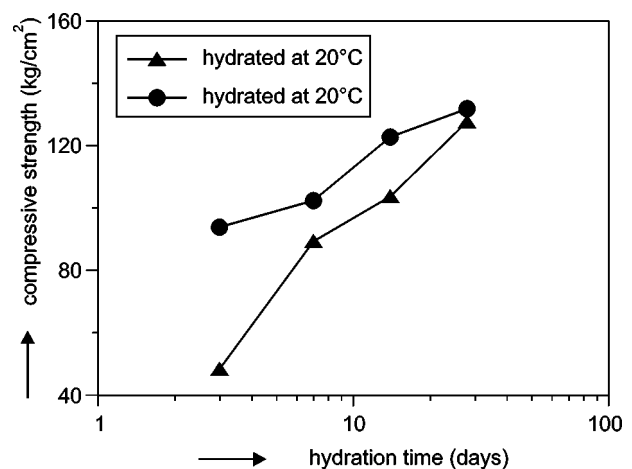Figure 6. Reacted lime during hydration of metakaolin-lime sludge-silica fume system at 20 and 60°C.

Figure 7. Compressive strength of metakaolin-lime sludge-silica fume system hydrated at 20 and 60°C.

Table 1. Loss of weight of CH phases from GTA thermograms.

Hydration time (days)	Hydration temperature (°C)							
	20				60			
	Original weight (mg)	Weight loss (%)			Original weight (mg)	Weight loss (%)		
		440°C	580°C	1007°C		440°C	580°C	1007°C
3	33.09	-8.609	-10.94	-20.69	34.87	-9.52	-12.17	-20.60
7	35.20	-10.09	-12.23	-22.56	31.03	-10.60	-12.75	-22.15
14	31.71	-10.59	-12.48	-22.09	32.91	-12.14	-14.06	-23.46
28	35.39	-14.72	-16.95	-24.59	32.27	-12.97	-14.89	-22.83

CONCLUSION

Studies carried out showed that curing temperature plays an important role on the rate of formation of hydrated phases as well as on the amounts of hydrates produced. The following conclusions are deduced from the above studies:

1. At early stages of the reaction, the CSH is the main phase for both temperatures. Subsequently, C_2ASH_8 (gelhenite) and C_4AH_{13} appear, and finally the C_3ASH_6 (hydrogarnet) is the predominant phase in the samples cured at 60°C.

2. At 60°C of curing temperature, there is a transformation of metastable phases (C_2ASH_8 and C_4AH_{13}) into hydrogarnet under the conditions studied. The hydrogarnet is produced as a result of the pozzolanic reaction between MK, SF and lime (reacted lime increase) as well as through a transformation reaction.

3. The hardened pastes cured at 60°C possess higher values of compressive strength than that cured at 20°C, due to pozzolanic reaction and transformation of C_2ASH_8 and C_4AH_{13} in to C_3ASH_6 .

Cement Chemistry Notation, C: CaO; CH: Ca(OH)$_2$; S: SiO$_2$; A: Al$_2$O$_3$; H: H$_2$O

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VLIV TEPLOTY NA KINETIKU HYDRATACE A STABILITU HYDRATOVANÝCH FÁZÍ SYSTÉMU METAKAOLIN–VÁPENNÝ KAL–KŘEMIČITÝ ÚLET

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Článek představuje experimentální studii účinku teploty na kinetiku hydratace systému metakaolin–vápenný kal–křemenný úlet. Kaolin byl aktivován 2 hodiny při teplotě 800°C. Metakaolin a vápenný kal byly smíšeny v hmotnostním poměru 1:1. K této směsi bylo přidáno 5 hmot.% křemičitého úletu. Hmotnostní poměr voda:pojivo je 0,93. Tuhnutí vzorků probíhalo při teplotě 20 a 60°C při 100% relativní vlhkosti. Fázové složení vytvořených hydratovaných fází bylo stanoveno rtg difrakční, termogravimetrickou (TG) a kalorimetrickou (DSC) analýzou. Výsledky ukázaly, že pevnost v tlaku vzorku s teplotou tuhnutí 60°C byla větší než u vzorku s teplotou tuhnutí 20°C. Bylo také ukázáno, že posloupnost tvorby hydratovaných fází je pro při teplotě tuhnutí 20°C CSH, C_2ASH_8 a C_4AH_{13}, zatímco při 60°C se vytváří C_2ASH_8, C_4AH_{13} a hydratovaný granát (C_3ASH_6)