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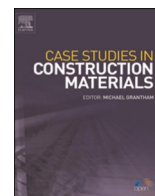
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Phase change materials incorporated into geopolymer concrete for enhancing energy efficiency and sustainability of buildings: A review

Iman Asadi^a, Mohammad Hajmohammadian Baghban^{b,*}, Mohammad Hashemi^c, Nima Izadyar^d, Behrang Sajadi^e

^a Department of Structural Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

^b Department of Manufacturing and Civil Engineering, Norwegian University of Science and Technology, Gjøvik, Norway

^c College of Civil Engineering, Hunan University, Changsha 410082, Hunan, China

^d School of Built Environment, College of Engineering and Science, Victoria University, Melbourne, Vic, Australia

^e School of Mechanical Engineering, College of Engineering, University of Tehran, Iran

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ABSTRACT

To reduce CO₂ emissions by 55% by 2030, applying sustainable and energy-efficient materials like geopolymer concrete containing Phase change materials (PCMs) for infrastructure development is necessary. This study reviews the geopolymer mortar and concrete containing PCMs, including their characterizations such as workability, density, compressive strength, heat capacity, thermal conductivity, and their effect on energy consumption in buildings. Existing literature reveals that using geopolymers instead of OPC can reduce thermal conductivity and power consumption. The latent heat and melting temperature of investigated PCMs were in the range of 96.1–230 J/g and 21.9–33.8 °C, respectively. Although microencapsulated PCMs (MPCMs) such as E-EVA and St-DVB have slightly reduced the compressive strength of geopolymers, they still show a high strength compared to typical strength classes in normal concrete. Also, the workability of geopolymer concrete can remain in the acceptable ranges when the PCMs are incorporated in the low percentages. Furthermore, a considerable increase in the heat capacity is reported at the PCM's melting temperature of geopolymer mortars and concretes, which can be deployed to conserve energy in the buildings.

1. Introduction

The cement industry accounts for about 5–7% of global CO₂ emissions [1]. The increment demand for cement to produce cement mortar and concrete may further impact the environment and cause climate change and global warming. Around four billion tons of cement were produced in 2013 [2], which would increase by 200% in 2050 [3]. The cement industry is significantly responsible for rising CO₂ emissions and global warming [4]. Around 0.8 tons of CO₂ is generated for one ton of cement production [5] by varying substantially between process types, producers, countries, and cement types. Also, another study showed that around 522 million tons of CO₂ were emitted by the cement industry in 2016 [6]. Concrete is a composite of cement, other powders such as pozzolan and filler

* Corresponding author.

E-mail address: mohammad.baghban@ntnu.no (M.H. Baghban).

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Nomenclature

k	thermal conductivity (W/m.°C)
C	specific heat capacity (J/g.°C)
Q	heat flow (W)
q	heat flux (W/m ²)
h	height of melting peak (m)
w	phase change temperature range
M	weight of samples (kg)
m	shape parameter
T	temperature (°C)
V	volume of samples (m ³)
∂T	temperature difference (°C)
∂x	distance (m)
ρ	density (kg/m ³)

Acronyms

GGBFS	ground-granulated blast-furnace slag
FA	fly ash
DSC	differential scanning calorimetry
GPC	geopolymer concrete
GPM	geopolymer mortar
LECA	lightweight expanded clay aggregate
LWA	lightweight aggregate
MG	milled glass
MPCM	microencapsulated phase change material
PCM	phase change material
WM	waste mud

Subscripts and superscripts

a	ambient
p	constant pressure
s	solid
r	right
l	liquid
L	left
m	melting

(including limestone filler with slight binder properties), water, chemical admixtures, coarse and fine aggregates with a wide variety of composition and applications. Concrete is one of the most frequently used building materials, while it is used twice as much as all other building materials such as plastic, wood, and steel [7]. Consequently, concrete is one of the primary sources of CO₂ emission to the

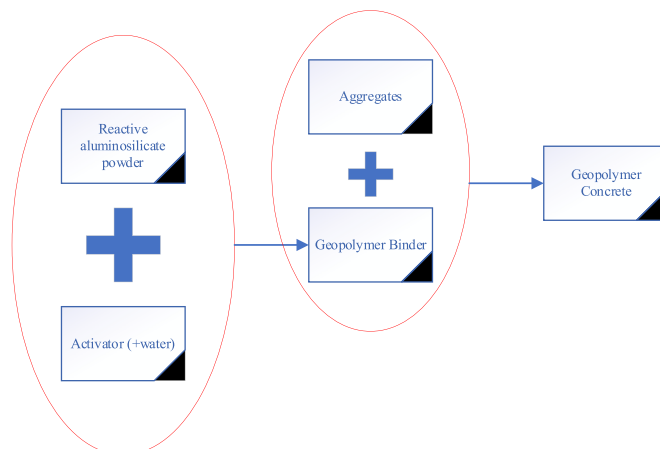


Fig. 1. Schematic of geopolymer concrete.

atmosphere and global warming. Therefore, an urgent change is needed to paradigm and produce more effective concrete and reduce harmful emission.

Ordinary Portland cement (OPC) is increasingly substituted by supplementary or pozzolanic cementitious materials such as fly ash and slag to prepare more environmentally friendly materials. It should be noted that many other materials can potentially substitute the cement with the content of CaO , SiO_2 , and Al_2O_3 , such as rice husk ash, metakaolin, and various natural pozzolana to produce concrete [8–11]. Geopolymer concrete, sometimes also called alkali-activated concrete, is a proper method to make conventional concrete more sustainable due to less or no Portland cement [12]. It was reported that the production of geopolymer instead of cement reduced the CO_2 emission by up to 80% [13].

Geopolymer concrete contains fine and coarse aggregate, aluminosilicate sources, and an activated solution [14,15] (Fig. 1). The aluminosilicate powders for use in geopolymer concrete are divided as 1. by-products from other industries (fly ash, low calcium slags, etc.), 2. natural reactive aluminosilicate powders (volcanic glass and tuffs, diagnosed silica gel from hot springs or acid environment, non-thermally activated clays, etc.), 3. activated aluminosilicates (calcined clays, metakaolin, etc.). It should be noted that all of them contain reactive silica and alumina. The characteristics of fly ash, metakaolin, silica fume, ground granulated blast slag (GGBFS), rice husk ash, red mud, and glass powder as common aluminosilicate precursors are discussed in ref. [16]. The $\text{CaO-SiO}_2-\text{Al}_2\text{O}_3$ system of various supplementary cementitious materials (SCMs) is shown in Fig. 2. The most common alkaline activator for activating aluminosilicate sources in geopolymer concrete is sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na_2SiO_3), and potassium silicate (K_2SiO_3).

Several studies reported that the mechanical properties of geopolymer concrete are like conventional concrete [17–20]. Some other studies showed that geopolymer concrete is a sustainable material with excellent compressive strength and durability [21,22]. Also, prior literature reported some other advantages for geopolymer concrete, such as high resistance against acid attack, high fire resistance, high resistance against chloride penetration, and low drying shrinkage [23–26]. Despite the mentioned advantages, some studies showed that activating solutions are potentially harmful to the environment due to sodium hydroxide and sodium silicate [27]. Mendes et al. discussed the traditional and alternative activators produced by waste (agricultural or industrial). Finally, they revealed alternative and ecological solutions to minimize the environmental impact of activators. Another drawback of geopolymer concrete is its low workability, discussed in Section 3.1.

Concrete's thermal behavior can directly impact the annual energy usage for heating and cooling in buildings. The thermal behavior of concrete depends on its thermal conductivity (k), specific heat capacity (C_p), and thermal diffusivity (α) [28–31]. These thermal parameters among the layer's density and thickness demonstrate the thermal capacity against the daily temperature sinusoidal cycle [30,32–35]. Incorporating the phase change materials (PCM) in concrete is proper to postpone buildings' maximum thermal load to low electricity demand [28].

Therefore, incorporating PCMs into the concrete can increase its heat storage capacity [36,37]. PCMs are divided into different categories such as organic, inorganic, and eutectic. Organic PCMs are subcategorized to paraffin and non-paraffin PCMs [28,38]. The melting point of paraffin wax varies from 20°C to 70°C with a latent heat range of 60–269 kJ/kg. The melting point of non-paraffin PCMs is $30\text{--}65^\circ\text{C}$, with the latent heat in the range of 153–182 kJ/kg [39–41]. The chemical structure of paraffin and non-paraffin PCMs are $[\text{C}_n\text{H}_{2n+2}]$ and $[\text{CH}_3(\text{CH}_2)_{2n}\text{COOH}]$, respectively. The most common type of inorganic PCMs is hydrated salt $[\text{MnH}_2\text{O}]$. The advantages and limitations of PCMs and various methods of incorporation for building applications have been discussed by Shafiqh et al. [28].

The GPC can increase sustainability and energy efficiency in different ways. It has been reported that the usage of cementitious materials instead of the OPC increased the sustainability of materials. However, considering the environmental impact of the activator in GPC should not be forgotten. Regarding energy-saving, GPC can decrease the embodied energy compared to the normal concrete and mortar by using optimal molar ratios [42] or reducing the curing period [43]. Despite the embodied energy, the operating energy

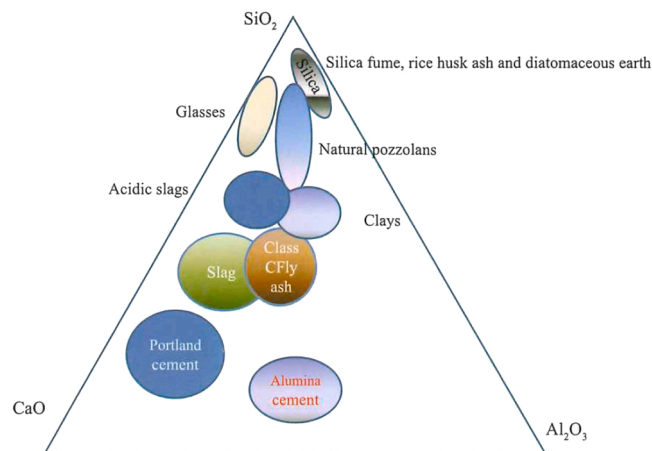


Fig. 2. $\text{CaO-SiO}_2-\text{Al}_2\text{O}_3$ system of some common SCMs.

Table 1
Chemical composition of binders (wt%).

Ref.	aluminosilicate	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	MgO	k ₂ O	TiO ₂	Na ₂ O	P ₂ O ₃	SO ₃	SrO	MnO	CO ₂	LOI
[79]	FA	29.3	57.5	6	2.95	1.36	–	–	2.6	–	–	–	–	–	–
[53]	FA	22.68	60.81	1.01	7.64	2.24	2.7	1.46	1.45	–	–	–	–	–	–
[37]	FA	25.71	52.65	6.236	5.307	1.402	1.981	1.2	1.1	1.01	0.935	0.19	–	1.74	–
	GGBFS	10.65	34.3	43.97	0.359	5.026	0.569	1.19	0.28	–	3.01	–	–	0.13	–
[54–58,80]	FA	23.15	50.83	6.87	6.82	1.7	2.14	1.01	1.29	1.14	1.24	0.19	–	3.07	–
	GGBFS	10.3	34.51	42.84	0.6	7.41	0.52	0.66	0.4	0.02	1.95	0.05	–	0.3	–
[65]	FA	23.1	48	3.2	12.5	1.5	–	–	–	–	–	–	–	–	1.1
	GGBFS	14.4	34.7	42	0.8	6.8	–	–	–	–	–	–	–	–	1.1
[67]	FA	20.58	36.02	18.75	15.91	–	–	–	–	–	2.24	–	–	–	0.07
	SF	1.17	88.30	0.48	4.76	–	–	–	–	–	1.05	–	–	–	–
[66]	FA	22.68	60.81	1.01	7.64	2.24	2.7	1.46	1.45	–	–	–	–	–	–
	Metakaolin	37.62	56.22	–	2.45	–	2.53	0.87	0.3	–	–	–	–	–	–
[64]	FA	23.1	48	3.3	12.5	–	–	–	–	–	–	–	–	–	–
	GGBFS	14.4	34.7	42	–	6.9	–	–	–	–	–	–	–	–	–
	DS	3	63.9	14.1	–	–	–	–	–	–	–	–	–	–	–
[75,76]	GGBFS	10.7	37.3	43	0.2	6.5	0.8 ^a	0.7	0.8 ^a	–	–	–	–	–	–
	Metakaolin	41	55	0.1	1.2	0.2	1.8 ^a	0.4	1.8 ^a	–	–	–	–	–	–
[73]	WM	19.56	47.66	–	12.6	–	3.85	–	1.41	–	11.63	–	–	–	–
	MG	–	73.93	12.83	–	–	0.69	–	9.72	–	–	–	–	–	–
[78]	Clay	21.73	49.28	2.39	8.44	8.86	0.95	–	1.06	–	–	–	0.12	–	–
	Slag	10.67	32.84	39.73	0.54	7.57	0.38	–	0.17	–	–	–	0.11	–	–

^a (Na₂O+ k₂O) eq

in buildings can be significantly improved using PCM technologies [44–46]. Recently, a few researchers incorporated the PCM into the geopolymer concrete and mortar (PCM-geopolymer concrete/mortar) to produce a sustainable and energy-efficient material.

This review evaluates PCM-geopolymer concrete/mortar studies in terms of density, compressive strength, thermal properties, and power reduction. The review process was designed based on published papers within the last six years (i.e., January 2016– January 2022) and among the documents, which consist of all three keywords of “Geopolymer” and “PCM” and “concrete” or “mortar” or “paste” in the title, summary, or keywords sections. Section 2 will summarize the materials used, and the studies in the context of physical and mechanical properties will be outlined in Section 3. Also, the thermal properties and their effect on energy saving will be reviewed in Sections 4 and 5, respectively.

2. Materials

Geopolymer concrete contains aluminosilicate sources, an activated solution (an inorganic binder), fine aggregate, and coarse aggregate [47]. The geopolymer binder is achieved by mixing aluminosilicate powder and alkali activators such as alkali hydroxide solution (NaOH, KOH, LiOH, RbOH, CsOH), alkali silicate solution, or water glass (Na₂O, K₂O, SiO₂, water) and calcium hydroxide [48–52]. Prior literature showed that researchers evaluated various PCM-geopolymer concrete/mortar properties using different types of geopolymer binders. The prior literature is categorized based on materials used as geopolymer binders in Section 2.1 and PCMs in Section 2.2.

2.1. Geopolymer binders

The FA was the most used material as the aluminosilicate powder in literature. In some cases, it was used solely [53], and in some other studies, it was mixed with the other aluminosilicate sources such as GGBFS [36,37,54–62] and dune sand (DS) [63–65], Metakaolin [66], and silica fume (SF) [67]. FA is a byproduct of the coal industry, and its physical and chemical properties can be varied based on the source of the coal and combustion conditions [68,69]. However, FA is generally considered a good geo-polymerization due to the high amount of Al₂O₃ and SiO₂ [70]. FA’s availability (Around 363 million tons of FA are produced yearly [71]) is the main reason for the vast usage of FA as the aluminosilicate powder. It should be noted that the main problem of using FA is reducing the PH of concrete, which can lead to carbonation [72]. Analyzing FA’s chemical compositions in the prior literature showed that the SiO₂, Al₂O₃, Fe₂O₃, CaO, and MgO were the most component in the ranges of 48–60.8%, 20.6–29.3%, 2.9–15.9%, 1–18.7%, and 1.2–2.2%, respectively (Table 1).

Despite FA’s studies, some researchers applied different binder types to prepare PCM-geopolymer concrete/mortar. For instance, Kastiukas et al. [73] used waste mud (WM) as a binder when 20% of its weight was replaced by the milled glass (MG) to increase SiO₂ content. In other studies, metakaolin [74], the mix of GGBFS and metakaolin [75,76], red mud [77], and the combination of clay and slag [78] were used as the binder. The characteristics of aluminosilicate powders for geopolymer concrete are defined in ref.[14] and

Table 2
Alkali activator in binders.

Ref.	Aluminosilicate powder	Alkali activator	ratios
[53]	FA	sodium hydroxide solution and sodium silicate solution	Na ₂ O = 13.5%, SiO ₂ = 58.7%, H ₂ O = 45.2%, Ratio of the weight of Sodium silicate solution to sodium hydroxide solution = 2.5
[37]	FA and GGBFS		Ratio of Na ₂ SiO ₃ and NaOH= 1.5
[54–60, 62]	FA and GGBFS		Ratio of NaOH and Na ₂ SiO ₃ = 1:1.5
[65]	FA and GGBFS		Na ₂ O: SiO ₂ = 1:2.24, NaOH:Na ₂ OSiO ₂ = 1:1
[67]	FA and SF		Na ₂ O = 13.5%, SiO ₂ = 58.7%, H ₂ O = 45.2%, Ratio of NaOH and Na ₂ SiO ₃ = 1:1.5
[66]	FA and Metakaolin		Na ₂ O = 11.47%, SiO ₂ = 27.53%, H ₂ O = 61%, ratio the weight of Sodium silicate solution to sodium hydroxide solution = 2.5
[63,64]	FA, GGBFS, DS		Na ₂ O = 4.79%, SiO ₂ = 15.5%, 35% water by mass
[75,76]	GGBFS and Metakaolin		SiO ₂ = 22.4%, Na ₂ O = 10.9%, SiO ₂ /Na ₂ O = 1.5, Na ₂ O concentration is = 4% of the total weight of slag and clay
[73]	WM and MG		
[78]	Slag and Clay		

ref. [16]. Also, assessing the prior literature showed that the researchers selected different alkaline activators to prepare geopolymer concrete containing PCMs (Table 2).

2.2. PCMs

Organic PCMs, such as paraffin, are the most common PCMs used in building applications due to their advantages such as safety, non-reactivity, chemical stability, and the ability to use in the form of microencapsulated [28,38,81]. Regarding the methods of incorporation, immersion, impregnation, and encapsulation are the most effective ways to incorporate PCMs with concrete [82–86]. It should be noted that the encapsulation method is divided into two subcategories entitled macro encapsulation and microencapsulation. Microencapsulation is the most used method for incorporating PCM into geopolymer concrete/mortar. In this method, PCM is the core material covered by a shell. The shell can be a metal, polymer, or plastic. It is a medium between PCM and the environment to control PCM volume during the phase changing and avoid leakage. Table 3 summarizes the types of PCMs and methods of incorporation into geopolymer mortar or concrete. Also, PCMs can be used in geopolymer mortar and concrete as an additive to the mixture or as the aggregate replacement in different percentages [79,87]. The prior literature showed that the PCM could be used as the fine aggregate replacement from 5% to 30% [36,37,55,66,76,78,79] and as an additive up to 80% weight of aluminosilicate powder [88].

The PCM-Geopolymer concrete/mortar can influence its physical, mechanical, and thermal properties. Also, PCM-Geopolymer concrete can reduce energy consumption significantly. The following section summarizes the prior literature regarding workability, density, compressive strength, thermal conductivity, heat capacity, and energy-saving.

3. Physical and mechanical properties

3.1. Workability and density

Some studies reported the workability of PCM-Geopolymer concrete through slump test based on EN 12350–2 and PCM-Geopolymer mortar through measuring flow time based on NF P18–452. The use of PCM in conventional concrete reduces its workability [37]. Also, the workability of geopolymer concrete is lower than the regular concrete due to the higher water demand of some aluminosilicate powder and the higher viscosity of some alkaline activators or the concentration of alkaline solutions [57, 89–93]. Furthermore, the workability of PCM-Geopolymer mortar is less than conventional cement mortar due to the rheology differences between geopolymer and cement [94].

Therefore, PCM-Geopolymer concrete/mortar workability is much lower than the typical concrete/mortar with PCM and geopolymer concrete/mortar without PCM [37,58]. It can be attributed to the differences in particle size of the sands and replaced PCM or the water absorption by MPCM shell [54,95]. However, adding superplasticizers (SP) like Naphthalene-based can improve PCM-Geopolymer concrete/mortar workability, especially in the FA-based geopolymer binders [54,96–98]. Also, using MPCMs with

Table 3
PCMs in geopolymer concrete.

Ref.	Method of incorporation	Type of PCM (technical name)	Melting temperature (°C)	Latent heat (J/g)	Type of coating
[73]	Impregnation into aggregate and coating with immersion and spray	Organic paraffine	22–26	230	Sika latex, Weber dry-lastic, Palatal, Palatal-powder
[36,37]	Microencapsulation	paraffin wax (Rubitherm®RT27)	28.4 ± 0.9	–	low density polyethylene (LDPE), ethylvinylacetate (EVA), (EVA/LDPE = 0.5)
[58–60, 62]		paraffin (Rubitherm®RT2)	24.9	100	polystyrene cross-linked with divinylbenzene
		paraffin (PCM26)	24.7	110	polymethyl methacrylate
		Paraffin (24D)	21.9	154	melamine-formaldehyde polymer
[53,66]		paraffin (BSF26)	26	110	–
[54–57]		paraffin wax (Rubitherm_RT27)	28.4 ± 0.9	98.1	ow density polyethylene (LDPE) and ethylvinylacetate (EVA)
			24.2 ± 0.9	96.1	styrene (St) and divinylbenzene (DVB)
[79]		paraffin	28	180–195	inert, stable polymer, or plastic
[88]		Paraffin	17.3–24.1	170.4	Alumina hollow spheres
[75,76]		Paraffin (Nextek 28 D)	26–28	180–190	urea polymer cross-linked with a polyethylene
[65]		Paraffin (RT31)	28–33.8	124.1	Geopolymer paste

the hydrophobic shells limits the water affinity's effect [54].

It was reported that adding the Naphthalene-based SP (up to 2% of the mass of FA) can increase the workability of concrete without any reduction in its compressive strength [99]. Also, another study [100] revealed that the Naphthalene-based SP could increase the workability of FA geopolymer (136% increment in the relative slump test) without any profound effect on its compressive strength. However, some other studies reported a significant reduction in the compressive strength of geopolymer concrete by adding Naphthalene-based SP (1.19% of FA mass) to the mixtures [101].

Some prior studies measured PCM-Geopolymer concrete/mortar density based on EN 12390-7, EN1015:10, ASTM C138, [102, 103]. Some studies revealed that geopolymer concrete/mortar density increased slightly by enhancing PCM content as aggregate [67, 78]. Some others showed a few reductions in density by adding PCM to the samples [36,53,58,66]. The summary of reported density for different samples is shown in Figs. 3 and 4. It should be noted that the density of samples that were prepared by the impregnation method (injection paraffin into the carrier agent like perlite or LWA) remained almost the same as the control sample (specimens without PCMs)(Fig. 3). It may be attributed to filling the porosity of lightweight aggregates by liquid PCMs. However, an increment in MPCMs content reduced the density of PCM-Geopolymer concrete/mortar (Fig. 4). It may be attributed to the lower density of MPCMs than the sand and higher porosity in samples containing MPCMs.

3.2. Compressive strength

Despite the strength of standard concrete, which depends on the formation of cement gel (C-S-H), the geopolymer gel is the most influential factor in the strength of the geopolymer concrete depending on the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ [42,104,105]. It should be noted that this ratio can be varied based on the type of aluminosilicate powders [106,107]. For example, the optimum strength for a metakaolin-based geopolymer concrete was achieved when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is 3.0–3.8, and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio is around 1 [108]. However, another study reported that the highest strength for a geopolymer mortar containing glass waste is achieved by a molar ratio of 2.5 [109].

Regarding the PCM-Geopolymer concrete/mortar, the studies that used carrier agents to incorporate the PCMs [67,78] reported a similar strength to the control samples (even a slight increment in compressive strength by enhancing PCMs was written). It may be attributed to the filling up of the voids by liquid paraffin. Except for the ref. [77], the other available literature showed that replacing sand with MPCMs reduced the compressive strength [37,56,64–66,73,75,76,79,88]. The compressive strength reduction can be attributed to the low stiffness of MPCMs compared to the sand and weaker bonding between MPCMs and the matrix [110–112].

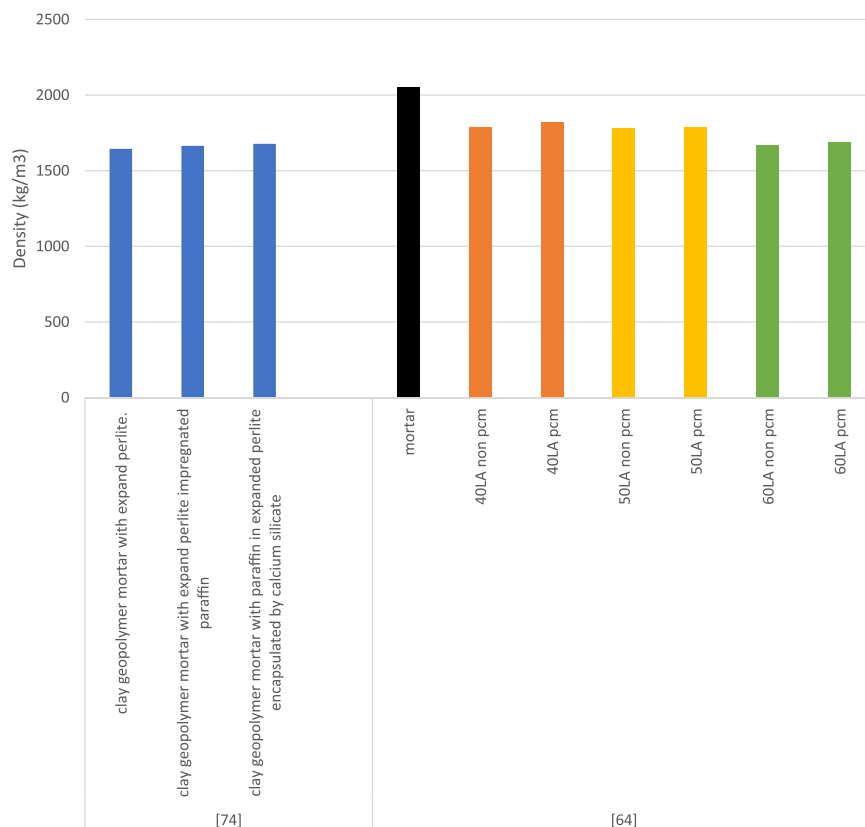


Fig. 3. Density of samples by adding PCMs through impregnation (xLA, where x is the percentage of coarse aggregate by volume).

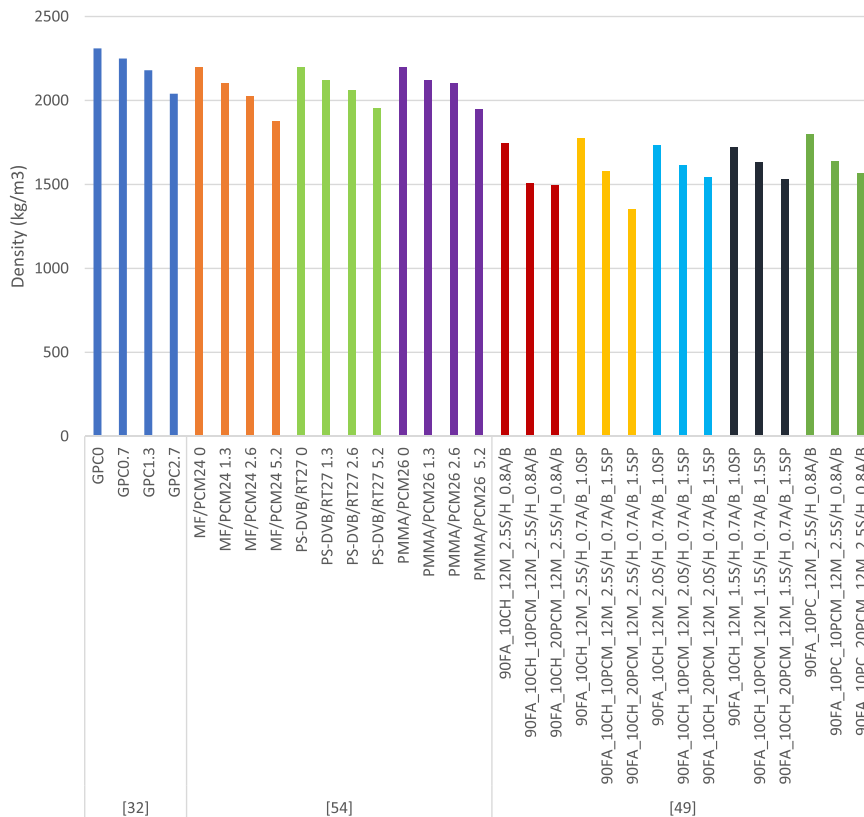


Fig. 4. Density of samples that decreased by adding PCMs.

Generally, the geopolymer concrete has sufficient compressive strength, and some studies reported a better compressive strength than Portland cement concrete [55]. For instance, the compressive strength of geopolymer concrete containing 20% MPCMs was more than the Portland cement concrete without MPCMs [54]. Thus, it was expected that incorporating PCMs into the geopolymer matrix would cause a lower reduction in compressive strength than the Portland cement concrete. However, the results were the reverse of the assumption. For instance, the compressive strength of PCM-Geopolymer concrete and PCM-Normal concrete decreased around 51%

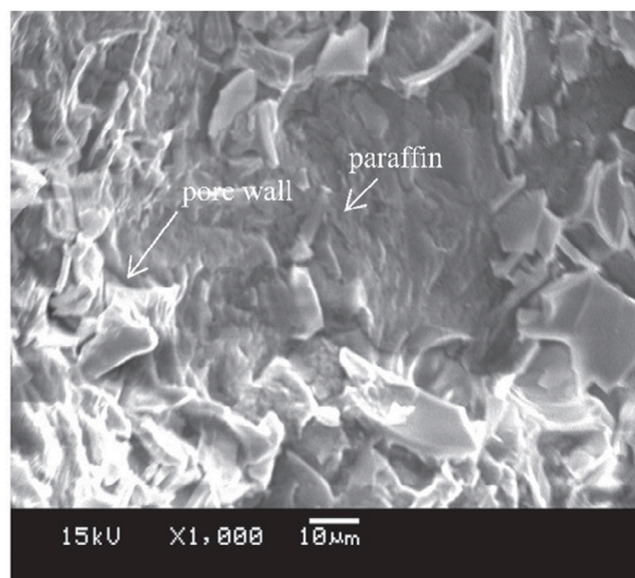


Fig. 5. SEM of expanded perlite [78].

and 42% by adding 2.7%wt and 3.2%wt of MPCMs, respectively [36]. It clearly shows that the compressive strength reduction in the presence of MPCMs in PCM-Geopolymer concrete is more than PCM-Normal concrete even with less MPCMs content. The main reasons are the higher porosity in PCM-Geopolymer concrete and the poor interface between MPCMs and binder.

In one study, Pilehvar et al. [55] reported a stable compressive strength for PCM-Geopolymer concrete after the freeze-thaw cycles test compared to the conventional concrete. They reported that MPCMs in geopolymer concrete increased the freeze-thaw cycle resistance due to increased porosity. Moreover, Pilehvar et al. [37] reported that curing temperature and method could affect the compressive strength of PCM-Geopolymer concrete. Regarding the PCMs phase (liquid or solid), Cao et al. [58] and Afolabi et al. [77] reported a higher compressive strength in the solid phase than in the liquid phase.

In summary, the unchangeable compressive strength of geopolymer mortar/concrete can be mentioned as the main advantage of impregnation (injection paraffine into the carrier agent like perlite or LWA). However, the leakage of phase change materials during the changing phase is the biggest drawback of this incorporation method.

3.3. Microstructural analysis

The void size and ITZ were the main reasons for changing the density and compressive strength of PCM-Geopolymer concrete/mortar. The SEM result of expanded perlite is shown in Fig. 5. This figure demonstrates the capability of perlite pores in the absorption of paraffine. Therefore, the perlite can be a good package for PCM during the phase-changing process.

However, most studies reported reducing density and compressive strength by adding MPCMs to the samples. They concluded that porosity increased in the geopolymer concrete due to large agglomeration and unfilled cavities formed by adding MPCMs [113]. Fig. 6 shows the agglomeration of the MPCMs presented by Pilehvar et al. [37]. They observed the porosity of normal concrete and geopolymer concrete with and without MPCMs using X-ray microtomography. They emphasized that many agglomerates of MPCM are produced for samples containing 20% MPCM. The increment of agglomerate MPCM is one of the main reasons for compressive strength reduction in concrete (Fig. 7). Also, another study showed that the usage of MPCMs increased the porosity due to making obvious gaps between MPCMs and concrete matrices. (Fig. 8) [36].

It should be noted that distinguishing between porosity and MPCM through X-ray scanning is not straightforward. By applying grayscale analysis, air voids and MPCMs seem dark colors. Therefore, a shape analysis was suggested to assume the spherical as void and irregular as MPCM [37]. However, the shape analysis is not a proper method in some cases (like using PMMA/PCM26) due to the spherical shape of MPCM too. Therefore, Cao et al. [58] suggested size analysis in these cases as the air voids have appeared much more considerable than MPCM.

Also, damage in MPCM shells due to alkaline reaction and mixing processes can affect PCM-Geopolymer concrete/mortar thermophysical properties. The microscopic analysis of MPCMs showed that the surfaces are resistant to alkaline solutions (Fig. 9a), but some are potentially broken during mixing (Fig. 9b).

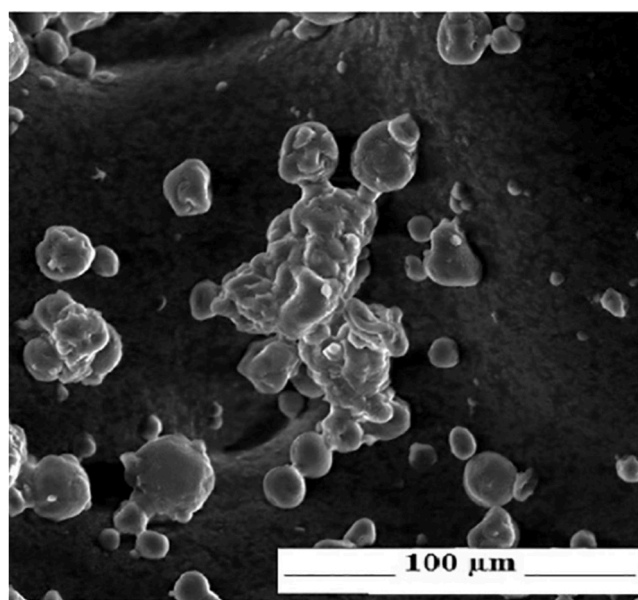


Fig. 6. SEM of agglomerate MPCM [37].

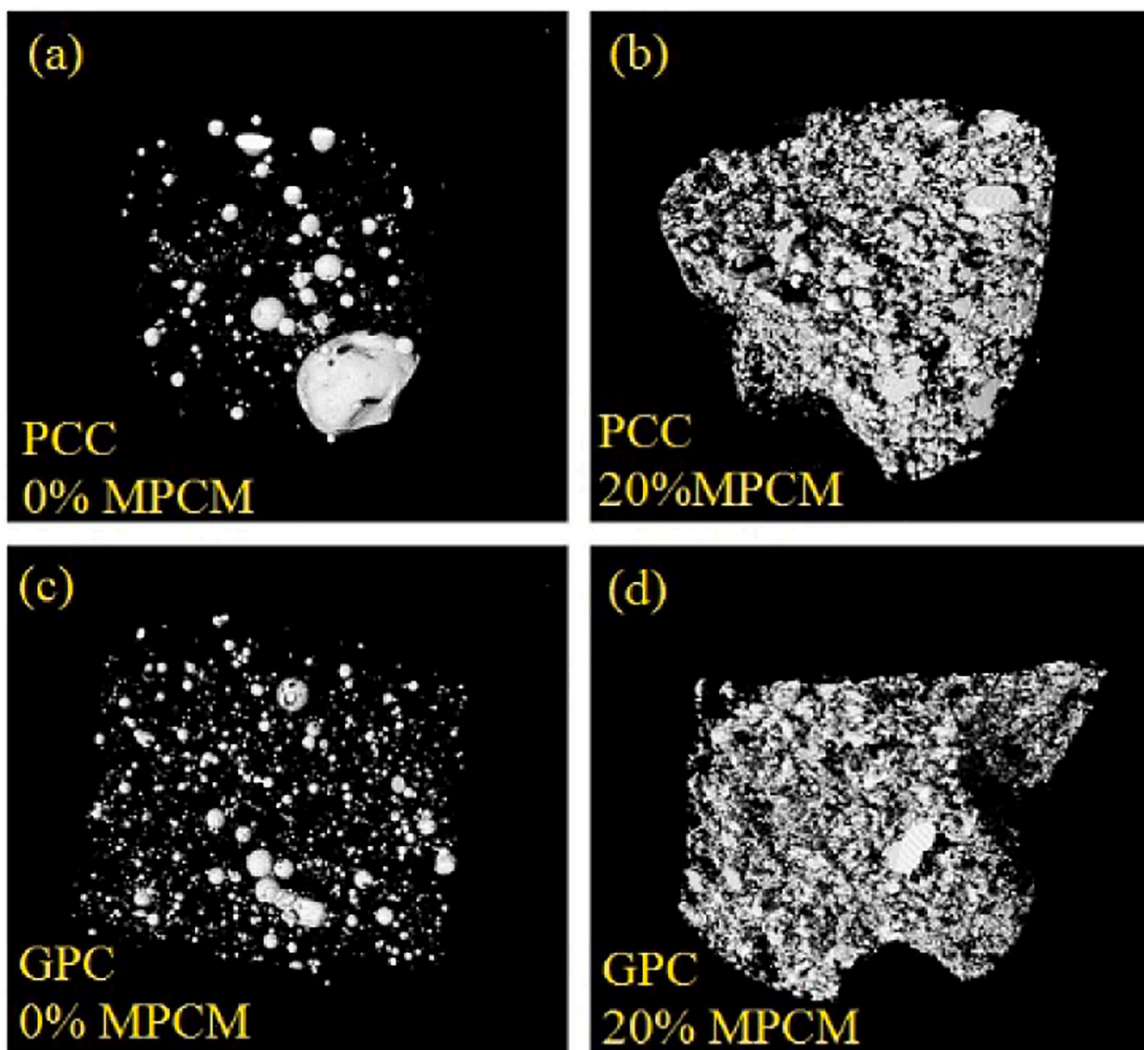


Fig. 7. 3D rendering of MPCM and air bubbles for a) normal concrete without PCM, b) Normal concrete with 20%PCM, Geopolymer concrete without PCM, b) Geopolymer concrete with 20%PCM [37].

4. Thermal properties

4.1. Specific heat capacity (C_p)

Incorporating PCMs can enhance buildings' energy storage capacity of buildings' walls [114–116]. PCM-geopolymer concrete/mortar is a solution to save energy in the building sector [53]. The amount of energy-saving is directly related to the thermal properties of mortar or concrete [117–119]. Using PCMs increases geopolymer concrete's energy storage capacity during changing phase due to the high latent heat capacity [120]. The prior literature showed that the thermal energy storage of PCMs used in geopolymer concrete/mortar was in the range of 96.1–230 J/g (Table 3).

Differential scanning calorimetry (DSC) is an excellent rapid method to evaluate the thermal performance of PCMs and the heat capacity of samples in a wide range [121]. The DSC was used in prior literature to assess the heat storage capacity of MPCM and PCM-Geopolymer concrete/mortar. Furthermore, other methods such as hot plates were used in some studies to determine samples' thermal conductivity and heat capacity. It should be noted that the peak temperature and latent heat for fusion and solidification are not the same. For instance, Wang et al. [78] reported that paraffine's peak melting point and peak solidification point are 41.44 °C and 32.16 °C, respectively. Consequently, the latent heat of fusion and solidification is around 135.46 J/g and 158.14 J/g, respectively.

Fig. 9 shows the specific heat capacity of different PCM-Geopolymer concrete. The heat storage capacity of different samples increased in the range of 21 °C to 28 °C, which can be attributed to the gained heat for changing the phase of PCM in this range. The results showed the type and amount of PCMs influence the heat storage capacity of geopolymer concrete. For instance, the heat capacity of GPC containing MF/PCM24 is higher than GPC containing PMMA/PCM26. Also, the geopolymer mortar's heat capacity

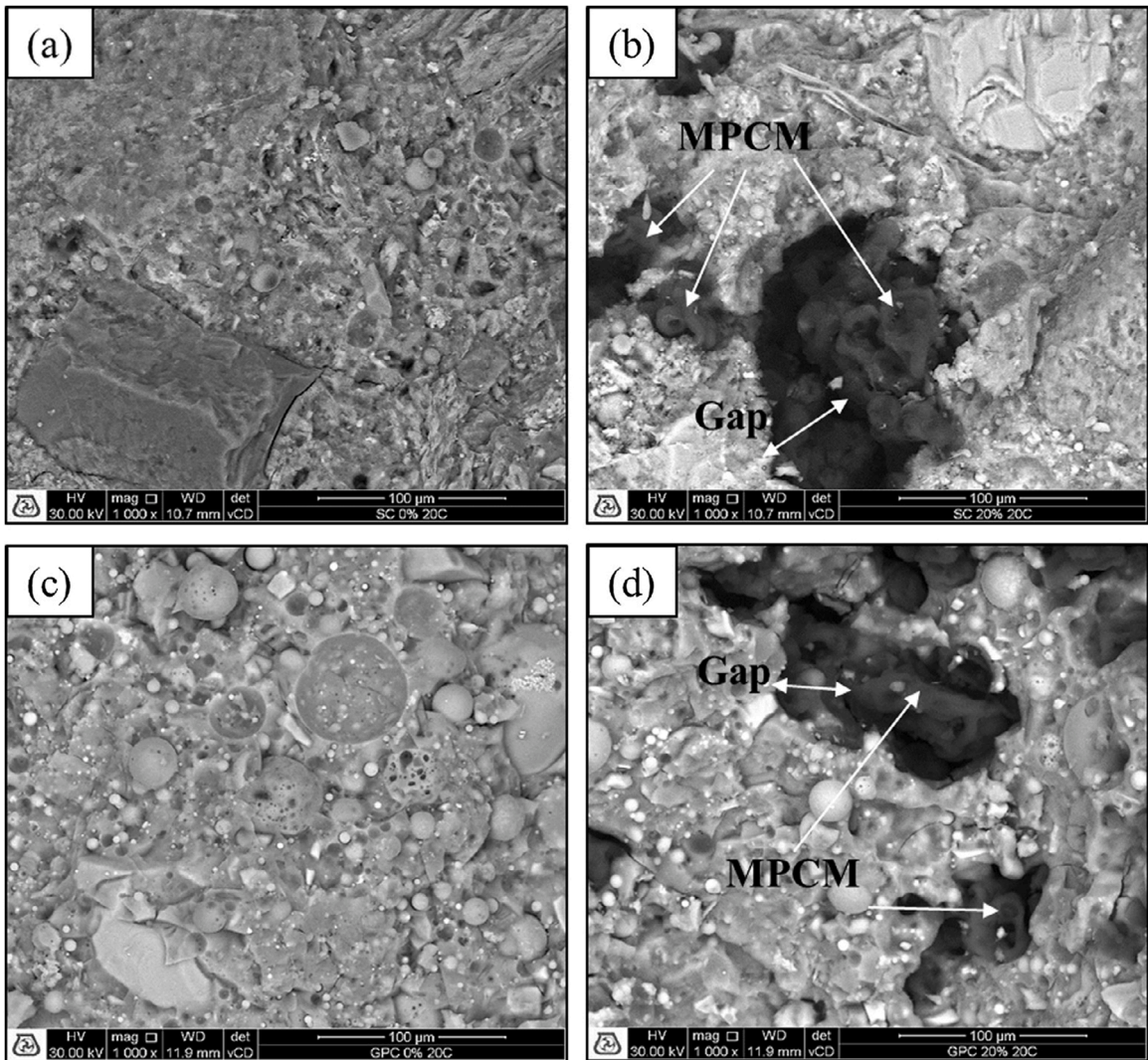


Fig. 8. SEM of a) normal concrete without PCM, b) Normal concrete with PCM, Geopolymer concrete without PCM, b) Geopolymer concrete with PCM [36].

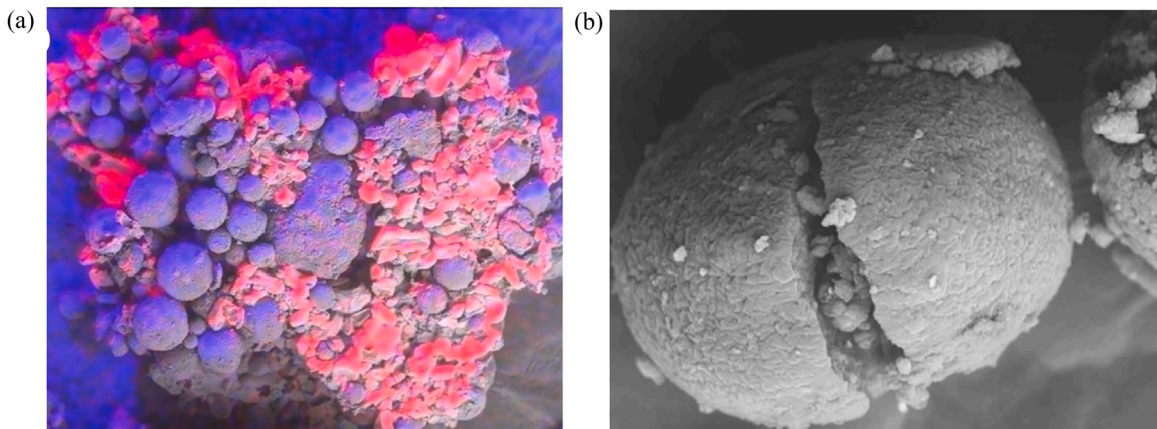


Fig. 9. Image of MPCM a) in alkaline solution b) after mixing [56].

containing 20% PCM is higher than the sample with 10% PCM. It should be noted that the heat capacity of geopolymer without PCM is a straight line in the range of 10–40 °C. (Fig. 10).

Regarding the numerical calculation of $C_p(T)$ Some studies assume the peak melting point is symmetrical and use a piecewise function (Eq. 1) [122,123] or Gaussian function [124,125](Eq. 2). However, Cao et al. [59] revealed that these equations are not in good agreement with the experimental results for Geopolymer concrete or mortar containing MPCMs. Therefore, they developed Eq. (3), which fits the experimental results (Fig. 8).

$$C_p(T) = \left\{ \begin{array}{ll} C_{ps} & \text{for } T \leq T_{ms} \\ \frac{L}{T_{me} - T_{ms}} + C_p & \text{for } T_{ms} \leq T \leq T_{me} \\ C_{pl} & \text{for } T_{me} \leq T \end{array} \right\} \tag{1}$$

$$C_p(T) = C_{s,l} + \frac{B}{W} \exp \left[- \left(\frac{T - T_m}{W} \right)^2 \right] \tag{2}$$

$$C_p(T) = \left\{ \begin{array}{ll} C_{ps} + h_l \frac{w_l^{2m_l}}{\left\{ \left((w_l^2 + (2^{m_l} - 1)) * (2T - 2T_m)^2 \right)^{m_l} \right\}} & \text{for } T \leq T_m \\ C_{pl} + h_r \frac{w_r^{2m_r}}{\left\{ \left((w_r^2 + (2^{m_r} - 1)) * (2T - 2T_m)^2 \right)^{m_r} \right\}} & \text{for } T > T_m \end{array} \right\} \tag{3}$$

Where B is the melting peak factor (j/kg), W is the difference in the temperature from melt when 84% of the latent capacity occurs. (Fig. 11).

4.2. Thermal conductivity (k)

Despite the heat storage capacity, thermal conductivity is a controversial issue. The higher thermal conductivity in MPCM is needed to speed up the phase-changing process, and the lower thermal conductivity of the building envelope is beneficial in reducing heat transfer [38,126,127]. It was found that the thermal conductivity of PCM-Geopolymer concrete/mortar decreased by adding MPCM. It can be attributed to the lower thermal conductivity of MPCM compared to the sand [128]. For example, paraffin and geopolymer shell's thermal conductivity is around 0.2 W/m.°C and 0.13–0.34 W/m.°C, respectively; however, the thermal conductivity of sand is up to 2.5 W/m.°C. Porosity and poor interface between MPCM and matrix also are the other vital parameters in thermal conductivity reduction [58,119]. As described in Section 3, the porosity of samples was increased by adding MPCM. El Moustapha et al. [75] attempted to minimize some drawbacks of MPCMs by adding metakaolin to the Slag based Geopolymer mortar. They revealed that the thermal conductivity of PCM-Geopolymer mortar (10% MPCM) increased around 31.28% in the presence of 20% metakaolin. Also, Sang et al. [88] developed an MPCM containing paraffine as the PCM and an alumina hollow sphere as the shell. They reported that thermal conductivity reduction in this type of MPCM is lower than in diatomite and expanded vermiculite.

In addition, the thermal conductivity of samples in the solid-state of PCM was higher than liquid phase [36,58]. It is attributed to the higher thermal conductivity of PCMs in the solid-state compared to the liquid form [127,129]. For instance, the thermal conductivity of paraffine is o 0.358 W/m.°C and 0.148 W/m.°C in solid and liquid phases, respectively [130].

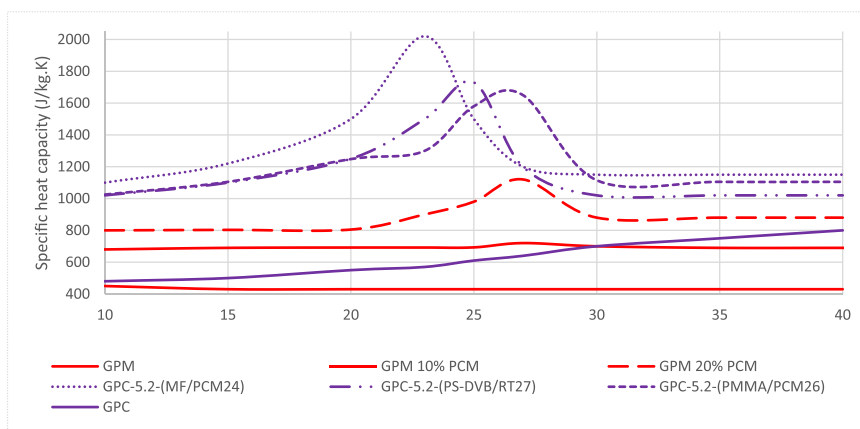


Fig. 10. The heat capacity of geopolymer mortar and concrete with/without PCM Adapted from [58,79].

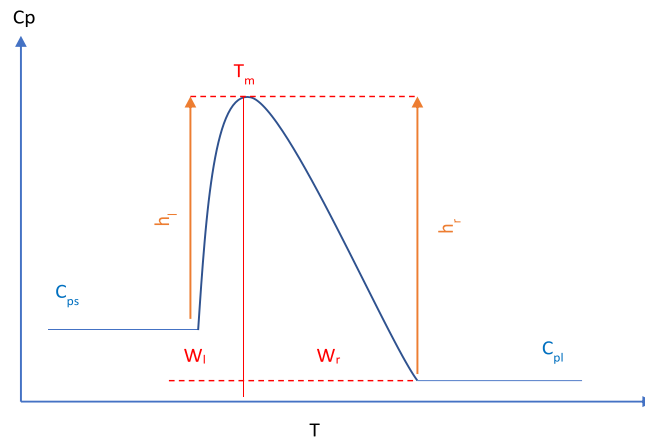


Fig. 11. The specific heat capacity of geopolymer concrete.

5. Energy saving

The aim of incorporating PCMs into the geopolymer concrete/mortar is to produce an energy-efficient and sustainable material [38, 60]. Prior literature revealed that the PCM-geopolymer concrete could reduce energy usage in buildings [36,54,77].

The experimental measurement of energy reduction in actual conditions is time-consuming and costly. Thus, numerical simulation is an alternative method to predict energy usage in different scenarios [61]. Previously, some researchers developed numerical methods to simulate energy usage based on indoor and outdoor temperatures [131,132]. Various studies also developed numerical methods to evaluate the thermal efficiency of materials containing PCMs [133–137]. Regarding the PCM-geopolymer concrete, Cao et al. [36] subjected one side of the samples to a heating and cooling cycle in the range of 23–20–32–20 °C as the outdoor temperature. The other side was kept at 23 °C as the indoor temperature. They used the following equation to calculate the total energy consumption for samples:

$$Q = \frac{\int_{t_1}^{t_2} |\dot{Q}_{indoor}| dt}{3600 \cdot 10^3} \quad (4)$$

They reported that the geopolymer concrete containing 2.7% MPCM could save energy for heating and cooling purposes up to 15%. However, they revealed that the energy usage reduction for normal concrete containing 3.2% MPCM is around 11% compared to those without MPCM. They concluded that the more decline in geopolymer samples than the Portland cement samples might be attributed to higher porosities after adding MPCMs. In another study, Cao et al. [58] used a small chamber to evaluate the amount of heat transfer and energy consumption through PCM-geopolymer concrete. They fixed the indoor temperature at 23 °C and calculated the sinusoidal outdoor temperature as follows:

$$T_{outdoor}(t) = \frac{T_{max} + T_{min}}{2} + \frac{T_{max} - T_{min}}{2} \sin\left(\frac{\pi}{43200}t - \frac{2\pi}{3}\right) \quad (5)$$

When T_{max} and T_{min} were 40 °C and 10 °C, the total heat transfer was calculated by applying Eq. (1). They concluded that the samples containing more MPCMs could keep the indoor temperature very close to the comfort temperature of humans (23 °C) by using less energy than the samples without MPCMs. Furthermore, the numerical method was applied to analyze the heat transfer of walls [59]. The results showed a good agreement between numerical simulation and experimental measurement. It was found that using 75 mm of PCM-geopolymer concrete containing 5.2 wt% MF/PCM24 can reduce the energy consumption by up to 35%. In another study, the numerical calculation based on the outdoor temperature and radiation was applied to determine the effect of climate (The climate of Oslo and Madrid), orientation, and season on the efficiency of PCM-geopolymer concrete for energy saving [62]. It was found that the PCM-geopolymer concrete is more effective for western and southern walls in both climates. Also, the PCM-geopolymer concrete was more effective during summer than winter in Oslo and Madrid. Moreover, Madrid's saved energy was more than in Oslo. The efficiency of PCM-geopolymer concrete in winter and Madrid is related to the melting temperature of MPC. [61]. Also, Cao et al. [62] calculated the effect of PCM-geopolymer concrete in a multi-layer wall house in Oslo, Norway. They revealed that the energy consumption could be reduced up to 32% in the presence of PCM-geopolymer concrete, PCM wall, and insulation layer.

6. Discussion

Several researchers recently developed sustainable materials to reduce energy usage and CO₂ emission in the building sector. Geopolymer mortar and concrete can reduce CO₂ emissions related to cement production. Incorporating the phase change materials (PCMs) into the building materials, such as concrete, can also reduce the heating and cooling power consumption. The PCM-Geopolymer concrete/mortar are energy-efficient materials considered future materials in the building sector. It is vital to assess

this material's recent development and summarize its advantages and disadvantages before practical usage in the building industry. Recently, a few studies considered its thermo-physical and mechanical properties.

By reviewing the prior literature, it was found that most studies used FA and GGBFS as a binder, and there is a lack of knowledge related to the PCM-Geopolymer concrete/mortar containing other aluminosilicate powder. As available resources for making geopolymer concrete/mortar such as fly ash and slag are expected to be insufficient soon, the different materials like clay should be a great alternative with local availability in various areas. Also, activating solutions are not entirely welcome from an environmental point of view. A few studies had developed the PCM-Geopolymer concrete containing kaoline. They reported the successful activation of using kaoline-based geopolymer. Thus, more studies should be focused on the PCM-Geopolymer concrete/mortar with local clay.

The significant reduction in the workability PCM-Geopolymer concrete/mortar was reported by prior literature. However, more research is required to evaluate the effect of different superplasticizers on the workability of PCM-Geopolymer concrete/mortar. Moreover, the reaction between various aluminosilicate powder, superplasticizers, and MPCMs are not discussed. The compressive strength is a vital mechanical property that can determine the applications of mortar and concrete. The prior literature revealed that geopolymer mortar and concrete's compressive strength reduces by adding PCMs. However, they reported that the compressive strength of PCM-Geopolymer concrete is higher than PCM-Normal concrete. It was concluded in several studies that PCM-Geopolymer concrete/mortar could satisfy the required compressive strength for building applications.

The specific heat capacity and thermal conductivity are influential thermal factors on buildings' energy usage. Geopolymer mortar and concrete's heat capacity increased significantly by adding MPCM. It was observed that more PCMs incorporation caused higher specific heat capacity. Also, they reported that the thermal conductivity of geopolymer concrete decreased by adding PCMs. Consequently, the prior literature indicated that using geopolymer mortar and concrete reduced power consumption significantly in buildings.

It should be noted that the current knowledge about the geopolymer mortar and concrete containing PCMs is still insufficient. It is vital to assess the effect of vast ranges of PCMs on other physical properties of geopolymer concrete, such as splitting tensile strength, flexural strength, Modulus of elasticity, durability, shrinkage, water absorption, and porosity, sorptivity, and other specifications. Furthermore, "life cycle assessment" and "cost and benefit analysis" are essential to commercialize the geopolymer concrete containing PCMs.

7. Conclusion

This study reviewed the thermos-physical properties of g PCM-geopolymer concrete/mortar in workability, density, compressive strength, heat capacity, thermal conductivity, and energy usage.

The outcome of this study can be concluded as follow:

- ✓ Fly Ash (FA) was selected as a binder by most researchers. Analyzing the chemical composition showed that the SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , and MgO were the most FA component. Thus, they could have been categorized as a good geo-polymerization due to the high amount of Al_2O_3 and SiO_2 . Also, Sodium Hydroxide and Sodium Silicate were the most selected alkaline activator.
- ✓ The compressive strength of geopolymer mortar and concrete increased at a higher temperature. The microscopic analysis demonstrated that the reduction in compressive strength of samples containing PCMs was related to the larger voids.
- ✓ The type and amount of PCMs can significantly change the heat capacity of geopolymer mortar and concrete. The reported heat capacity in prior literature increased from 21–28 °C. The thermal conductivity of geopolymer mortar and concrete decreased by adding PCMs to the samples.
- ✓ Incorporating PCMs into the geopolymer concrete can reduce the power consumption for heating and cooling buildings.

The PCM-geopolymer concrete/mortar can reduce heat transfer and power consumption. Also, it seems to be a very environmentally friendly material to mitigate global warming. Despite these, the reduction of workability and compressive strength are mentioned as the main disadvantages of PCM-geopolymer concrete/mortar. However, most studies used organic PCMs and the other types are not used in the relevant literature yet. Besides, most researchers reported that using 20% MPCMs maintains its compressive strength in acceptable ranges for structural applications. Thus, the further research question in this field can be implemented in the field of application, standardization, and commercial production of PCM -geopolymer concrete/mortar.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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