Chapter 72
Thermal Performance of Fly Ash Geopolymeric Mortars Containing Phase Change Materials

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This paper reports experimental results on the thermal performance of fly ash-based geopolymeric mortars containing different percentages of phase change materials (PCMs). These materials have a twofold eco-efficient positive impact. On one hand, the geopolymeric mortar is based on industrial waste material. And on the other hand, the mortars with PCM have the capacity to enhance the thermal performance of the buildings. Several geopolymeric mortars with different PCM percentages (10%, 20%, 30%) were studied for thermal conductivity and thermal energy storage.

1 Introduction

Climate change-related effects are associated mainly to the emissions of energy sector [1]. This in turn is dependent on the population rise that will be responsible for a very high increase of electricity demand [2]. The energy needs of the building sector are expected to grow more than 70% [3]. The European Union adopted very ambitious plans in order to tackle this paramount problem. The European Energy Performance of Buildings Directive (EPBD) 2002/91/EC has [4] required that by the end of 2018, all new buildings must have a nearly zero-energy consumption. The use of innovative materials like PCMs will make it easier for this target to be met [5]. These materials use chemical bonds to store or release heat thus allowing for a reduction on the energy consumption. The capability to store or release thermal

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energy in these materials depends strongly on the heat storage capacity, thermal conductivity, the melting temperature and the outdoor environment. Recently the use of PCMs on OPC-based materials has merit increased attention [6–8]. Also according to the Roadmap to a Resource Efficient Europe, all waste is to be managed as a resource [9]. This is a very important goal concerning the circular economy and zero-waste target [10]. Thus, materials that have the ability for the reuse of several types of wastes such as geopolymers must receive a special attention on this context [11]. This includes waste like fly ash because they are generated in high amount [12]. In this context this paper reports experimental results on the thermal performance of fly ash geopolymeric mortars containing PCMs because this is a research line that so far has received little attention.

2 Experimental Programme

The binder precursor was composed by 90% of fly ash and 10% of calcium hydroxide. Solid sodium hydroxide, which was obtained from commercially available product of Ercos, SA, Spain, was used to prepare the 12M NaOH solution. The chemical composition of the sodium hydroxide was 25%Na_2O and 75%H_2O. The sodium silicate liquid was supplied by MARCANDE, Portugal. The chemical composition of the sodium silicate was 13.5%Na_2O, 58.7% SiO_2 and 45.2% H_2O. The fly ash was obtained from the PEGO Thermal Power Plant in Portugal, and it was classified as class F according to ASTM-C618 standard [13]. It was used as the base material for the production of the geopolymers. The chemical composition of the fly ash is presented in Table 72.1.

Calcium hydroxide was supplied by LUSICAL H100 and contains more than 99% CaO. The sand was used as inert filler provided from the MIBAL, Minas de Barqueiros, SA, Portugal. The superplasticizer was commercially available in polyacrylate from Acronal series, with a density of 1050 kg.m^3 from BASF. One type of organic microencapsulated PCM was considered: BSF26 with melting temperature of 26 °C. The properties of the selected PCM for this study are provided by the manufacturer and are presented in Table 72.2.

Table 72.1 Major oxides in fly ash (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2
60.8	22.7	7.6	1.0	2.2	1.5	2.7	1.5

Table 72.2 Properties of PCMs

Operating temperature range (°C)	Latent heat of fusion (J/g)	Melting point (°C)	Apparent density at solid state (kg/m3)	Particle size distribution range (μm)
10–30	110	26	350	5–90

The specimens were cured in laboratory conditions (25 °C and 65% relative humidity (RH)). The thermal conductivities of the mortars were determined in four representative measurements of each mortar formulation, using a steady-state heat flow metre apparatus (ALAMBETA, Model Sensora), following recommendation of ISO 8301:1991 [14]. Mortars were casted into cylinder moulds with diameter of 10 cm and length of 1 cm. Then thermal conductivity of the specimen is calculated based on heat conduction heat transfer theory according to [15]. Specific enthalpies of the mortars were determined using, it is relevant to submit the sample into the differential scanning calorimeter-DSC testing (Model NETZSCH 200 F3 Maia) and measure the corresponding heat fluxes at controlled environment. Based on this, the specific heat as a function of temperature can be obtained, and the specific enthalpy is determined. The DSC has an accuracy of ±0.2 °C for temperature measurements. All the specimens were tested within aluminium crucibles with volume of 40 μL under nitrogen (N_2) atmosphere with a flow of 50 mL/min. The specimens were weighted using analytical balance (model PerkinElmer AD-4) with accuracy of ±0.01 mg. Each specimen was sealed in the pan by using an encapsulating press. An empty aluminium crucible was considered a reference in all measurements. A heating/cooling rate of 5 °C/min was considered for all experiments.

3 Results and Discussion

The thermal conductivity results are presented in Table 72.3. The lowest thermal conductivity is noticed for the mixtures based on a sodium silicate/sodium hydroxide ratio of 2.5 and an activator/binder ratio of 0.7. For a similar activator/binder ratio, the reduction of the sodium silicate/sodium hydroxide ratio to 2.0 leads to highest results of thermal conductivity. Results show that the addition of PCM into the different mortars results in a consistent reduction of thermal conductivities. The highest reduction is noticed for the mixtures based on a sodium silicate/sodium hydroxide ratio of 2.0 and an activator/binder ratio of 0.7. The DSC curves for the testing of mortars at heating/cooling rate of 5 °C/min are shown in Fig. 72.1.

Table 72.3 Thermal conductivity of mortars

Formulations	Group name	Thermal conductivity (W/m. K)
12M_2.5S/H_0.8A/B	A	0.77
10PCM_12M_2.5S/H_0.8A/B	A	0.70
20PCM_12M_2.5S/H_0.8A/B	A	0.69
30PCM_12M_2.5S/H_0.8A/B	A	0.44
12M_2.5S/H_0.7A/B_1.0SP	B	0.52
10PCM_12M_2.5S/H_0.7A/B_1.5SP	B	0.47
20PCM_12M_2.5S/H_0.7A/B_1.5SP	B	0.44
30PCM_12M_2.5S/H_0.7A/B_1.5SP	B	0.42
12M_2.0S/H_0.7A/B_1.0SP	C	0.94
10PCM_12M_2.0S/H_0.7A/B_1.5SP	C	0.90
20PCM_12M_2.0S/H_0.7A/B_1.5SP	C	0.77
30PCM_12M_2.0S/H_0.7A/B_1.5SP_3.0 W	C	0.35

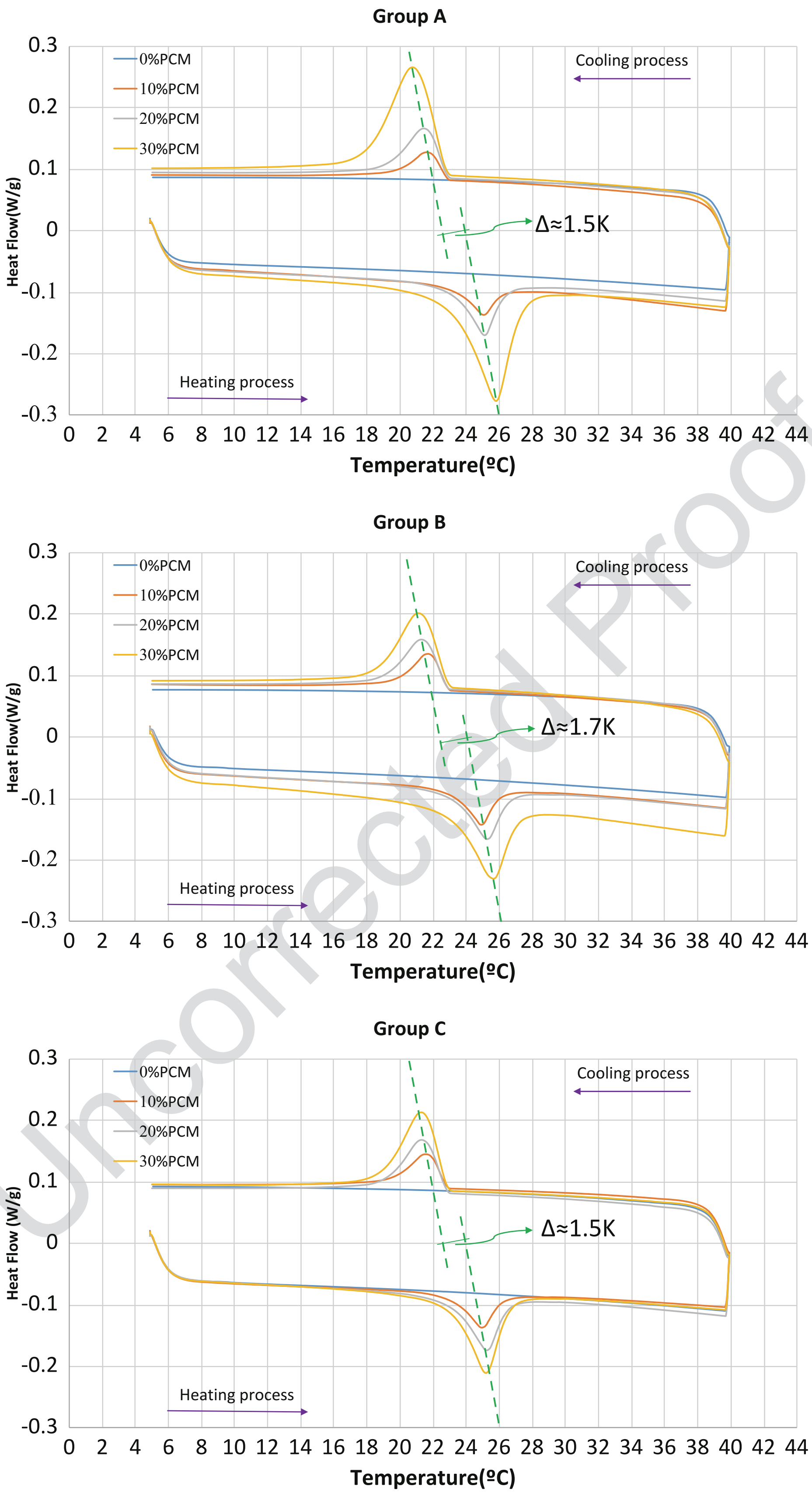

Fig. 72.1 DSC curves of the alkali-activated mortars with and without PCM upon a cooling and a heating cyclic test with a rate of 5 °C/min: (**a**) group A based on 12M_2.5S/H_0.8A/B; (**b**) group B based on 12M_2.5S/H_0.7A/B_1.0SP; (**c**) group C based on 12M_2.0S/H_0.7A/B_1.0SP AU3

Overall, the results suggested that the PCM peak temperature shifts in the direction of the imposed flux and further confirming higher peaks for mortars with higher mass fraction of PCM into the mix. The two dashed lines per graphic have been plotted by uniting the peak temperatures of all heating and all cooling thermograms: there is a clear linear relationship between the peak temperature of the thermogram and the percentage of PCM embedded. When the two dashed lines for a given group are compared, it can be noticed that they are approximately parallel and that the distance between them ranges from $\Delta \approx 1.5$ K to $\Delta \approx 2.5$ K. The difference observed in this hysteresis is known to depend on the internal thermal gradients upon the tested sample, which tend to lag or raise heat exchange from DSC. The average specific enthalpies for all the studied groups are ≈1.5 J/g, ≈2.5 J/g and ≈4 J/g for the mortar with 10%PCM, 20%PCM and 30%PCM, respectively.

4 Conclusions

The lowest thermal conductivity is noticed for the mixtures based on a sodium silicate/sodium hydroxide ratio of 2.5 and an activator/binder ratio of 0.7. For a similar activator/binder ratio, the reduction of the sodium silicate/sodium hydroxide ratio to 2.0 leads to highest results of thermal conductivity. Results show that the addition of PCMs results in a consistent reduction of thermal conductivities. The average specific enthalpies for all the studied groups are ≈1.5 J/g, ≈2.5 J/g and ≈4 J/g for the mortar with 10%PCM, 20%PCM and 30%PCM, respectively.

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