Case Studies in Construction Materials 16 (2022) e00922

Contents lists available at ScienceDirect

Case Studies in Construction Materials

journal homepage: www.elsevier.com/locate/cscm

Impact of Ca^+ content and curing condition on durability performance of metakaolin-based geopolymer mortars

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A R T I C L E I N F O

Keywords:
Metakaolin (MK)
Microstructure properties
Durability
Sorptivity
Aggressive environment
MK based geopolymer matrix (MK-GPM)

A B S T R A C T

To overcome massive pollution and energy consumption resulting from cement production in addition to concrete's durability problems, geopolymer concretes (GPC) and mortars (GPM) are recently gaining increasing interest. GPCs are manufactured based on different ingredients such as Fly Ash, GGBS, and other Alumina-Silicate rich materials and polymerized by using alkali activator. However, based on the major polymeric constituent material and curing condition, the properties of GPC are determined. In Egypt, metakaolin (MK) is available in several locations, which after calcination exhibits satisfactory pozzolanic activity. MK is a good replacement of cements in concrete and GPC as it consumes less fuel and produces much lower pollutants. In this research, the durability of MK mixes, that can be utilized in normal construction locations are investigated. Metakaolin based geopolymer mortars (MK-GPM) with up to 60% OPC are made to investigate the effect of OPC inclusion on durability related characteristics. The influence of curing conditions at ambient temperature (23 ± 2 °C) as well as at 60 °C heat curing is also investigated. Water transport properties are evaluated. Durability related characteristics in terms of change in weight and compressive strength with time after exposure for 10 weeks to chemical solution (10% $MgSO_4$, H_2SO_4 (pH=3) and 10% NaCl). Furthermore, microstructure properties are investigated through X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) with energy dispersive X-ray spectroscopy (EDS) to identify the phase and chemical composition. The results reveal that, heat curing of MK-GPM reduces its sorptivity by 9 ± 2% and water absorption by 13 ± 3%. On the other hand, the inclusion of OPC in MK-GPM (by more than 5%) increases water absorption and sorptivity and consequently reduces durability. Although, MK-GPM shows better durability when exposed to aggressive environmental attacks, incorporating cement up to 20% demonstrates better durability performance than OPC mortar. The study of the microstructure of tested mixes explains and confirms the experimental results.

1. Introduction

Due to global warming problems, many researchers are seeking an alternative material to replace the heavily CO_2 producing OPC

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https://doi.org/10.1016/j.cscm.2022.e00922
Received 16 November 2021; Received in revised form 25 January 2022; Accepted 27 January 2022
Available online 3 February 2022

manufacturing process. Geopolymer is then proposed as a reasonable substitute because its relatively high mechanical strength and outstanding durability, besides its environmental friendliness [1].

Geopolymer is an inorganic matrix similar to that of OPC, produced by the chemical activation of aluminosilicate with highly alkaline solution and preferably cured under elevated temperatures [2]. Because the raw materials used in geopolymer production come from various industrial waste materials such as ground granulated blast furnace slag (GGBS), fly ash (FA), waste-glass powder (WGP) and silica fume (SF), it helps in minimizing waste disposal problems, as well as reduces CO_2 emissions by reducing OPC use. In addition of being greener, geopolymer is reported to possess mechanical and durability properties that competes with OPC counterpart [3–5]. However, the frequent necessity for geopolymer heat curing (for 24–48 h) at 60–120 C° during the manufacturing process has become one of the drawbacks of its applications especially in field construction. Therefore, researchers focus on the utilization of carefully selected aluminosilicate materials to overcome the slow setting of geopolymer [6–8]. While other research adds a small amount of Ca^{+} (Cement, GGBS, Limestone) to aluminosilicate materials as another alternative to avoid heat curing [9–11].

Thermally activated kaolinite clay (metakaolin (MK)) has been utilized recently in geopolymer system as an aluminosilicate rich material [12–14]. Lothenbach et al. [15] classified MK as calcium-free aluminosilicate raw materials. The absence of calcium in GP mix may result in a longer geopolymer setting time and sometimes slows the strength gain and increases shrinkage at early age especially with high SiO_2/Al_2O_3 molar ratio [16,17]. To overcome GP setting time inadequacy, it is important to speed up the curing process by heat curing and/or the inclusion of high calcium incorporating addition (Cement and/or GGBS) [18–27]. The effect of OPC on geopolymer activation process have been reported by Garcia-Lodeiro et al. [21–23]. It has been suggested that incorporating aluminosilicate binder with calcium source has a positive impact on mechanical performance of geopolymers [21–25]. Moreover, hybrid cement prevents the occurrence of efflorescence, considerably improve setting time, and accelerate hardening [28–30].

Studies on the durability of Alkali-activated materials (AAMs) showed that calcium-free or low-calcium AAMs have better durability in aggressive environments than OPC in sulfate environment [31–35] and acidic solutions [36-38]. GP better durability is a consequent to the absence of sulpho-aluminate products formation, such as ettringite and gypsum, during the polymerization process [31] and due to the formation of N-A-S-H gel, with its superior resistance to acid attacks [37]. On the other hand, calcium-rich AAMs usually produce calcium-containing hydrates such as C-S-H gel and C-(A)-S-H gel which have lower sulfate resistance and decreased acid resistance compared with the N-A-S-H gel [35,39–41]. The vast majority of the recent geopolymer studies have been conducted based on low calcium fly ash (class F) as aluminosilicate raw materials. While there is still lack of knowledge regarding metakaolin-based geopolymers with source of calcium (OPC) on the mechanical performance as well as long-term durability concern of these materials.

In this paper, experimental program is conducted to study the impact of incorporating cement on MK based geopolymer properties to make it useable in field construction under ambient temperature curing condition. The main objective of this study is to investigate the impact of OPC inclusion on compressive strength and durability related characteristics under ambient temperature curing condition. Sorptivity and water absorption as well as loss in weight and compressive strength are investigated after 10 weeks of GPM exposure to highly aggressive chemical solution (10% $MgSO_4$, H_2SO_4 and 10% NaCl). Moreover, microstructure of tested samples is also investigated. The results are compared with similar MK-GPM samples under heat curing and conventional OPC mortar samples as reference.

2. Experimental program

2.1. Materials

CEM I 42.5 N Portland cement complying with ESS 4756–1/2007 [42] is used. MK is purchased from local market. The physical properties and chemical composition of OPC and MK are illustrated in Tables 1 and 2 respectively. XRD for OPC and MK are illustrated in Fig. 1. Characteristic peaks of phases alite (A), belite (B), and ferrite (F) are found in cement. In comparison, MK's XRD patterns indicate that MK's crystalline phases composed of kaolinite (K), mica (M), and quartz (Q).

The used fine aggregate is clean siliceous river sand with fineness modulus of 1.74, 1.5% water absorption and 2.5 specific gravity. The used alkali activator consists of two solutions: sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). The alkali solutions are mixed with (Na_2SiO_3/NaOH) ratio of 2.5. NaOH solution of molarity 14 M is made by mixing (NaOH) pellets with distilled water whereas (Na_2SiO_3) is prepared by mixing 16.20% Na_2O, 34.72% SiO_2 and 49.08% water.

2.2. Mix proportions

Six geopolymer mortar mixtures are prepared by replacing MK with OPC. The replacement ratio varied from 0% to 60% by weight.

Table 1
Physical properties of OPC and MK.

Property	OPC	MK
Specific gravity	3.15	2.5
Blaine fineness (m^2/kg)	350	12,000
Average particle size (μm)	12	1
Color	Gray	White

Table 2
Chemical composition of OPC and MK.

Compound (%)	OPC	MK
SiO_2	20.7	53
Al_2O_3	5.4	44
Fe_2O_3	3.8	0.5
MgO	2.1	0.2
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

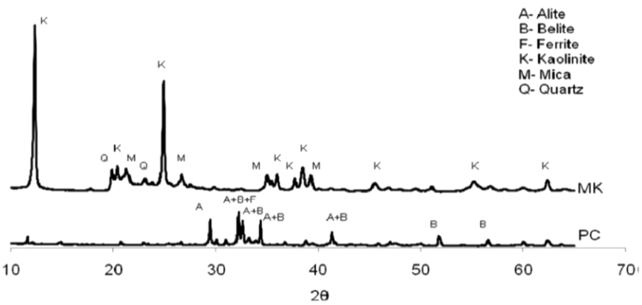


Fig. 1. The X-ray diffraction patterns of OPC and MK.

OPC mortar with the same mix ingredients was also prepared as shown in Table 3. All mixes have the same binder content (730 Kg/m^3),alkaline activator /binder ratio of 0.40, alkaline activators content (292 Kg/m^3) and sand content (1178 Kg/m^3) and no extra water or superplasticizer was added.

2.3. Mixing and casting

To avoid the liberation of excess heat due to the mixing of NaOH and Na_2SiO_3, the preparation of the activator solution is done 24 h before final mixing [43,44] Geopolymer mixes are mixed manually. First, dry powders and fine aggregates are blended together, thereafter alkaline solutions are added to the binder and remixed together till complete homogeneity achieved. After then the fresh mortars are cast into the molds and compacted using tamping rod. The samples are then wrapped in polyethylene sheets and left in molds at room temperature of 23 ± 2 °C for 24 h then samples are demolded and cured.

2.4. Curing conditions and chemical solutions

To compare the behaviour of MK-based geopolymers containing OPC exposed to chemical solutions to that of OPC, two different curing conditions after sample demolding were followed; (i) curing at normal ambient air temperature 23 ± 2 °C to 28 days, (ii) curing at 60 °C for 24 h inside oven and then left at normal ambient temperature the remaining period (27 days). After curing specimens are immersed in three different chemical solutions; (i) 10% magnesium sulphate ($MgSO_4$), (ii) 10% sodium chloride (NaCl), (iii) sulphuric acid with pH level of 3 (H_2SO_4).

Table 3
Details of MK and OPC Based proportions of geopolymer mortar mix.

Mix no.	Code	Quantity of mortar mixture (kg/m^3)	L/B
		Sand MK OPC SS SH	
1	MK	1178 730 0 208.6 83.4	0.4
2	MK/5 C	1178 693.5 36.5 208.6 83.4	0.4
3	MK/10 C	1178 657 73 208.6 83.4	0.4
4	MK/20 C	1178 584 146 208.6 83.4	0.4
5	MK/40 C	1178 438 292 208.6 83.4	0.4
6	MK/60 C	1178 292 438 208.6 83.4	0.4
7	OPC	1178 0 730 - -	0.4

2.5. Testing properties and procedures

2.5.1. Fresh properties

The setting time of the fresh mortar was determined using the Vicat needle device according to ASTM C 807–13 [72]. The Mortar Flow Table Apparatus (MFTA) was proposed for determining the flowability of fresh mortar, according to the ASTM C 1437–20 [73].

2.5.2. Transport properties

Durability properties of concrete can be acceptably assessed by sorptivity because the rate of chemical infiltration can be influenced by water ingress via capillary suction. The sorptivity rate and water absorption are calculated according to ASTM C1585–04 [45] and ASTM C642–06 [46] respectively. These tests are performed at the age of 56 days on 50 × 50×50 mm cubes.

Sorptivity (S), can be determined as follows: $S = \frac{I}{t^{0.5}}$, where t is the elapsed time in minutes, and $I = \frac{\Delta m_t}{a \times b}$, where Δm_t represents the change in specimen mass in grammes during time t, a and b represents the exposed area of the specimens in mm^2.

2.5.3. Durability related properties

Test series have been proposed for the durability assessment of MK-GPM and OPC mortars. After curing the specimens were exposed to highly aggressive environments, 10% solution of magnesium sulfate,10% solution sodium chloride and sulfuric acid (PH=3) and kept immersed up to 10 weeks. To monitor the effects of solutions on all the immersed specimens regularly over the exposure period both change in weight and compressive strength were performed every two weeks up to 10 weeks. To determine the weight change, using 50 mm cubic specimens over the exposure time as a percentage of original weight before the immersion in the aggressive solutions. After the stated exposure times, the samples were allowed to dry at room temperature until they reached a constant mass, and then weighed on an electronic scale (accuracy of ± 0.01 g). Compressive strength degradation was also determined in accordance with ASTM C 109 [47] as a percentage of the compressive strength of specimens after 28 days curing period and before immersion in aggressive solutions.

2.5.4. Microstructure analysis

After specified exposure period (10weeks after curing for 28 days), pieces of the synthesized geopolymer broken samples were crushed and immerged in (1:1) methanol/acetone mixture for 24 h to avoid rehydration. The specimens were then filtered off, wiped with methanol and left to dry in an oven at 50 °C for another 24 h then, the samples were ground to powder form, sieved through 150 μm mesh to obtain homogeneous sample and kept in desiccators containing silica gel until analysis. X-ray diffraction (XRD) analysis were conducted at 2θ = 5–90° with pixel density of 0.02°/step and scan speed of 0.5 s/step. Quantitative XRD analysis is used to check the amorphous phase of geopolymer pastes. In SEM/ EDS analysis, selected samples are taken from the broken pieces of specimens after durability testing.

3. Results and discussion

3.1. Fresh properties

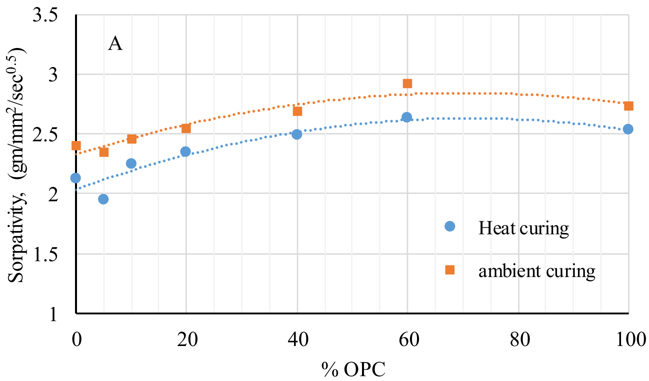
All fresh mortar mixes generally appear stiff and cohesive due to low liquid content and absence of additional water. As shown in Table 4. the setting time of geopolymer mortar is longer than that of OPC mortar. When OPC is incorporated in the mixture, initial setting time and initial flow of geopolymer slightly improved. Mixture having 5% OPC achieved initial setting time of 168 min, which decreased to 160, 150 and 135 min for inclusion of 10%, 20% and 40% OPC in mixtures respectively. Furthermore, it can be seen that flow of mortar is influenced by the inclusion of OPC in the binder. A general increasing trend in the initial flow values can be observed with the increase of OPC content. These obtained results is in the line with that by Chen et al. [72,73]. It should be noted that cement addition leads to increasing flowability, nevertheless the difference is rather limited.

3.2. Transport properties

The effect of incorporating OPC on sorptivity and water absorption of MK-GPMs are illustrated in Fig. 2 under both ambient and heat curing conditions at 28 days before exposure to aggressive solutions. It is clear that MK-GPM has less sorptivity and water absorption than normal OPC mortar for both curing conditions. This result obtained consistent with that obtained elsewhere [48–62]. The reduction in sorptivity of MK-GPM reaches 14% and 19.3% compared with OPC mortar for ambient and heat curing specimens respectively. On the other hand, the figure shows that the value of both sorptivity and water absorption for all studied heat cured mortars are less than that cured in ambient air. The percent of reduction in sorptivity of MK-GPM are 12% and 16% compared with

Table 4
Effect of OPC content on mortar fresh properties.

OPC content, %	GP= 0	5	10	20	40	60	OPC= 100
Initial setting time, min	175	168	160	150	135	105	55
Final setting time, min	625	620	615	610	594	565	350
Initial flow, %	180	181	183	185	188	194	205



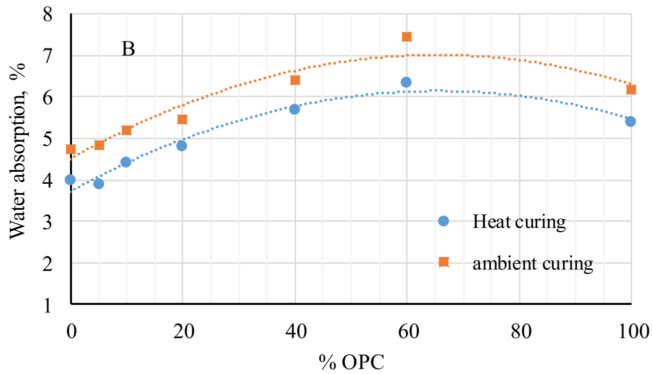


Fig. 2. Effect of OPC ratio and curing condition on transport properties of MK-GPM and OPC mortars after 28 days, a) Sorptivity & b) Water absorption.

OPC mortar for ambient curing and heat curing specimens respectively. Moreover, for MK-GPM the values of both sorptivity and water absorption slightly decrease by replacing MK by 5% OPC and then increase as cement content increase for both curing conditions. These results agree with the results obtained elsewhere, [64,65].

Addition of 5% OPC to MK geopolymer mix decreases its sorptivity by 2.5% and 8% for heat curing and ambient curing specimens respectively. However, replacing 10%, 20%, 40% and 60% OPC increases its sorptivity by 2.5%, 5.8%, 12.1% and 21.7% for ambient cured and 6.1%, 10.8%, 17.4% and 24.1% for heat cured specimens respectively.

On the other hand, the transport properties of MK-GPM containing cement up to 40% are almost less than that for normal OPC mortar for both curing conditions. Percent of reduction in sorptivity of MK-GPM containing cement with respect to OPC mortar reach 23%, 11%, 7% and 1.6% for heat curing and 14%, 10%, 7% and 1.5% for ambient curing for replacing ratios of 5%, 10%, 20% and 40% OPC.

It can be noticed from Fig. 2b that water absorption follows similar sorptivity trend. It can be comprehended that heat curing and incorporating 5% OPC to MK-GPM reduces mortar water absorption and enhances its resistance to penetration of aggressive solutions and hence improves its expected durability. In contrast, inclusion of MK by higher than 5% OPC has reverse effect on mortar durability as it gradually raises water absorption with the increase of OPC replacement level. We can also notice the clear drop in the value of mortar's water absorption when 100% OPC is used as it indicates the presence of different behavior for OPC mortar (hydration reaction) than geopolymer or OPC modified geopolymer (polymerization reaction) mixes. It can be noticed that the water absorption of OPC mixes is almost equal to that of 40% OPC replacement GPM.

The transport properties results reveal that, heat curing reduces mortar sorptivity by 9 ± 2% and absorption by 13 ± 3%. Moreover, the inclusion of 5%OPC in MK-GPM slightly improve the studied transport properties for both curing conditions and consequently improves durability. This could be attributed to the formation of C–S–H from the OPC and N–A–S–H from aluminosilicate ingredients [51,54]. García et al. [21] Reported that these gel in presence of aluminum and calcium evolve respectively, into C–A–S–H (tobermorite) and (N,C)–A–S–H in calcium-rich activated alkali materials. Similar conclusion was reported by Kaja et al. [23], they found that Calcium ions, dissolved from cement phases, contribute to a faster precipitation of products and in consequence, to a denser microstructure of composite pastes and a higher early age mechanical performance. However, the increase in transport properties due to inclusion of higher replacement ratio (higher than 5%) also explained by Kaja et al. [23], is attributed to the adverse effect of the excessive cement content which impedes the gel formation due to hindered hydration of cement in high alkalinity at later ages and low compatibility between calcium deficient and calcium rich phases which lower the silica availability.

3.3. Compressive strength

Fig. 3. illustrate the compressive strength tests results of for all studied mixes at 28 days for both ambient temperature and heat curing conditions. It is clear that MK-GPM compressive strength slightly increases with 5% OPC replacement level while, declines with further increment. Moreover, it can be also noted that compressive strength of MK-GPM and that containing OPC up to 40% is higher than conventional OPC mortar. The compressive strength values of MK-GPM, containing different percentages of cement (0, 5, 10, 20, 40, 60%) and conventional OPC mortars reach 45.3, 46, 43.8, 42, 40.5, 39, and 39 MPa respectively, with ambient temperature curing, while these values increase by heat curing to reach 56, 56.9, 54.6, 50.6, 48, 45 and 46 MPa respectively. The percentages of increase in compressive strength of MK-GPM incorporating different percentages of cement 0, 5,10%, 20% and 40% reach 16.2%, 17.9%, 12.3%, 7.7% and 3.8% higher than that for conventional OPC for ambient air curing, respectively. On the other hand, these ratios enhanced with heat curing to 21.7%, 23.7%, 18.7%, 10% and 4.3% for heat curing at the same curing age. It is obvious that heat cured specimens achieve higher compressive strength which is nearly 23.6% than ambient temperature curing specimens and this percent decreases with increasing OPC content. This result confirm that heat curing favors the alkaline activation process, contributing to the increase in strength of geopolymer mortar, but impairs the gain in strength of OPC mortar, due to the loss of hydration water. This complies with the results obtained by [60]. The limited improvement in compressive strength of 5%OPC blended MK-GPM could be attributed to the formation of more densified microstructure as a result of formation of C–S–H gel from the OPC and N–A–S–H gel from aluminosilicate mix constituents [51,54]. On the other hand, the poor strength development of composites of aluminosilicate geopolymer with higher cement due to the retarded development of C–S–H because of the preferential removal from the system of available Si because geopolymer formation is more rapid than the hydration of the cement minerals [55].

Comparing the results obtained by other authors who worked with similar materials is interesting. Kumar and Ramesh [56] found the compressive strength of MK based geopolymer concrete of 61 MPa, (alkaline activator/binder ratio 0.4, $Na_2SiO_3/NaOH= 2.5$ and NaOH molarity=10). The authors performed air curing till test age (28 days). Moreover, the authors observed decline in compressive strength with incorporating GGBS (a source of $Ca+$). Salim et al. [57] obtained compressive strength of MK based geopolymer mortar of 19 MPa (alkaline activator/binder ratio 0.6, $Na_2SiO_3/NaOH= 2.5$ and NaOH molarity=14). Other researchers [21–23,26,28,58] incorporate OPC into geopolymer based on other base materials like FA and RHA to control setting time and accelerate early strength at ambient curing. The authors found different optimum OPC contents with respect to compressive strength improvement. In this study the lower OPC content (5%) which enhances compressive strength of MK/OPC geopolymer matrix could be attributed to absence of excess water in design mixes (Table 3) required to complete hydration reaction excess OPC resulting densified CSH gel and depending only on water presents in alkaline solution.

3.4. Relationship between transport properties and compressive strength

The results of transport properties of the mortar can be attributed to the corresponding pore structure and interconnections which affect the amount of penetrated solution into matrix. Low sorptivity and water absorption of MK-GPM are attributed to the low permeability and more densified microstructure than MK-GPMs containing cement. Based on the results obtained in this study, the relationship between compressive strength and transport properties is shown in Fig. 4. Using linear regression analysis, Fig. 4 shows a good direct correlation between transport properties and compressive strength for all studied mortar mixes. Specimens with less water absorption and water sorptivity have more strength than those with higher corresponding values. This result agreed with that obtained by Thokchom et al. [41,48,49].

3.5. Durability properties

3.5.1. Chloride attack

Steel corrosion in concrete is mostly caused by chloride salts penetration. Fig. 5(a, b) illustrates the effect of incorporating cement on weight change results of MK-GPMs immersed in 10% sodium chloride solution for 10 weeks after 28 days of either heat and ambient

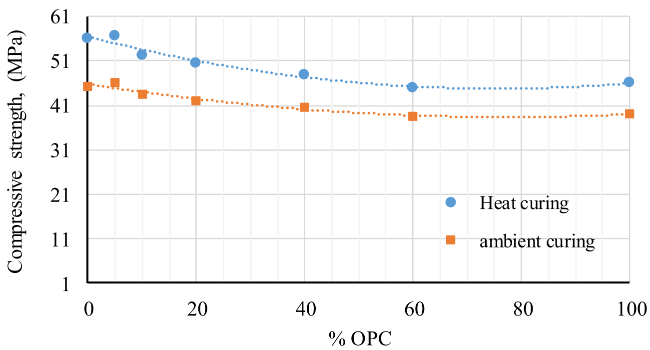


Fig. 3. Effect of OPC ratio and curing condition on compressive strength of MK-GPM and OPC mortars after 28days.

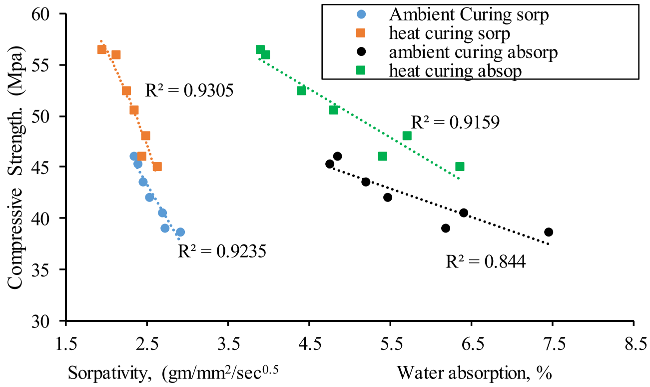


Fig. 4. Relationship between compressive strength with both transport properties (sorptivity, water absorption).

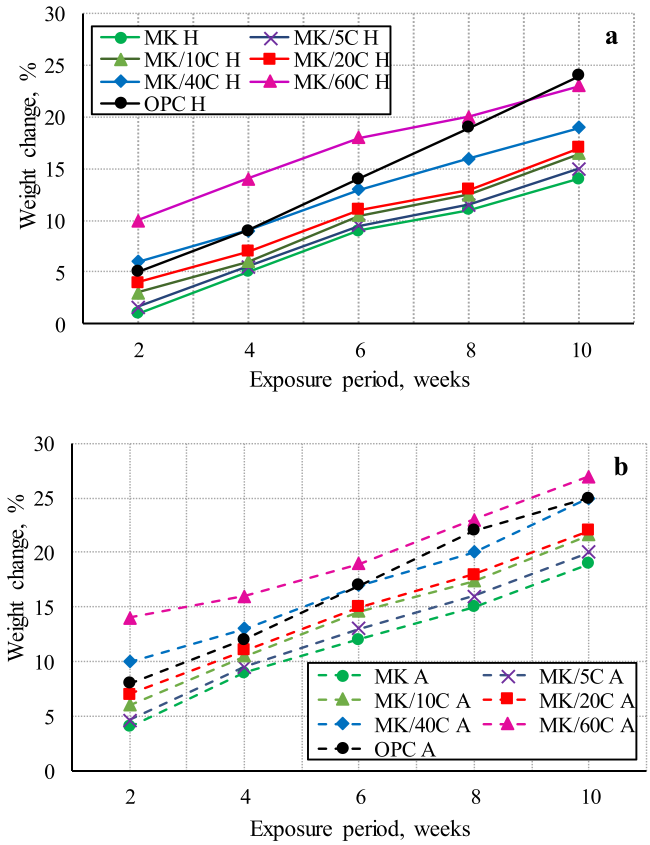


Fig. 5. Effect of cement content on weight change of different MK-GPMs cured at a) heat curing, b) ambient air curing and immersed on NaCl solution.

curing. It can be seen that MK-GPM has the lowest percent weight change. The change in the weight increases with increasing the period of immersion and with increasing cement replacement level and it is more significant at normal ambient curing than heat curing. However, the percent of weight increments after 10 weeks immersion for MK-GPMs containing OPC up to 40% are less than that for the conventional cement mortar at both curing conditions. The percent of weight increments after 10 weeks immersion of geopolymer MK, MK/5 C, MK/10 C, MK/20 C, MK/40 C, MK/60 C and OPC mortars reached 14%, 15%, 16.5%, 17%, 19%, 23% and 24% respectively, at heat curing, while these values increased at ambient curing to reach 19%, 20%, 21.6%, 22%, 25%, 27% and 25% respectively at the same immersion period. Therefore, it is evident that geopolymer mortars containing cement up to 40% have better performance than OPC mortar in sodium chloride solution.

The weight gain might be attributed to an increase in the mass of chemical particles that penetrates the mortar within the solution and increased the weight of the samples. Pasupathy et al. [61] observed higher absorption parameters represent a lower resistance to chloride diffusion at the concrete surface. The author characterized the water absorption into two stages: the initial water absorption rate and the secondary water absorption rate. The initial absorption rate is associated with the capillary pores in the concrete surface, which are related to chloride transportation to the concrete [61]. The lower percent of weight increase in heat cured MK-GPM could be attributed to its more densified matrix as a result to polymerization reaction and formation of dense alkali aluminosilicate gel (NASH) which leads to reduction in the amount of penetrated solution. While the increase of weight gain of MK-GPM containing OPC can be attributed to the formation of both dense NASH gel and less densified CASH gel [61].

The strength degradation of the samples exposed to sodium chloride solutions is appraised through measuring compressive strength as a percentage of the control specimens that were tested at 28 days curing (Fig. 3). Degradation of compressive strength for several mortars specimens immersed in sodium chloride solutions are demonstrated in Fig. 6(a, b). It is clear that the compressive strength loss for all studied mortars increases with increasing exposure period as well as with increasing cement content. Moreover, MK-GPM samples possess the least compressive strength degradation for both curing conditions. The percent of compressive strength degradation after 10 weeks immersion for MK, MK/5 C, MK/10 C, MK/20 C, MK/40 C, MK/60 C and OPC mortars reached 10%, 10.8%, 13.5%, 15%, 17%, 20% and 23% respectively, at heat curing, while these percentages increase at ambient curing to reach 11%, 12.6%, 14.6%, 17%, 20%, 23% and 25% respectively at the same immersion period.

The porosity of the cementitious paste is the most important factor impacting chloride ion penetration [49,62]. Although geopolymer mortars have a dense microstructure; similar to OPC systems, the relationship between chloride penetration and porosity follows the same pattern [63]. Continuous immersion in calcium chloride solution tends to change the integrity of the matrix due to formation of expansive calcium components and internal cracks formation resulting compressive strength degradation. The marked decrease in degradation of compressive strength of MK-GPM is largely due to the high reactivity of MK as well as its micro filler effect. This helps the formation of more densified geopolymer network resulting in a decreased pore size or more tortuous pore network So, it is concluded that, the compressive strength in case of heat curing is higher than ambient curing. [64,65].

3.5.2. Sulphate attack

Effect of cement content on weight change of different MK-GPMs cured at both heat curing and ambient curing and exposed to 10% magnesium sulphate solution for different immersion periods is illustrated in Fig. 7(a, b). The results show an increase in weight along the exposure period compared to initial weight after curing period. MK-GPM sample demonstrates less percent of weight increment than OPC sample. This positive effect is more pronounced for heat cured samples than ambient cured. The weight change for MK-GPMs containing cement increases with increasing the period of immersion and with increasing OPC content and this increment is more

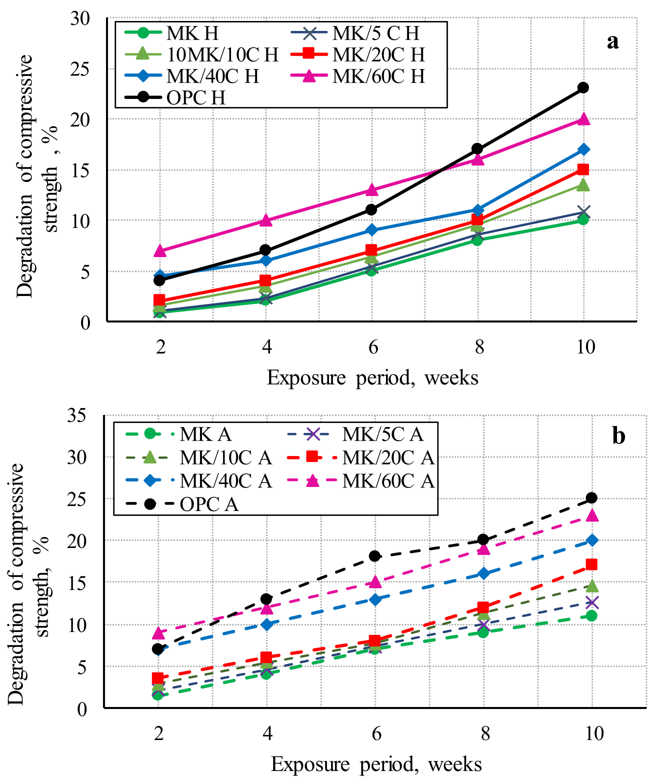
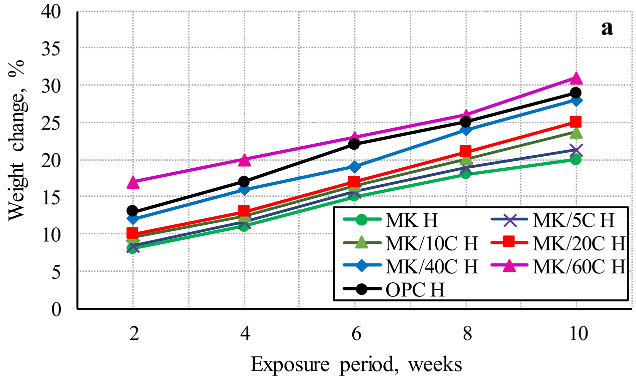


Fig. 6. Effect of cement content on compressive strength degradation of different MK-GPMs cured at a) heat curing, b) ambient air curing and immersed on NaCl solution.



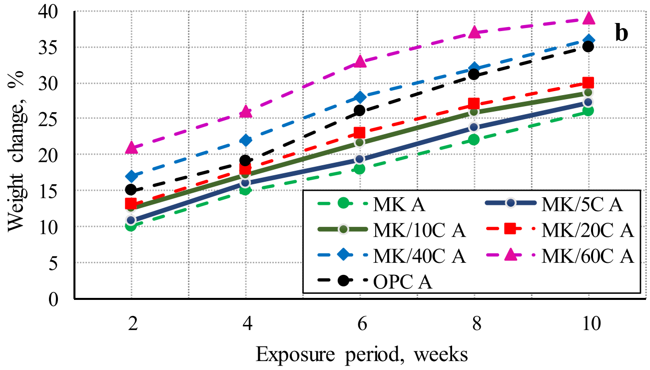


Fig. 7. Effect of cement content on weight change of different MK-GPMs cured at a) heat curing, b) ambient air curing and exposed to magnesium sulphate.

significant at normal ambient curing than heat curing. However, the weight change of MK-GPMs containing cement up to 40% after 70 days immersion period is almost less than that for OPC mortar at heat curing and this replacement ratio decreases to 20% at ambient curing. The percent of weight increments after 10 weeks immersion for MK, MK/5 C, MK/10 C, MK/20 C, MK/40 C, MK/60 C and OPC mortars reach 20%, 21.3%, 23.7%, 25%, 28%, 31% and 29% respectively, at heat curing, while these values increase at ambient curing to reach 26%, 27.2%, 28.6%, 30%, 36%, 39% and 35% respectively at the same immersion period. This reveals that MK and MK containing OPC up to 40% samples possess higher resistance to magnesium sulphate attacks than conventional OPC sample. The same results were obtained by Alcamand et al. [41], however, they demonstrated that partial replacement of MK with blast furnace slag (BFS) (as a source of Ca^{+}) causes reductions in the mechanical properties after sulfate attack and they attributed this behavior to the formation of ettringite and gypsum in the presence of calcium from BFS.

Fig. 8(a, b) clarifies the degradation of compressive strength of geopolymer mortar specimens immersed in magnesium sulphate solution. It is clear that the MK geopolymer mortar has the highest resistance to sulphate attack and the percent of strength degradation increase with increasing OPC content and immersion period. The figure illustrates that resistance to sulphate attack is improved by heat curing compared to ambient air curing. However, the degradation of compressive strength of MK-GPMs containing cement up to 40% after 70 days immersion period is almost less than that for OPC sample for both curing conditions. The amount of compressive strength degradation at the end of immersion period for MK, MK/5 C, MK/10 C, MK/20 C, MK/40 C, MK/60 C and OPC mortars reach 14%, 15.4%, 17.7%, 19%, 22%, 27% and 30% respectively, for heat cured samples. The similar values increase at ambient air curing condition to reach 18%, 18.8%, 20.1%, 21%, 25%, 30% and 35% respectively at the same immersion period.

Both Figs. 7 and 8 demonstrate that MK-GPM has better resistance to sulfate attack than MK-GPM containing cement or conventional OPC mortar. This can be attributed to that MK is free from Ca+ that has an undesirable outcome on sulfate resistance as geopolymer containing MK do not produce sulfate-aluminate compounds such as ettringite and gypsum through the hydration procedure and exposure to sulfate solution [41]. On the other hand, the MK-GPM containing cement (as a source of Ca) possess lower resistance to sulfate attack as presence of Ca+ help the formation of ettringite and gypsum during sulfate attack. Because the reaction products are comparable, the sulphate resistance mechanism of calcium-rich geopolymer cement is similar to that of OPC. Calcium-rich geopolymers contain C-(A)-S-H gel with a lower Ca/Si ratio than that of C-S-H in an OPC system. The formation of ettringite and gypsum during sulfate attacks help the formation of internal microcracks and increase the porosity and consequently increase the compressive strength degradation [66].

3.5.3. Acid attack

Fig. 9(a, b) illustrates the effect of cement content on weight change for all mortars exposed to sulphuric acid at different immersion

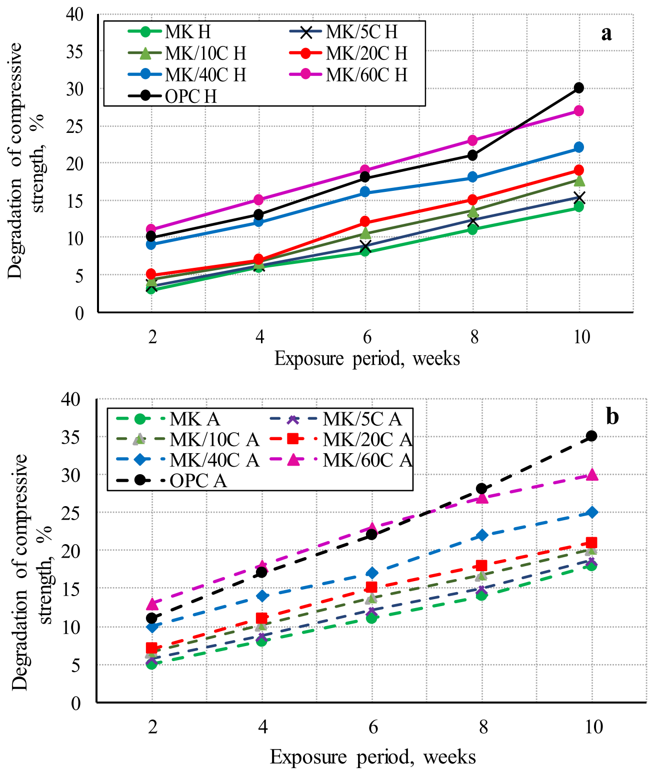


Fig. 8. Effect of cement content on compressive strength degradation of different MK-GPMs cured at a) heat curing, b) ambient air curing and exposed to magnesium sulphate.

periods for heat and ambient curing conditions. It can be seen that MK-GPM has the lowest percent of weight increment, and the weight increases with increasing the period of immersion and with increasing cement content. Moreover, the weight increment is more significant at normal ambient curing than heat curing. The percent of weight increments after 10 weeks immersion for MK, MK/5 C, MK/10 C, MK/20 C, MK/40 C, MK/60 C and OPC mortars reached 40%, 41%, 43.8%, 45%, 49%, 51% and 45% respectively, at heat curing, while these values increased at ambient curing to reach 45%, 46.3%, 47.8%, 49%, 55%, 58% and 52% respectively at the same immersion period.

Fig. 10 indicates the effect of cement content on compressive strength degradation for all MK-GPMs samples absorbed in sulphuric acid solutions. It is clear that the MK-GPM has high resistance to sulphuric acid attack than OPC mortar at both curing conditions and the resistance decreases with incorporating OPC to MK-GPM and with increasing the immersion period. Resistance to sulphuric acid attack is more pronounced in heat curing than ambient curing. The compressive strength degradation at the end of immersion period for MK, MK/5 C, MK/10 C, MK/20 C, MK/40 C, MK/60 C and OPC mortars reach 22%, 22.9%, 24.3%, 25%, 27%, 33% and 42% respectively, at heat curing, while these values increase at ambient curing to reach 25%, 26.5%, 30%, 32%, 35%, 37% and 49% respectively at the same immersion period.

Effect of cement content on weight change and compressive strength degradation of different MK-GPMs cured at both curing conditions and exposed to different aggressive solution after 10 weeks immersion period is summarized in Figs. 11 and 12 respectively. It is clear that MK-GPM has better chemical resistance at the end of exposure period than OPC mortar. This complies with [32]. This chemical resistance decreases with increasing cement content and is more significant with heat cured specimens than ambient air cured one. However, the resistance of MK-GPM containing cement up to 40% is better than the corresponding OPC mortar specimens under heat curing condition and up to 20% under ambient curing condition. It is clear from the figures that sulphuric acid exposure has higher negative effect than chloride and sulphate solutions for all studied MK-GPMs and OPC mortar. However, MK-GPM and MK/20 C have a better performance than OPC mortar in an acidic environment.

Comparing the results obtained by other authors Duan et al. [65] investigated durability and microstructure of fluidized bed fly ash and metakaolin based geopolymer exposed to acid attack (sulfuric acid (2%) plus hydrochloric acid (2%)). The authors found geopolymer samples possesses higher acid resistance than OPC. They found after 28 days of immersion in acids the compressive strength loss of geopolymer sample is only 10.4% while it reaches 34.4% for OPC samples. These ratios agreed with the results of the present study which are (12%, 29% for MK-GPM and OPC sample respectively. Kumar and Revathi [67] concluded that blended geopolymer concrete (MK-bottom ash GPC) develops a better performance against sulphate and acid resistance than the conventional concrete in terms of sorptivity, rapid chloride and water absorption.

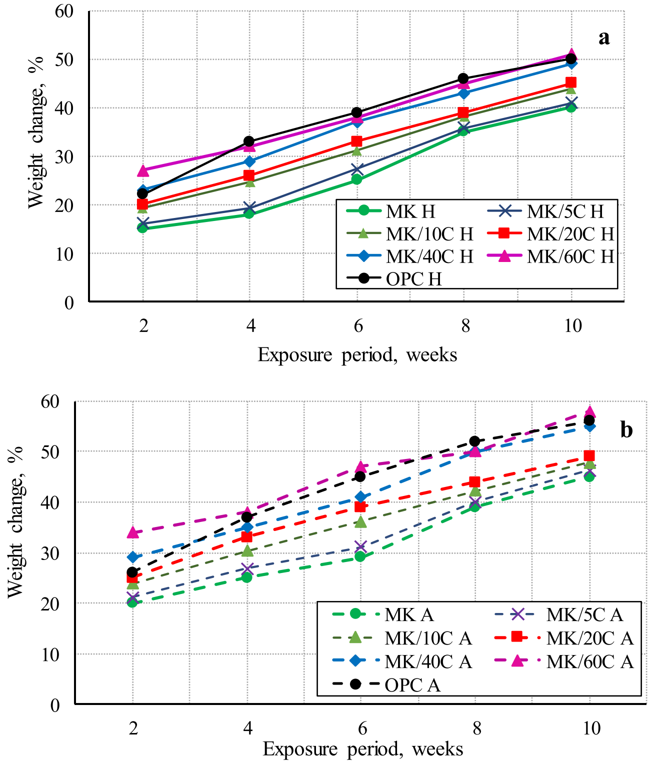


Fig. 9. Effect of cement content on weight change of different MK-GPMs cured at a) heat curing, b) ambient air curing and exposed to sulphuric acid.

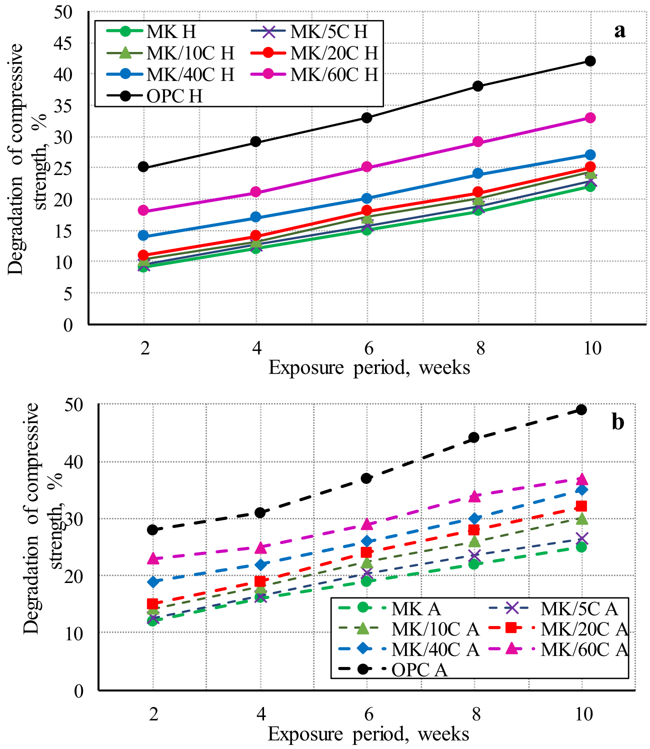


Fig. 10. Effect of cement content on compressive strength degradation of different MK-GPMs cured at a) heat curing, b) ambient air curing and exposed to sulphuric acid.

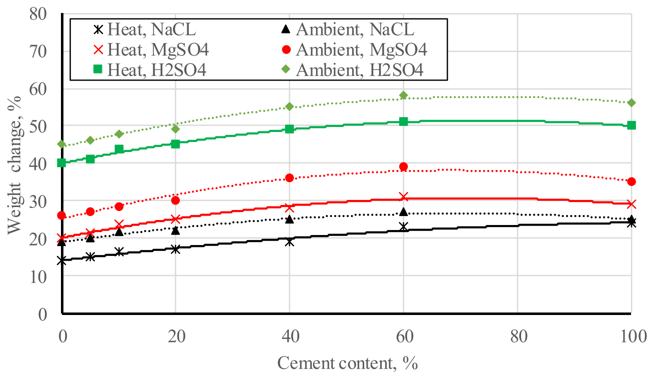


Fig. 11. Effect of cement content on weight change of mortars exposed to different aggressive solution at both curing conditions.

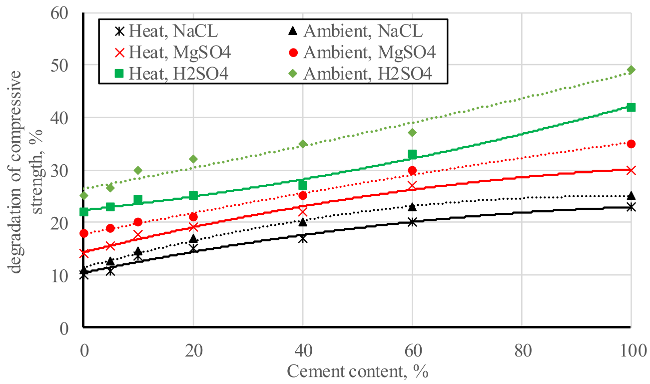


Fig. 12. Effect of cement content on compressive strength degradation of mortars exposed to different aggressive solution at both curing conditions.

3.5.4. Relationship between weight change and compressive strength degradation

The relationship between weight change and compressive strength degradation of MK-GPM and that containing OPC exposed to different aggressive solution at both curing conditions was derived from the linear regression analysis as shown in Fig. 13. Strong correlation coefficient can be obtained for these expressions indicating the authenticity of the regression curves. The compressive strength degradation found to be directly proportional to weight change i.e. the higher the compressive strength degradation, the higher will be the weight change. The relation between water absorption, pore structure and compressive strength of both geopolymer and OPC samples was studied by Duan et al. [65]. They attribute the lower strength degradation after exposure to aggressive environment to the less porosity and densified microstructure which related to better permeability resistance and hence lower water absorption.

3.5.5. Microstructure analysis

The X-ray diffraction pattern for MK-GPM, MK/20 C-GPM and OPC exposed to sulphuric acid at 10 weeks after 28 days of both heat and ambient air curing conditions are shown in Fig. 14, respectively. For the specimens of MK-GPM, major peaks were identified as quartz, nepheline, albite and gypsum. The decomposition of the C-(A)-S-H phase which is responsible for durability can produce new crystalline gypsum phases, as shown by the lower corresponding peak of diffraction, which is similar to other researcher's previous observations [68].

On the other hand, gypsum is found in specimens incorporating 20% OPC and 100% OPC as shown in Figs. 15 and 16. This may be due to the dissolution of part of C-S-H, which forms a lot of good crystalline gypsum with H_2SO_4. Secondly, Ca $(OH)_2$ in OPC, consumed entirely by H_2SO_4. This is also the main reason for weight loss in samples with long-term exposure to acid [69,70]. It is notable that Gypsum phase intensity is the lowest in MK-GPM compared to MK/20 C and OPC mortar. In addition, the percentage of the gypsum is less in MK-GPM at heat curing than air curing conditions.

3.5.6. SEM and EDS

SEM analysis with EDS for selected samples MK-GPM, MK/20 C-GPM and OPC exposed to sulphuric acid for 10 weeks after cured at 28 days under heat and air curing conditions are shown in Figs. 17–19. The SEM image of MK-GPM after 10 weeks of exposure to H_2SO_4 pH 3 shown in Fig. 16, a greater number of freshly created micro-cracks with less micro-cracks incompletely filled with gypsum crystals. This could be resulted in microstructural deterioration in the shape of a microstructure that is more permeable. EDS elemental

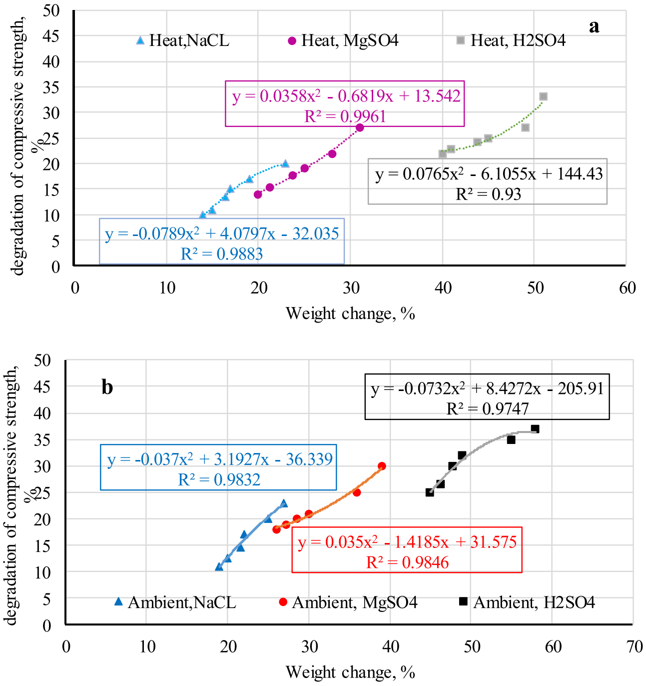


Fig. 13. Relationship between weight change and compressive strength degradation of different MK-GPMs cured at a) heat curing, b) ambient air curing exposed to different aggressive solution.

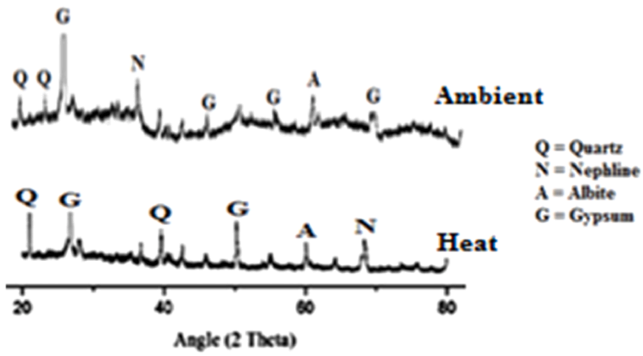


Fig. 14. XRD patterns of MK-GPM after 10 weeks of exposed sulphuric acid. heat and ambient curing conditions.

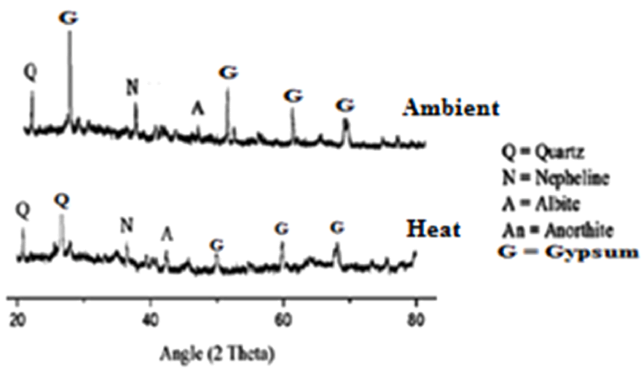


Fig. 15. XRD patterns of MK/20 C after 10 weeks of exposed sulphuric acid. heat and ambient curing conditions.

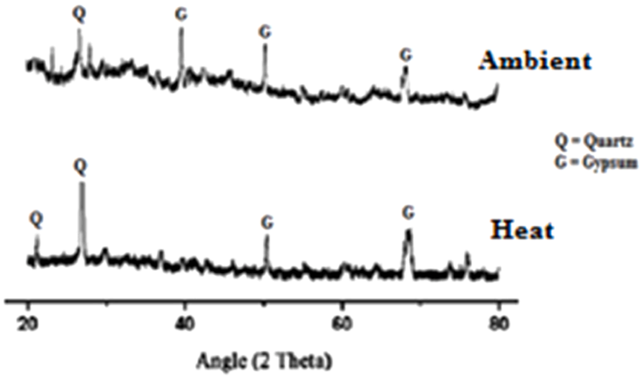


Fig. 16. XRD patterns of OPC after 10 weeks of exposed sulphuric acid. heat and ambient curing conditions.

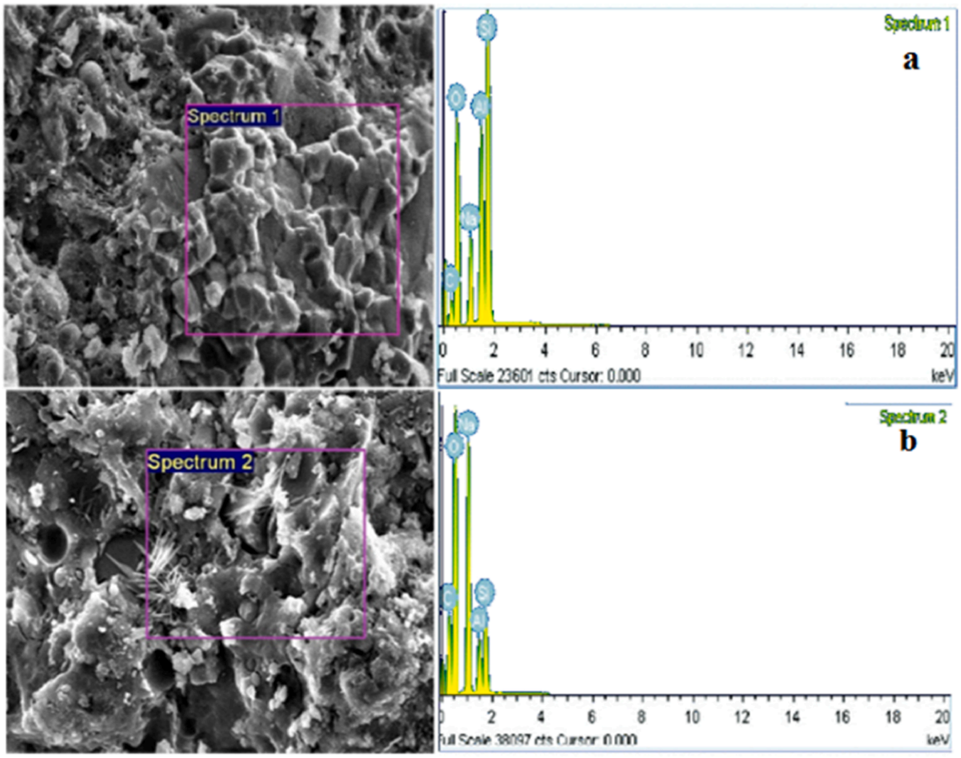


Fig. 17. SEM/EDS analysis of MK-GPM at 10 weeks of exposed sulphuric acid (a) heat curing and (b) ambient curing.

analysis with SEM observations has confirmed that some of the larger microcracks contain gypsum crystal due to reactions of sulphate acid ions and calcium compounds. This result is evident in the samples that were cured in the ambient curing condition. As stated earlier the MK-GPM presented some of microcracks at the surface. However, cracks were fewer than OPC mortars because the end product of polymerization is N-A-S-H that displays high resistance to acid attack as illustrated in Fig. 17. In terms of differences in chemical and phase compositions, MK-GPM is better than OPC when exposed to sulfuric solutions.

As previously confirmed, the main components of the EDS of MK-GPM mortar in the drop area are Si, Ca, Al and O which confirming the presence of gypsum. In addition to the previous reasons, SEM image (Fig. 18) shows a lack in homogeneity when adding OPC to the MK-GPM. This may be due to the presence of some unreacted MK and OPC particles with microcracks as well as the formation of improper gypsum and ettringite, lead to less strength compared with MK-GPM. Comparing microstructure of heat and ambient curing conditions Fig. 18b shows more unreacted MK and OPC particles and more microcracks with improper gypsum and ettringite formed, yet less strength is detected for ambient air cued matrix. Consequently, silica and alumina are less accessible for polymerization at higher OPC content and led to lower polymerization product (NASH) formation. Moreover, higher calcium requires increase in the water demand for hydration, some of these waters released and form additional void areas. The induced heating due to the exothermic

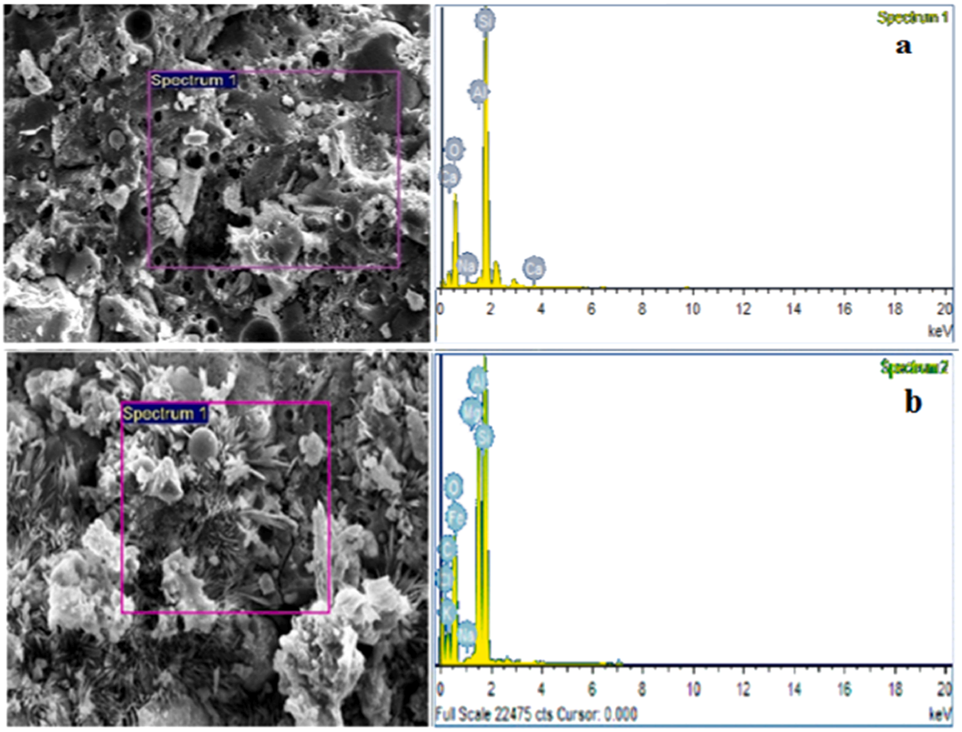


Fig. 18. SEM/EDS analysis of MK/40 C-GPM at 10 weeks of exposed sulphuric acid (a) heat curing and (b) ambient curing.

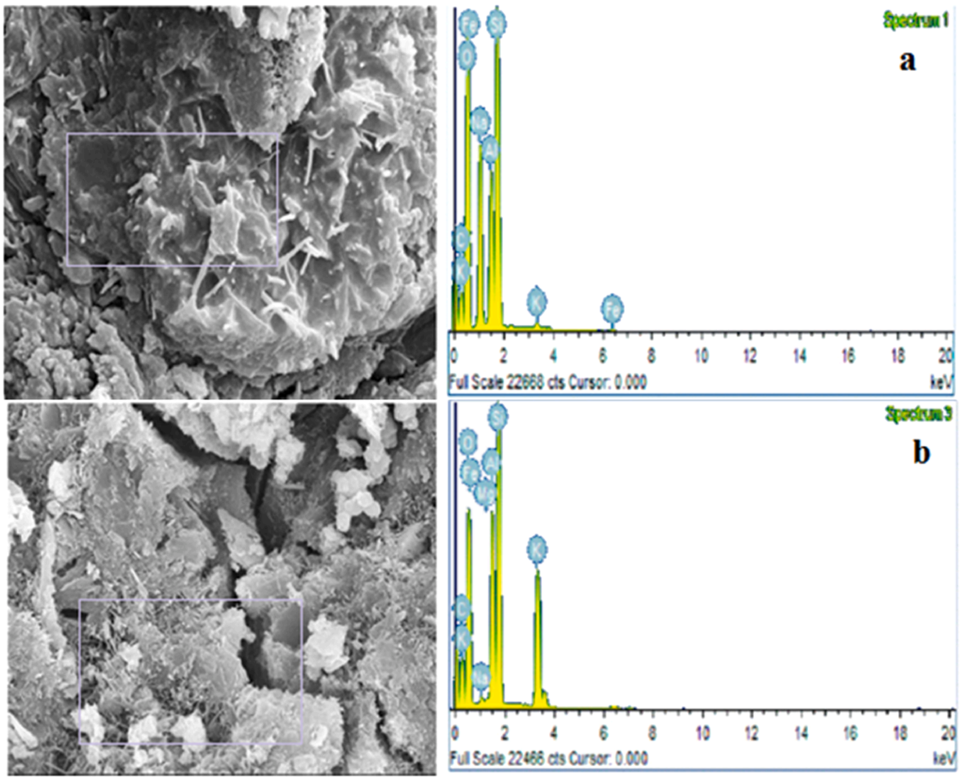


Fig. 19. SEM/EDS analysis of OPC mortar at 10 weeks of exposed sulphuric acid (a) heat curing and (b) ambient curing.

nature of hydration also increases the effectiveness of heat in the GPM technique, so that the moisture is further evaporated and microcracking and voiding are achieved [71].

As the large presences of the Ca, O and S show, the EDS spectrums reveal the presence of lengthened crystalline gypsum structures ($CaSO_4$) and ettringite crystals in MK-GPM/20% OPC and OPC samples. After exposure to sulphuric acid the OPC mortar has fine white surface depositions and becomes very porous. Moreover, SEM image of normal OPC mortar shown in Fig. 19 reveals the formation of large amount of gypsum and ettringite crystals with more microcracks and some pores filled with unreacted cement more than MK-GPM /20 OPC matrix. The study proves that samples containing reduced-calcium hydrate products are more durable than samples containing high-calcium hydration products when exposed to acid environment.

4. Conclusions

This study investigates the durability of MK geopolymer, MK geopolymer cement mortars and compares the results with OPC mortar. The following conclusions may be drawn:

1. Heat curing effectively decreases sorptivity and water absorption while increases compressive strength of MK-GPM and consequently improves its durability when exposed to aggressive environmental attacks better than ambient curing.
2. Incorporating 5%OPC into MK-GPM slightly decreases sorptivity and water absorption, while these properties increase with further increasing OPC content.
3. Inclusion of 5%OPC into MK-GPM increase the reduction of water transport properties for heat cured sample than that ambient cured.
4. Heat curing improves the durability properties of MK-GPM more than ambient temperature curing at all aggressive environments. However, the difference between them is insignificant and couldn't restrict the use of geopolymers in field applications.
5. Despite the fact that incorporating OPC up to 20% into MK-GPM decrease its resistance to chemical attacks, MK/GPM containing up to 20% cement shows better durability than OPC matrix when exposed to aggressive environmental attacks.
6. Microstructure of MK geopolymer paste is extra homogenous and more densified than normal OPC paste. Whereas inclusion of OPC causes lack in homogeneity of MK geopolymer paste microstructure with the presence of microcracks and pores.
7. After 10 weeks of sulfuric acid exposure for different geopolymer mortars, SEM/EDS micro-graphs show a gypsum and ettringite crystal formation. When compared to MK/20 C and OPC mixes, a MK-GPM produces dense microstructure and less micro cracks.

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.

Acknowledgements

This research was conducted at the Construction Material Laboratory of shoubra faculty of Engineering, Beha University and 6 October High institute, Culture & Science City. Housing and Building National Research Center (HBRC). This study was not funded by any public, commercial, or non-profit agencies.

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