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Impact of Cement and curing conditions on MK geopolymers characteristics

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ملخص البحث :

للحد من انبعاث ثاني أكسيد الكربون ، تركز معظم البلدان على استبدال خرسانة OPC التقليدية باستخدام أنواع أخرى من مواد رابطة صديقة للبيئة. أثبت الجيوبوليمر القائم على الميتاكولين (MK) أنه أحد المواد البديلة المحتملة للأسمنت البورتلاندي ، ليس فقط بسبب قوته العالية ومتانته ، ولكن أيضا بسبب توفره. ومع ذلك ، فإن استخدام الجيوبوليمر كمواد رابطة بديلة في الخرسانة مقيد بحقيقة أن ؛ تطور قوتها بطيئ في ظل ظروف المعالجة في الهواء المحيط وبتكلفة أعلى. في هذه الدراسة تم تصنيع الأسمنت الهجين عن طريق الاستبدال الجزئي لـ MK بالأسمنت البورتلاندي في مونة (MKGP) بنسبة 5٪ و 10٪ و 20٪ و 40٪ وعولجت العينات في حالة الهواء المحيط (23 ± 2 درجة مئوية) وكذلك المعالجة الحرارية عند 60 درجة مئوية لمدة 24 ساعة بعد الصب.

ABSTRACT

To reduce the emission of CO_2, most countries are focusing on replacing the traditional OPC concretes by using other types of environmentally friendly binders. Metakaolin (MK)-based Geopolymer has proven to be one of the potential alternative materials to Portland Cement, not only due to its high strength and durability, but also because of its availability. However, geopolymer use as an alternative binder in concrete is limited by the fact that; its slow strength development under atmospheric condition and, higher cost. In this study hybrid cement was synthesized by partially replacing MK by Portland cement in (MKGP) mortar by 5%,10%,20% and 40% and the samples were cured at ambient air condition (23 ± 2 °C) as well as at 60 °C heat curing for 24 hours after casting. The fresh properties; (Setting time, flowability and flowability loss) and mechanical characteristics; (compressive and splitting tensile strength) of hybrid cement at dissimilar curing ages were investigated. These results were compared with conventional OPC mortar as well as MKGP mortar. The results demonstrated that both fresh and mechanical properties of MKGP mortar improve by replacing MK by 5% OPC. Moreover, not only the fresh properties of hybrid cement mortar were better than MK geopolymer mortar, but also the mechanical properties of hybrid cement (up to 40% OPC replacement) exceed those of conventional OPC mortar at 28 days of age in ambient air curing condition In short, hybrid

cement based on metakaolin and OPC (95% MK and 5%OPC) can be conveniently used for casting in situ concrete under ambient air curing condition.

Keywords: Metakaolin, Fresh properties, Mechanical Properties, Heat curing, Ambient air curing.

INTRODUCTION

The construction sector is experiencing an exponential increase in request for binder components, such as OPC. Nonetheless, questions regarding its environmental risks from clinker development have been raised over in recent years [1,2]. In detail, the manufacture of a ton of cement is expected to require approximately 1.5 tons of raw materials and emit almost a ton of carbon dioxide into the environment [1–4]. As an alternative to cement, it is therefore significant to use aluminosilicate materials, particularly to reduce emissions of carbon dioxide in the atmosphere [3–6].

The resulting Al_2O_3 and SiO_2 undergo polymer reactions, resulting in 3D aluminosilicate grids with a strength that may be even greater than normal concrete [7]. For curing purposes, heat from 65 C° to 105 C° is generally applied to geopolymer samples for approximately 24–48 h and can then remain for use at ambient temperature. Using the maechanism described above, any material that can dissolve (Si) and (Al) in the arrangement and form geopolymers in the attendance of robust alkali and high temperatures can be used. For example, GGBS was found effective in various studies in which it was used to raw material for geopolymer concrete, a waste product from the iron industry [7,8]. Likewise, additional products for example fuel ash [9], fly ash [10], oil fuel ash [11], rice husk ash [6,12], metakaolin [3] are used, as well. Once used as a raw material in geopolymer mechanism, these waste materials from various industries not only minimize the disposal issues but also decrease the use of OPC for concrete implementations13,14].

Aside from all of the perks of geopolymers, the only thing that prevents them from being used in field applications is their curing technique. As previously stated, it needs a heat-curing time of 24–48 h at 60–100 C° which in actual field applications becomes very difficult. Therefore, this research aimed to perform the curing process in two ways heat and ambient curing conditions and investigate the effect of different curing at the different properties. Researchers are concentrating their efforts on developing geopolymers with diverse additives such as GGBS, metakaolin, Portland cement, and other materials [15,16]. The adding of calcium located in OPC to the geopolymer arrangement may have a good effect on other qualities not only when cured at a heat temperature, but also when cured at ambient temperature [17-19].

Experimental Program

Materials

Local Ordinary Portland Cement CEM I 42.5N complying with ESS 4756-1/2007 [20] was used in the study. The metakaolin (MK) used was brought from local market. X-ray diffraction (XRD) for OPC and MK are shown in Fig.1. chemical composition and physical properties of OPC and MK are illustrated in Tables 1.

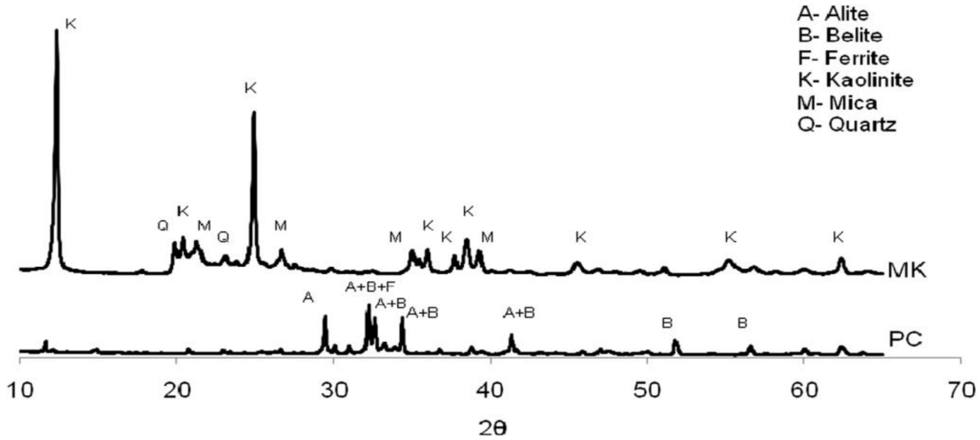

Fig.1 The X-ray diffraction patterns of OPC and MK

Table 1 Chemical composition and Physical properties of OPC and MK

Compound (%)	OPC	MK	Property	OPC	MK
SiO_2	20.7	53	Specific gravity	3.15	2.5
Al_2O_3	5.4	44	Blaine fineness (m^2/kg)	350	12000
Fe_2O_3	3.8	0.5	Average particle size (μm)	12	1
MgO	2.1	0.2	Color	Gray	White
CaO	64.3	0.2			
Na_2O	0.2	0.3			
K_2O	0.4	0.2			
SO_3	2.1	0.2			
Loss on ignition	0.9	1.1			

The fine aggregate was clean siliceous river sand with fineness modulus of 1.74, 1.5% water absorption and, 2.5 specific gravity, grading of fine aggregate compared with standard domain illustrated in Table 2.

Table 2 Grading results for fine aggregate

Sieve opening (mm)	4.75	2.36	1.18	0.6	0.3	0.15	0.075
% Passing by weight for sand	100	97	80	50	20	3.5	0.5
ASTM Standard domain	100	95-100	70-100	40-75	10-35	2-15	-

The used alkali activator consists of two solutions; sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). The alkali solutions were mixed in a ratio of (Na_2SiO_3/NaOH) of 2.5.

Mix proportions

MK geopolymer, OPC mortar mix and four hybrid cement mortar mixes were made by partial replacing MK with 5%,10%, 20% and 40%OPC as shown in Table 3. All mixes have the same binder content (730 Kg/m^3), water/binder ratio of 0.35, activators content in geopolymer mixes (292 Kg/m^3) and sand content (1178 Kg/m^3).

Table 3 Details of mortar mix proportions

Mix no.	Code	Mortar mixture quantity (kg/m^3)					W/S
		Sand	MK	OPC	SS	SH	
1	GP	1178	730	0	208.6	83.4	0.35
2	HC05	1178	693.5	36.5	208.6	83.4	0.35
3	HC10	1178	657	73	208.6	83.4	0.35
4	HC20	1178	584	146	208.6	83.4	0.35
5	HC40	1178	438	292	208.6	83.4	0.35
6	OPC	1178	0	730	-	-	0.35

Mixing and Casting

Because mixing alkaline solutions generates a lot of heat [21,22], the alkaline solutions were combined 24 hours before usage to bring the temperature down to ambient. The geopolymer mixtures were mixed by hand. After mixing the dry powders and fine aggregates, the alkaline solutions were added to the dry mixture and stirred until perfect homogeneity was attained. The fresh mortars were then poured into the moulds and compressed with a tamping rod. After that, the samples were wrapped in polyethylene sheets and kept in the moulds for 24 hours at a temperature of 23 ± 2 ºC. The samples were demolded and cured after 24 hours.

Curing conditions

Half the specimens for each mix were cured at normal ambient temperature of 23 ± 2 ºC till time of testing (3, 7, 28, 90 days) and the other half were cured at 65 ºC for 24 hours inside oven and then left at normal ambient temperature the remaining period till testing age (3, 7, 28, 90 days).

Testing Properties and Procedures

Fresh Properties

Vicat needle instrument was used to calculate the setting time of the fresh mortar rendering in accordance with ASTM C 807-13 [23] and BS EN 480-2 [24].

For measuring the flowability and rate of flow loss of fresh mortars, the Mortar Flow Table Apparatus (MFTA) was proposed. ASTM C230-80 [25] contains a detailed description of MFTA. The flowability of the mortar was assessed using MFTA immediately after mixing, according to ASTM C 1437-20 [26].

2.5.2 Mechanical Properties

In line with ASTM C 109 [27], compressive strength experiments were carried out on cubic models 50 mm at various ages (3, 7, 28, 90 days). The experiment was carried out using a UTM compression machine with a 300 KN capacity. The compressive strength rating for each age is the average of three tested specimens. A splitting tensile strength test was carried out in line with ASTM C 496-11[28].

Results and discussion

Fresh properties

Setting time

The initial and final setting times for all studied mortar are illustrated in Fig.2. The result shows that setting time of geopolymer mortar in ambient temperature is longer than that of OPC mortar. The final setting time for geopolymer (GP) mortar reaches 625 min. This is attributed to the lack of Ca^{+} content in MK mixes that may result in a longer setting time of geopolymer. Furthermore, OPC inclusion slightly accelerates both initial and final setting time of hybrid cement (HC) mortar with increasing OPC replacement ratio. The final setting time reaches 610 min for mix with 5% OPC replacement ,594 min for mixes incorporating 10% OPC ,565min for mix with 20% OPC replacement,520 min for mix with 40% OPC replacement and 350 min for OPC mortar mixes, representing 97.6%, 95.0%,90.4%,83.2% and 56.0% of corresponding GP mix respectively. On the other hand, initial setting time is 175 min, 150 min, 135 min, 105 min,85min, and 55 min for GP, 5%, 10%, 20%, 40% and 100% OPC replacement mixes. The initial setting time for 5%, 10%, 20%, 40% and 100% represents 85.7%, 77.1%, 60%, 48.5%, and 31.4% respectively of GP mix.

The results indicate that the reduction in initial setting time is proportional to OPC replacement level and decrease by increasing OPC% in a linear manner Fig.3. On the other hand, mortar final setting in less affected by the OPC replacement, nevertheless, the rate of reduction in setting time increases by increasing OPC replacement level. The decreases in final setting time can be represented by a 2nd order equation. The reduction due to OPC inclusion in all cases is obviously higher in initial setting compared to final setting.

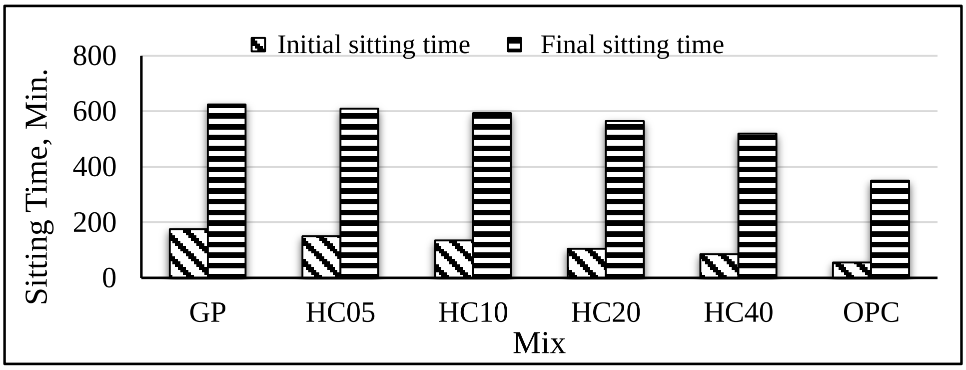

Fig.2 Initial and final setting times of GP, HC and OPC fresh mortar.

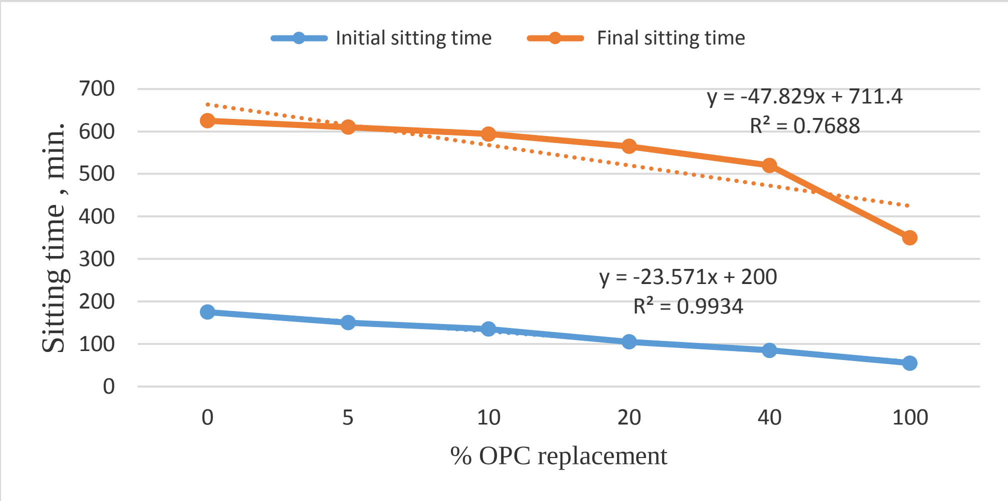

Fig.3 Effect of cement replacement on sitting time.

Flowability

Initial flow of fresh mortar was conducted immediately after mixing. The rate of flow loss is also investigated for all studied fresh mortars. As shown in Fig.4 the initial flow of GP fresh mortar recorded the lowest value compared to HC and OPC mortars. This is clearly observed during the mixing and casting processes. The initial flow of fresh mortars is improved by increasing OPC content in the mix. The low value of initial flow for GP mortar could be attributed to the higher surface area MK and its lower particle size.

The replacement of MK by 5%,10%,20% and 40% OPC in reference GP mortar mix improves its flow by 1.67%,4.44%,7.78% and 11.12% respectively. The complete replacement of MK by OPC results in an increase of 13.9% in mortar flow. The relationship between mortar flow and OPC content is shown in Fig.5, where we can notice that the relationship can be acceptably represented by a straight line with R^2 value of 0.796.

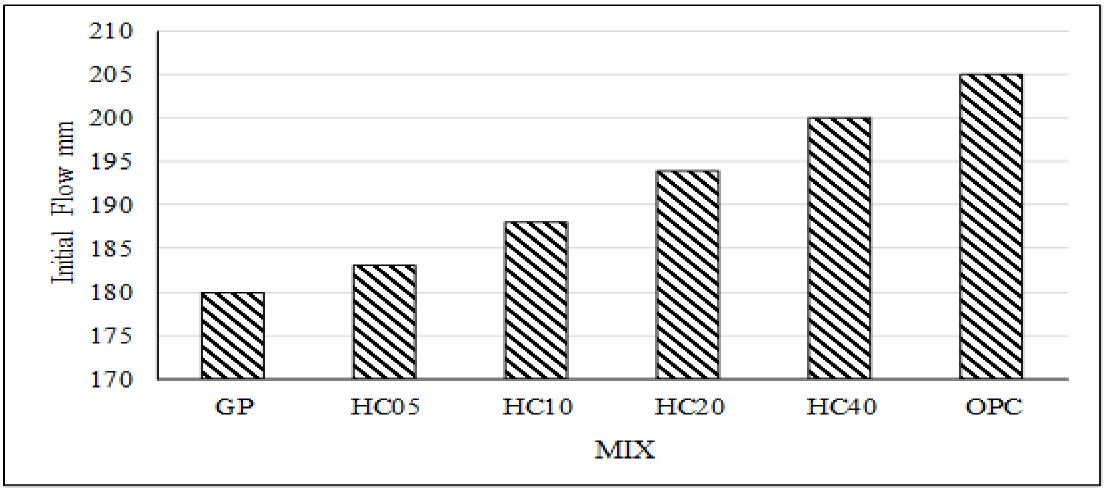

Fig.4 Initial flow of GP, HC and OPC mortar mixes.

The rate of flow loss of GP fresh mortar was measured by mean of the difference between instantaneous flow and the flow at different elapsed periods 30, 60, 120, and 240 minutes. The results are presented in Fig.6. As seen, GP fresh mortar possessed the lowest rate of flow losses among all studied fresh mortars. While the rate of flow loss of HC fresh mortar increases with increasing OPC content. The results of flow loss of GP mortar start by 2% after 30 min and increased gradually to reach 8% after 240 min. Replacing MK by OPC up to 40% results in increasing the loss in flow. The increase in flow loss due to replacing MK by OPC can be simply explained by the introduction of hydration reaction into mortar mix, which is faster than that of polymerization reaction associated with GP mortar.

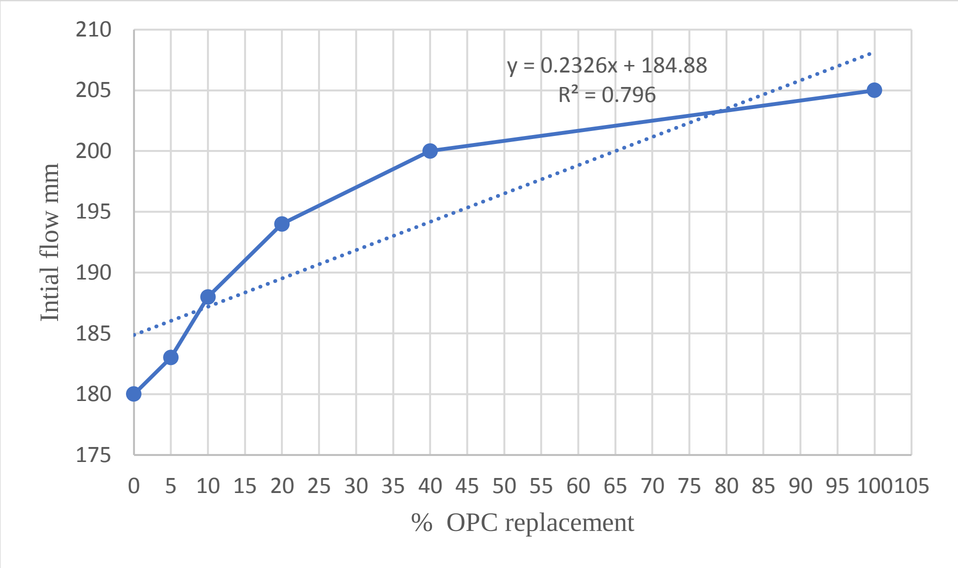

Fig.5 Relationship between mortar flow and OPC content

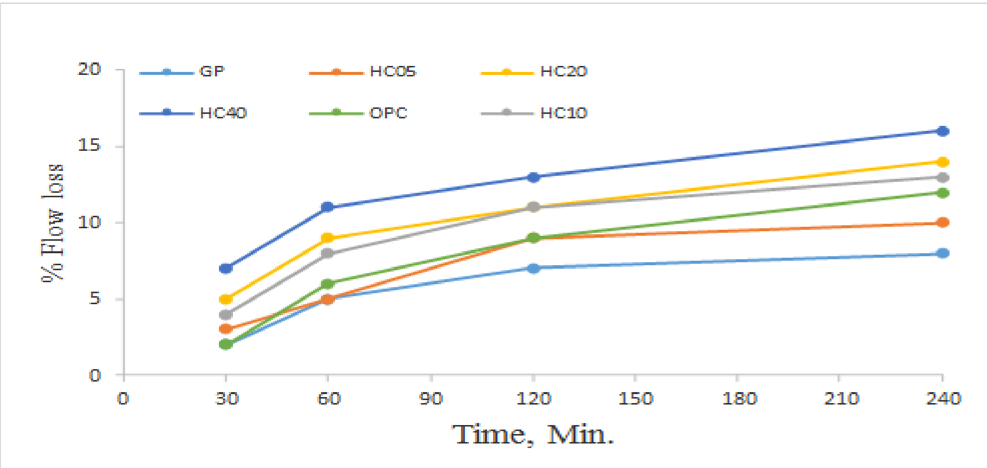

Fig.6 Flow losses of studied mortars

Mechanical Properties

Compressive strength

Fig.7 illustrate the results of the compressive strength tests for different mixes for both ambient temperature and heat curing conditions at different curing ages. It is clear that HC containing 5% OPC develops slightly higher compressive strength at all ages and for both curing conditions, compared to GP and OPC mortars. Beyond OPC content of 5%, the compressive strength of mortars decreases to values even lower than that of GP mortars. However, HC mortars also achieve higher compressive strength than OPC mortar for mortars with OPC replacement level up to 40%.

The percent of strength increments for GP, HC05, HC10, HC20 and HC40 reached 35.6%, 44.4%, 29.5%, 16.9% and 8.7% respectively higher than OPC at 3 days. The compressive strength at (3 days) for heat cured samples of GP, HC05, HC10, HC20, HC40 and OPC mortars reach 12.2%, 14.4%, 12.8%, 8.9%, 6.3% and 15% higher than that cured in ambient air. This rise in mortar compressive strength in elevated temperature in attributed to the effect of heat on accelerating polymerization reaction, high reactivity of MK as well as its micro filler effect.

The 28 days compressive strength of GP, HC05, HC10, HC20, HC40 and OPC mortars reach 40.3, 42.0, 39.2, 38.6, 35.9, and 33.0 MPa respectively, with air curing, while, these values increase by heat curing to reach 48.7, 50.6, 46.3, 45.0, 42.3, and 40.0 MPa respectively. The compressive strength of GP, HC05, HC10, HC20 and HC40 mortars reach 21.7%, 26.5%, 15.7%, 12.5% and 5.7% higher than that for OPC for heat curing, respectively. These same ratios are 22.1%, 27.2%, 18.7%, 16.9%, and 8.7% for ambient air curing at the same curing age. Identical performance can be noticed for other curing ages of 3, 7, and 90 days for bath air and heat curing, see Table 4.

The GP mortar strength decreases by replacing MK by OPC, and mortar strength decreases by increasing OPC replacement ratio till Mortar mix HC40, except (HC05). This phenomenon is due to the reaction of part of OPC with hydration in addition to the polymerization reaction. When comparing GP and HC mortars strength with OPC mortar, it can be expected that replacing MK by more than 40% OPC is not beneficial to strength. It should also be clear that the nature of reaction in GP and HC mortars is polymerization reaction, whereas it is hydration reaction in OPC mortar.

It can also be observed that mortar strength is improved with time due to either polymerization of hydration reaction. The average 3, 7, 90-day strength resembled 67.0%, 86.0% and 119.2% of 28-day mortar strength for ambient air curing condition and 61.8%, 79.6%, and 114.9% for heat cured samples, consecutively. The results reveal that despite the fact that mortar strength is higher in heat treated sample, yet, the ratio of 3, 7 and 90-days strength to that of 28 days of air cured samples is always 6% approximately higher than those treated by heat. The results also indicate that heat curing enhancement to mortar strength decrease with increasing OPC content to reach its lowest level for OPC mortar.

Further, it can be deduced from the results that heat treatment improvement to mortar strength increases with age.

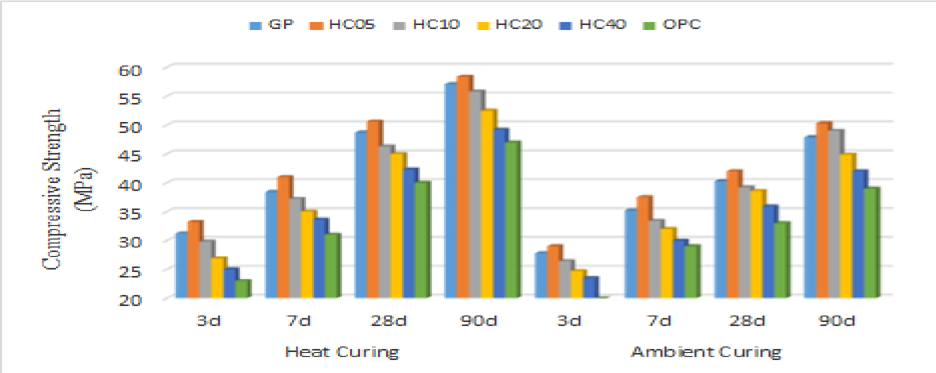

Fig.7 Compressive strength of mortars exposed to heat and ambient air curing conditions.

Splitting tensile strength

Tensile performance of all building materials is important, including geopolymer, because it indicates its ability to combat cracking. Fig.8 shows the tensile strength of the studied mortars under both ambient air curing and heat curing conditions at different ages. As shown in Fig.8, the pattern of tensile strength growth for all examined mixtures is comparable to that of compressive strength development (Fig. 7). The splitting tensile strength for the studied mortars (GP, HC05, HC10, HC20, HC40 and OPC) reaches 5.0, 5.5, 4.7, 4.4 and 3.8 MPa respectively, at 28 days without heat curing. The value of splitting tensile strength of all mortars increases by using heat curing, for all ages. The splitting tensile strength values for all studied mortars (GP, HC05, HC10, HC20, HC40 and OPC) reaches 5.9, 6.7, 5.3, 5.0,4.5 and 4.1 MPa respectively, at 28 days for heat cured samples.

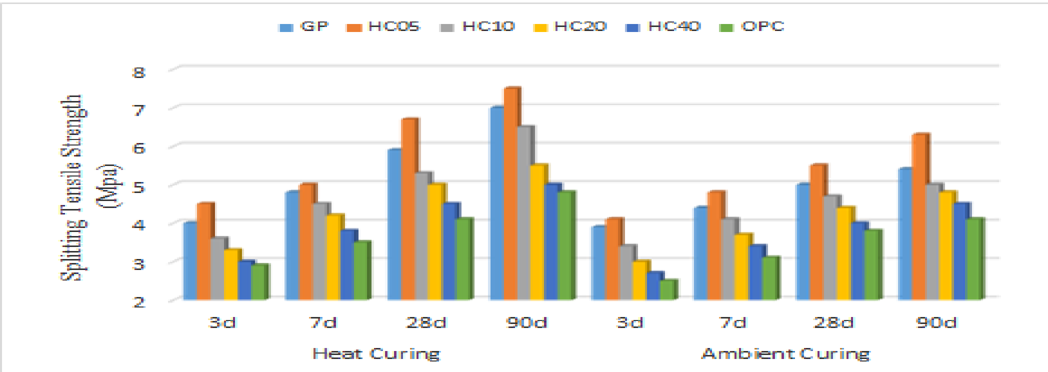

Fig.8 Splitting tensile strength of studied mortars under curing conditions

CONCLUSIONS

The following conclusions may be written:

Setting time of GP paste is longer than OPC paste, while OPC inclusion accelerate the setting time of the HC paste and this effect is more pronounced with increasing OPC content (HC40) in the paste.

GP mortar is much stiffer than normal OPC mortar, while OPC incorporation enhances the initial flow of the HC and the percentage of initial flow increased with increasing OPC content.

GP mortar imposes compressive and tensile strengths higher than normal OPC mortar at the same curing condition, while OPC inclusion (up to 40%) reduces the compressive and tensile strength of HC but still higher than normal OPC mortar at all ages without the need to heat curing.

Heat curing improves the mechanical properties of GP than ambient air curing, while OPC incorporation improves mechanical properties of GP at ambient temperature better than heat curing. Therefore, these results treat one of the factors that restrict the use of geopolymers in field applications.

Considering the overall investigated characteristics for all studied mixes, it can be concluded that, ambient temperature cured GP mortar incorporating OPC with replacement ratio up to 40% has shown significant feasibility and can be used for structural applications in the field as environmentally friendly sustainable construction material, which may in the future be a suitable substitute for the conventional cement mortar in green building industry.

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