Behaviour of fly ash geopolymer binders under exposure to alkaline media

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Abstract

Alkaline agents are primary binder components of geopolymer systems. In the converse, however, the hardened geopolymer binders can be adversely affected under exposure to strong alkalis. This paper presents an investigation conducted to evaluate the effects of highly alkaline exposure environment on fly ash geopolymer binders. In the study, a combination of sodium silicate and 12M NaOH solution was used as the alkali activator to prepare a low calcium (Class F) fly ash - based geopolymer binder. Fly ash geopolymer pastes or mortars were cast into 50 mm cubes and 25 x 25 x 285 mm prisms, then immersed in different media consisting of water or 1M to 3M NaOH solutions maintained at varied temperatures of 23, 38 and 80^0C. The tests done include compressive strength, expansion, weight changes. Analytical studies were done using X - ray diffraction, X - ray fluorescence, Fourier transform infrared spectroscopy, scanning electron microscopy. Leaching analysis of storage solutions was also conducted.

Results showed that alkali attack occurred when the concentrations of storage solutions exceeded 1M NaOH. The severity of attack increased with increase in NaOH concentration and in storage temperature. It was found that the alkali attack causes damage to the polymeric structure of the binder, leading to release of Al and Si. A gel - like substance forms, causing expansion and microcracking. New crystalline zeolite phases comprising *phillipsite*, *zeolite - P* and *chabazite*, also formed under exposure of the fly ash geopolymer binder to elevated alkali concentrations.

1. Introduction

Geopolymers are inorganic polymers that are synthesized from aluminosilicate materials. They are activated into binders by using strong alkali activators. During geopolymerization, the aluminosilicate raw materials dissolve in the highly alkaline activator solution, then precipitate into aluminosilicate gel to form a polymeric structure made of amorphous or partially amorphous phases composed of Al, Si and O elements [1–3]. The properties of geopolymer binders largely depend on the composition of starting materials and the reaction processes that occur during geopolymerization [4,5].

Metakaolin (MK), ground granulated blast - furnace slag (GGBS), fly ash (FA), natural pozzolans such as volcanic ash etc. [2,6-8], are among the commonly used aluminosilicate raw materials for formulating geopolymer cements (GPCs). FA and GGBS are artificial industrial waste by - products that are generated in large quantities worldwide. However, only small proportions of these artificial wastes are used beneficially e.g. as pozzolans in ordinary Portland cement (OPC), while most of these materials are disposed - off in landfills. The potential re - use of these wastes as alternative binder materials, would promote pollution control and environmental sustainability. However, for these alternative binders to be used at industrial scale, extensive scientific research into their performance properties is necessary, so as to develop full understanding of their material characteristics and engineering behaviours.

GPC concretes are widely understood to generally possess superior durability characteristics over OPC concretes. As such, there is interest in utilizing the GPC – based concretes under highly aggressive environments. Such applications may include special concrete structures that are used for storage of chemicals, hazardous materials or industrial wastes, which may be acidic or alkaline [9-13]. Alkali - silica reaction (ASR), is a well - established attack

2

process involving alkalis in concrete. It comprises the interaction of reactive phases in aggregates and free alkalis from cementitious materials [14-17]. Various studies have shown that GPC mixtures are much less susceptible to ASR damage than OPC mixtures [18-21].

1.1 Objectives

The present study focused on the effects of highly alkaline environment on GPC binder systems. In the absence of ASR, OPC binders are known to be durable under exposure to a highly alkaline environment. However, there is limited scientific literature available on the behaviour of GPC binders under strongly alkaline conditions. In the present study, fly ash geopolymer (FA – GPC) pastes and mortars containing non - reactive aggregates were immersed in highly alkaline solutions to assess possible occurrence of alkali attack. Compressive strength, expansion monitoring and leaching tests, were done. Also conducted were analytical studies done using X - ray diffraction (XRD), X - ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS).

1.2 Research significance

Special concrete structures or tanks are often used for containment or storage of chemicals, hazardous materials and industrial wastes which may be acidic or alkaline. Pertaining to these applications, there is limited literature on the limits of chemical stability for GPC binders particularly under highly alkaline exposure conditions. As such, the present study focussed specifically on the response of these binders to strongly alkaline exposure environment. In addition, the accelerated mortar bar test for ASR is based on use of 1M NaOH storage solution [22]. The method is used to evaluate OPC mixtures but it has been widely used for ASR testing

of GPC binders as well. In the present study, the behaviour of GPC mixtures under varied NaOH concentrations was investigated, which would provide some insights into the range of alkali concentrations suited for evaluating GPC binders.

2. Literature review

Various researches on the alkali and/or acid resistance behaviours of GPC binders are subsequently discussed with a view regarding the potential future applications of these binders under aggressive exposure conditions. Palomo et al. [23] studied the influence of different aggressive environments on metakaolin geopolymer cement (MK - GPC) mortars. In their study, a solution of 17M NaOH + $Na_2O \cdot SiO_2$ of silicate modulus 3.0 and solids content 36.5%, was used as the alkali activator. Silica sand was employed as the fine aggregate. MK - GPC mortar prisms of size 10 x 10 x 60 mm were immersed in different storage solutions comprising deionized water, sea water, 4.4% Na_2SO_4, 0.001M H_2SO_4, for varied periods of up to 270 days under room temperature. Results showed that all the samples stored in the various immersion solutions, gave slightly improved flexural strengths after 90 days of storage. Studies indicated the formation of faujasite - type crystalline zeolites in the samples that were immersed in sea water and in acid solutions, for a prolonged period of 180 days. Similar phases were also detected in samples that were stored in deionized water or Na_2SO_4 solutions for 56 days. It was suggested that the improvement in strength of the samples could be attributed to the transformation of some amorphous aluminosilicate gel into crystalline zeolite, which then served as reinforcement within the binder matrix.

New crystalline phases comprising Na - chabazite and faujasite were also reported by Sindhunata et al. [24] to have formed in FA - GPC paste samples, following storage of samples in 5M and 8M NaOH for 90 days at room temperature. However, no new crystalline phases formed in samples that were immersed in distilled water, 2.2M Na_2CO_3 or 2.2M K_2CO_3

solutions. In their study [24], NaOH or KOH mixed with $Na_2O \cdot SiO_2$, were used as the alkali activators. The H_2O/Na_2O and H_2O/K_2O ratios of the alkali activators were kept constant at 14.85, while SiO_2/Na_2O or SiO_2/K_2O ratios were varied to 0.0, 0.2 and 0.79. It was suggested that the formation of new crystalline phases under NaOH immersion solution could be attributed to continued geopolymerization during storage. A leaching study showed that the alkali storage solutions caused significant leaching of Al and Si from the samples, thereby damaging the aluminosilicate gel network.

In another study, Temuujin et al. [25] investigated the leaching behaviour of FA - GPC paste stored in acid and alkaline immersion solutions. From their results, significant concentrations of dissolved Al, Fe and Ca elements were detected in the immersion solution, having been leached from GPC pastes after 7 days of storage in 18% HCL. For the GPC paste samples immersed in 14M NaOH, high concentrations of Si and Al were leached out from the specimens. When the hardened FA - GPC paste samples were heat - treated at 600^0C prior to immersion in 18% HCL or 14M NaOH solution, the leaching of Al and Si elements decreased. The reduction in leaching was attributed to occurrence of partial crystallization at the surfaces of unreacted FA spheres, during heat treatment. This hardened surface layer which forms under heat treatment, tends to protect the FA particles against leaching during exposure to alkalis or acids.

Jin et al. [26] also studied the effects of acid and alkaline environments on leaching of GPC pastes made using municipal solid waste incineration (MSWI) FA. Paste mixtures of MSWI - FA/MK binder system were prepared using $NaOH + Na_2O \cdot SiO_2$ as the activator. In the mixtures, the ratios of Na_2O/SiO_2, SiO_2/Al_2O_3 and FA/MK used were 0.3, 4.7 and 0.67, respectively. A leaching study on the paste samples was done using an immersion solution of $H_2SO_4 + HNO_3$, mixed at H_2SO_4/HNO_3 ratio of 2.0. The pH level of the storage solution was varied to 3.0, 4.0 and 5.0. Also, the resistance of the MSWI - FA/MK pastes to alkali attack was evaluated by

immersion of the samples in NaOH solutions maintained at pH levels of 9.0, 11.0 and 13.0 i.e. 0.00001M, 0.001M, and 0.1M NaOH, respectively. Results showed that the compressive strengths of pastes that were subjected to the acid leaching test, reduced as the pH of acidic immersion solution decreased. Also, concentrations of the leached Cr, Zn, Cu and Pb increased with decrease in pH of the acid solution. However, the paste samples that were immersed in 0.1M NaOH did not show significant leaching of heavy metals. Also, no major reduction in compressive strength was reported in these samples.

Bakharev [27] investigated the effects of different alkali activators on acid resistance of FA - GPC. The different activators used in the study were 10M NaOH, $Na_2O \cdot SiO_2$ or 10M NaOH + 10M KOH. The FA - GPC pastes made using the different activators were immersed in 5% H_2SO_4 or 5% acetic acid. It was shown that FA - GPC pastes made using the NaOH activator, provided better resistance against acid attack, while the specimens that had been made using $Na_2O \cdot SiO_2$ or NaOH + KOH as the activator, exhibited significant reductions in strength. The deterioration of FA - GPC binders under exposure to acidic media, was attributed to depolymerisation of the GPC gel network, resulting from breakage of the Si - O - Al bonds and liberation of Si - OH and Al - OH groups. It was also suggested that the formation of zeolite crystals along with condensation of siliceous polymers, contributed to the strength loss observed in the FA - GPC pastes. Results indicated that the use of NaOH solution as alkali activator, leads to the formation of a more stable, cross - linked aluminosilicate polymeric structure, with an intrinsic ordering which provides better stability against an aggressive environment.

3. Experimental procedures

3.1. Materials and sample preparation

Class F, FA obtained from Lethabo power plant of ESKOM SOC Ltd, South Africa was employed in this study, as the aluminosilicate raw material for preparing GPC pastes and mortars. Table 1 gives the chemical composition of the FA used.

Table 1. Chemical composition of the fly ash used.

Oxides	Al_2O_3	CaO	Fe_2O_3	MgO	P_2O_5	K_2O	SiO_2	Na_2O	TiO_2	LOI
(%)	30.27	4.59	3.58	1.06	0.38	0.77	56.45	0.14	1.57	0.42

*LOI - Loss on ignition

Commercially available standard silica sand of particle sizes 0.4 - 0.85 mm, was obtained from Rolfes (pty) Ltd and used as fine aggregate to prepare GPC mortars. The alkali activator used in the study was prepared by mixing NaOH of technical grade and $Na_2O \cdot SiO_2$ solution of composition 64% H_2O, 8.3% Na_2O and 27.7% SiO_2 by mass. Both chemical supplies were obtained from Merck (pty) Ltd. Clearly, utilizing $Na_2O \cdot SiO_2$ in conjunction with NaOH as the activator, attracts considerable costs. However, studies show that this combination of the chemicals is perhaps the most effective activator for geopolymerization and the associated strength development in hardened GPC binder systems [28-33]. Accordingly, the foregoing GPC mixtures were employed while focussing on achieving good mechanical properties. It may also be noted that $Na_2O \cdot SiO_2$ can be produced from waste materials such as glass cullets, using simple processes [34]. Such innovative considerations could be exploited in future towards lowering the costs of chemicals that are used for GPC mixture synthesis. Already, the commonly used starting materials including FA, GGBS etc are typically low cost, waste materials.

The activator was prepared by first dissolving NaOH pellets in distilled water to obtain 12M NaOH, which was then mixed with $Na_2O \cdot SiO_2$ solution according to the proportions given in Table 2. The activator solution prepared was stored under normal laboratory conditions for 24

hours, prior to its use. Table 2 also gives the mixture quantities of FA and silica sand that were

used to prepare GPC pastes and mortars. Accordingly, the mortar mixture prepared consisted of

2.25 aggregate /binder ratio, alkali activator solution of SiO_2 /Na_2O = 1.4, and activator /FA ratio

= 0.5.

Table 2. Mix proportions used to prepare the fly ash geopolymer pastes and mortars.

Ingredients	Mortar (g)	Paste (g)
Fly ash	600	600
Sodium silicate	200	200
12M NaOH solution	100	100
Fine aggregate	1350	0.0

The mortars were prepared by mixing silica sand and FA at a low speed for 1 min, using a

mortar mixer. With the mixer still running, the alkali activator was added while mixing continued

for another 2 minutes, in accordance with ASTM C 305 [35]. A similar procedure was followed

in the mixing of pastes. The fresh pastes and mortars were used to cast 50 mm cubes and 25 x 25

x 285 mm prisms for conducting compressive strength measurements and expansion tests,

respectively. After casting, the fresh cubes and prisms in their moulds were sealed with a plastic

cling film and dry - cured for 24 hours in an oven maintained at 80^0C. Heat curing was employed

to promote rapid geopolymerisation of the GPC mixtures. Studies [36-41] show that the

geopolymerization reaction and the associated strength development are most effectively

achieved at curing temperatures of 75 to 85^oC. After curing of the samples, they were demoulded

and again sealed with a plastic cling film, then placed back for storage at 80^oC until testing. The

sealing of samples using a cling film was done to prevent evaporation of the liquid ingredients

during oven dry - curing at the elevated temperature of 80^0C. Various studies have shown that

moisture loss during curing of GPC mixtures adversely affects the geopolymerization reaction, which is responsible for strength development [38-40,42,43].

3.2 Alkali storage solutions

To evaluate the behaviour of the FA - GPC binder under alkali environment, the prepared paste and mortar cubes or prisms were subjected to alkali immersion test. The storage solutions used comprised tap water, 1M, 2M, 3M NaOH. In the test set - up, the volume of storage solution to the sample volume was kept constant at 4.7. In each set, three prisms were submerged in water or NaOH solution placed inside a tightly sealed plastic storage container. The assembly was then stored at varied temperatures of 22, 38, and 80^{0}C. Prisms were immersed in solution after 48 hours of curing. Thereafter, the expansions and weight changes of the paste or mortar prisms were measured at 1, 3, 7, 14, 28 days, and various ages of up to 90 days. Similarly, mortar cubes were dry - cured at 80°C for 48 days, then stored in water, 1M, 2M, 3M NaOH solutions also maintained at 80°C. The compressive strength of cubes was determined at 14 days of storage. Table 3 gives details of the samples and the different storage conditions employed.

3.3 Characterization studies

Microstructural studies were done on the FA - GPC samples before and after their immersion in the various storage solutions. Analytical studies were conducted using a Rigaku Ultima IV XRD, and Thermofourier FTIR. Microscopy was done using VEGA3 Tescan SEM equipped with an Oxford X - max EDS. Chemical compositions of the materials were determined using a Rigaku ZSX Primus II XRF equipment. Following conduct of the immersion tests, the storage solutions used in the test were analysed for leaching of elements, using the inductively coupled plasma mass spectrometry (ICP - MS) technique.

Table 3. Samples and storage conditions used for the fly ash geopolymer pastes and mortars.

Sample code	Type	Storage after two days of dry-curing at 80°C	Storage solution	Storage duration (days)	Storage temperature (°C)
M/0/2	Mortar	Dry exposure	-	-	80
M/0/14	Mortar	Dry exposure	-	14	80
M/W	Mortar	Immersion	Water	14/28	80
M/1M	Mortar	Immersion	1M NaOH	14/28	80
M/2M	Mortar	Immersion	2M NaOH	14/28	80
M/3M	Mortar	Immersion	3M NaOH	14/28	80
M/W/23	Mortar	Immersion	Water	84	23
M/1M/23	Mortar	Immersion	1M NaOH	84	23
M/2M/23	Mortar	Immersion	2M NaOH	84	23
M/3M/23	Mortar	Immersion	3M NaOH	84	23
M/W/38	Mortar	Immersion	Water	84	38
M/1M/38	Mortar	Immersion	1M NaOH	84	38
M/2M/38	Mortar	Immersion	2M NaOH	84	38
M/3M/38	Mortar	Immersion	3M NaOH	84	38
P/W	Paste	Immersion	Water	28	80
P/1M	Paste	Immersion	1M NaOH	28	80
P/2M	Paste	Immersion	2M NaOH	28	80
P/3M	Paste	Immersion	3M NaOH	28	80

4. Results and discussion

4.1 Compressive strength

Compressive strengths of the FA - GPC mortars were determined after 14 days of storing the cube samples under water or under 1M to 3M NaOH solutions at 80^0C. Fig. 1 shows the strength results of samples before and after storage in the different solutions. At immersion of samples in the various solutions, the cube samples had attained 53.2 MPa following 48 hours of curing, as given by the control M/0/2. It can be seen that the samples M/W/14, that were stored in water gave 14% lower compressive strength relative to their non - immersed counterparts, M/0/14. This strength reduction is attributed to the lubricating effect associated with the saturated condition of samples. This influence of the moisture condition of samples on strength, also occurs in OPC systems [44]. It is also evident that the GPC mortar cubes M/1M/14, that were stored in 1M NaOH solution gave a slightly lower strength of 48.9 MPa as compared to 50.6 MPa for those stored in water (M/W/14). However, strength decreased significantly with

increase in the alkali concentrations of storage solutions, giving only 14.6 MPa for samples M/3M/14 that were stored in 3M NaOH. This severe strength reduction of 71% at the alkali concentration of 3M NaOH could be related to the release of Si and Al from the aluminosilicate gel network under alkali attack [24, 25]. These mechanisms are discussed later in the paper.
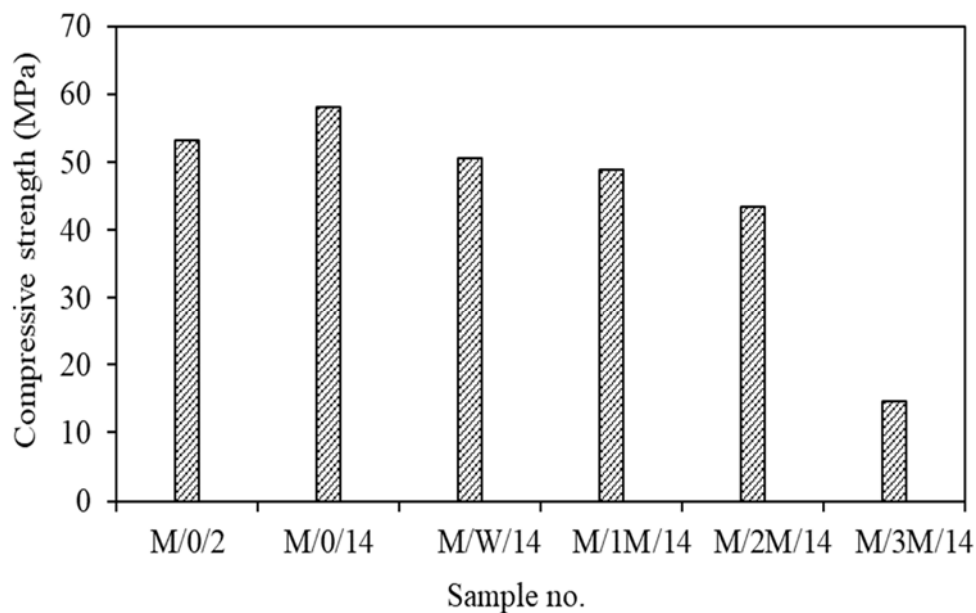

Fig. 1 Compressive strengths of mortars stored in alkali solutions of varied concentrations: M/0/2 – mortar cured for 2 days, M/0/14 – mortar cured for 14 days, M/W/14 - mortar immersed in water, M/1M/14 - mortar immersed in 1M NaOH, M/2M/14 - mortar immersed in 2M NaOH, M/3M/14 - mortar immersed in 3M NaOH.

4.2 Expansion results

4.2.1 Mortars and pastes stored at 80 ^{0}C

Results of the expansions for FA - GPC mortar prisms that were stored in water or in 1M to 3M NaOH solutions at 80^{0}C, are given in Fig. 2. It can be seen that there was an initial expansion in all samples, after one day of immersion. This early age expansion is a result of initial water sorption by the partially dry samples cured at 80^{0}C, prior to their immersion into the storage

solutions. After 7 days of storage, the samples that had been immersed in alkali concentrations exceeding 1M NaOH exhibited further expansions, while those that were stored in water or 1M NaOH showed no further expansions. While expansion was moderate for samples stored in 2M NaOH, there was high expansion for prisms stored at the elevated alkali concentration of 3M NaOH.

Fig. 3 gives the expansion results of paste prisms, also stored under water or in 1M to 3M NaOH solutions at 80^{0}C. Generally, the mortar samples (Fig. 2) gave higher expansions compared to the corresponding paste expansions (Fig. 3), but both sets of samples exhibited similar trends, showing higher expansions with increase in NaOH concentrations. The 14 - day expansion values of the mortar prisms stored at 80°C in water, 1M, 2M, 3M NaOH solutions were 0.008%, 0.010%, 0.051%, 0.104%, respectively compared to the corresponding 0.012%, 0.012%, 0.017%, and 0.063% for the paste prisms. It appears that the 14 - day expansion of mortar prisms approximately doubled for every 1M increase in alkali concentration of NaOH. Also, only the mortar prisms stored in 3M NaOH at 80°C gave expansions exceeding 0.10% at 14 days, while the prisms stored in all the other solutions gave lower expansions. Based on these results, it may be surmised that severe alkali attack on FA - GPC binder systems occurs at alkali concentrations no less than 3M NaOH.

Fig. 4 gives the weight changes for mortar prisms stored in water or in NaOH solutions. It can be seen that there was significant gain in weight of the samples during the initial stage of storage, regardless of the immersion solution used. However, the samples did not show further weight gain after the first day of storage. It is clear that the weight gain observed was a result of initial water absorption upon transfer of the oven - dry samples into the storage solutions. The results also show that samples exhibited higher weight gain with increase in concentration of the NaOH storage solution. This observation may be attributed to changes in density values of the NaOH storage solutions made at different concentrations. The density of NaOH solution

increases with increase in its concentration, which explains the higher gain in weight of samples with increase in concentration of the NaOH storage solution.

Within two days of storage of the FA - GPC mortar in 3M NaOH, fine longitudinal cracks appeared at surfaces of the samples. The sizes of these cracks increased with longer storage of the samples in the alkali solutions. Fig. 5 shows photographs of the paste and mortar samples stored in NaOH solutions of different concentrations. It can be seen that no visible cracks developed in paste samples that were stored in alkali solutions of less than 3M NaOH concentration.
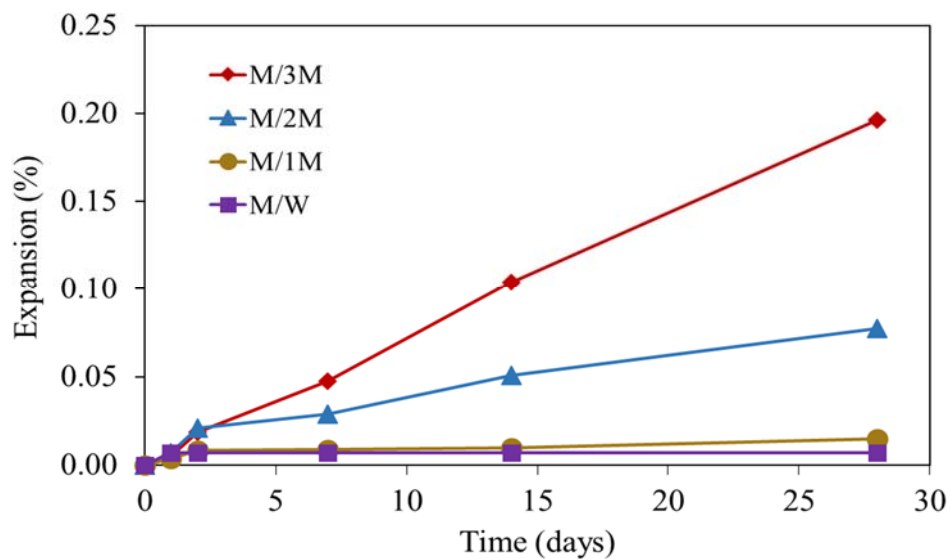
Fig. 2 Expansion measurements for 25 x 25 x 285 mm prisms of fly ash geopolymer mortars stored in water or 1M to 3M NaOH solutions at 80^0C: sample nos. as defined in Fig. 1 caption.
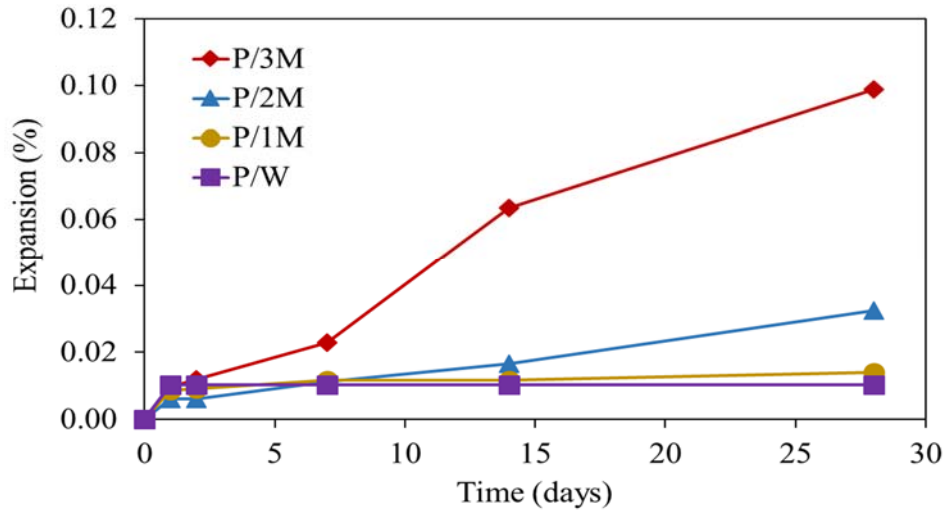
Fig. 3 Expansion measurements for fly ash geopolymer paste prisms stored in water or 1M to 3M NaOH solutions at 80^{0}C: P/W – paste immersed in water, P/1M - paste immersed in 1M NaOH, P/2M - paste immersed in 2M NaOH, P/3M – paste immersed in 3M NaOH.
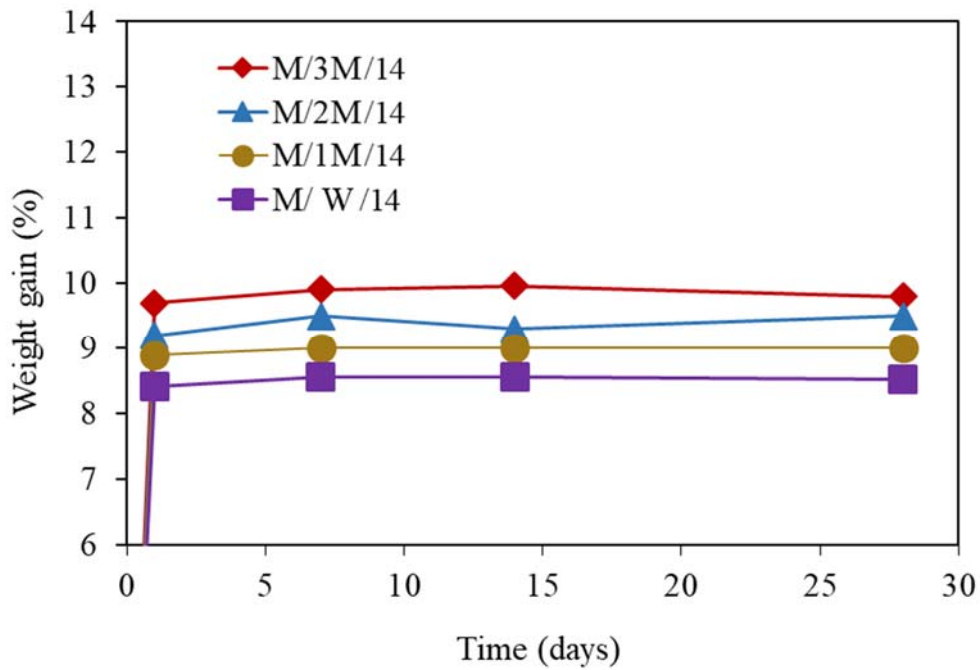

Fig. 4 Weight changes for 25 x 25 x 285 mm prisms of fly ash geopolymer mortars stored in water or 1M to 3M NaOH solutions at 80^{0}C: sample nos. as defined in Fig. 1 caption.

Fig. 5 Photographs of 25 x 25 x 285 mm geopolymer paste or mortar prisms stored at 80°C in NaOH solutions of different concentrations: P/2M - pastes stored in 2M NaOH, P/3M - pastes stored in 3M NaOH, M/3M - mortars stored in 3M NaOH.

4.2.2 Mortars and pastes stored at 23 ^{0}C or 38 ^{0}C

In Fig. 6 are shown the length changes for FA - GPC mortar specimens stored at 23 or 38^{0}C in water, or in 1M to 3M NaOH solutions. Clearly, there was no significant expansion in mortars stored in water, or in 1M to 2M NaOH solutions. However, the mortars that were immersed in 3M NaOH gave significant expansions of 0.115% and 0.184%, after 56 days of storage at 23^{0}C and 38^{0}C, respectively. These observations are consistent with results of the mortar samples stored at 80^{0}C (Fig. 2), showing that severe alkali attack occurs at concentrations no less than 3M NaOH.
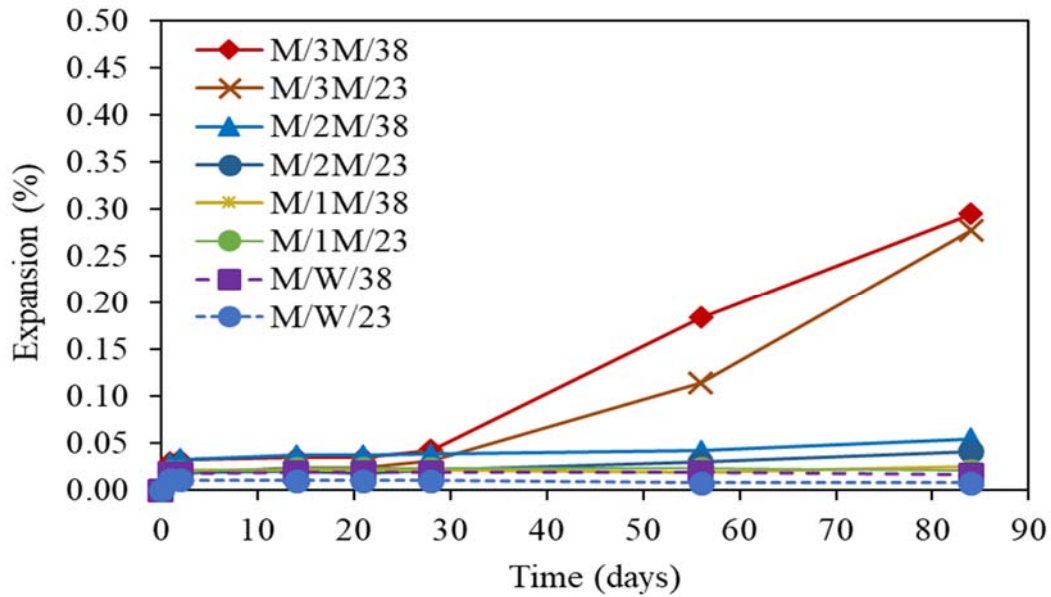
Fig. 6 Expansion of fly ash geopolymer mortar prisms stored in different concentrations of NaOH solutions at 23^0C or 38^0C: M/W/38 – mortars stored in water at 38^0C, M/3M/38 – mortars stored in 3M NaOH at 38^0C, M/3M/23 – mortars stored in 3M NaOH at 23^0C, etc.

4.3 Leaching

Fig. 7 shows the concentration of elements that leached from the FA - GPC paste prisms into the immersion solutions, after 28 days of storage at 80^0C. It can be seen that significant concentrations of Si and Al were leached out when the paste samples P/3M, were stored in 3M NaOH, while little or no leaching occurred under storage in water (P/W). The concentrations of leached Si and Al in the 3M NaOH storage solution were 97% and 78% higher than those in water. The high leaching of Al and Si under storage of samples in the 3M NaOH solution indicates the occurrence of alkali attack at this elevated alkali concentration. Such an attack could result from two possible mechanisms comprising, (i) dissolution of unreacted FA particles present in the geopolymer paste, upon its exposure to the elevated alkali concentration. This process can occur in a manner similar to the first stage of geopolymerization [1,45,46], (ii) release of Si and Al elements from the geopolymeric chain structure as a result of damage to the gel network [24].

16

At high alkali concentrations, it appears that the hydroxyl ions from the alkali may attack the Si - O - Al bonds of the aluminosilicate gel network, causing disintegration of the polymeric structure by forming new Si - OH and Al - OH bonds, accordingly releasing the Si and Al species into the immersion solution. However, results show a disproportionately higher leaching of Si relative to Al, which may indicate that the Si - O bonds may be more vulnerable to alkali attack than the Al - O bonds.

The chemical compositions of FA - GPC paste samples were also determined before and after their storage in 3M NaOH solution at 80^0C. Table 4 gives the chemical analyses results for the paste samples. These results show a 21.8% decrease in SiO_2 content of the pastes, after 28 days of their storage in the elevated alkali solution. These observations indicate that severe leaching of the Si species occurred from the paste into the storage solution. These results, which show a significant decrease in SiO_2 content of the pastes after storage in 3M NaOH solution, are in agreement with the chemical analyses results of the storage solutions, which showed a corresponding increase in SiO_2 content, as already discussed (Fig. 7).
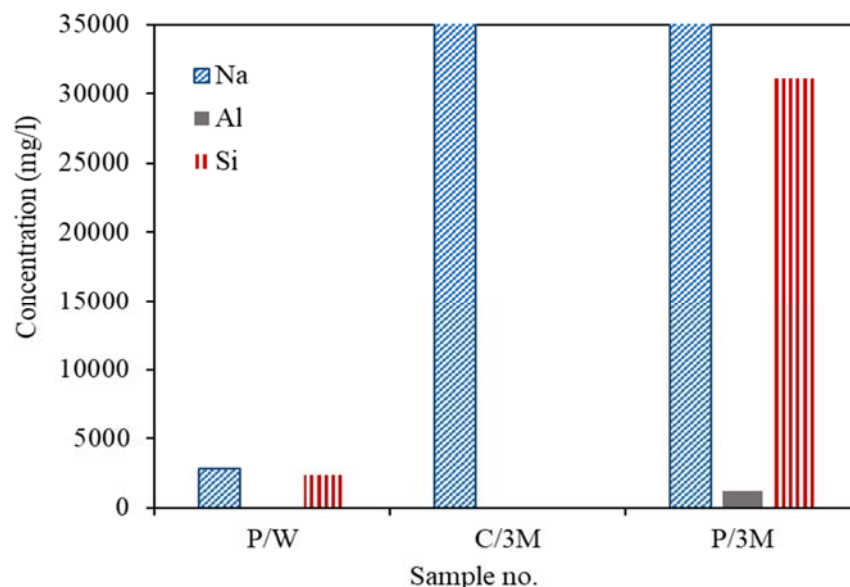

Fig. 7: Leaching of geopolymer pastes after 28 days of storage in water or 3M NaOH solution at 80^oC: P/W - pastes stored in water, C/3M – plain 3M NaOH solution, P/3M - pastes stored in 3M NaOH solution.

Table 4. Chemical compositions of the fly ash geopolymer pastes before and after storage in 3M NaOH solution.

Oxides	Fly ash (%)	Paste samples before storage in 3M NaOH (%)	Paste samples after storage in 3M NaOH for 28 days (%)
Na_2O	0.14	7.1	14.2
MgO	1.06	0.7	1.1
Al_2O_3	30.27	25.7	28.0
$SiO2$	56.45	53.2	41.6
P_2O_5	0.38	0.4	0.1
K_2O	0.77	0.9	0.5
CaO	4.59	5.0	6.2
TiO_2	1.57	2.0	2.2
Fe_2O_3	3.58	3.9	5.0

4.4 Microanalyses

4.4.1 X - ray diffraction

Fig. 8 gives the XRD patterns of FA - GPC pastes before and after their storage in water, 1M or 3M NaOH solutions at 80^0C for 28 days. By comparing the pattern of the control sample P with that of sample P/W, it can be seen that storage of the pastes in water did not cause any significant changes in crystalline phases. However, major phase alterations occurred in pastes that were stored in 1M or 3M NaOH solutions. Evidently, the samples P/1M and P/3M formed new phases including the Na - zeolite mineral, referred to as *zeolite - P*. Other studies [47-52] have reported the formation of *zeolite - P* mineral phase during synthesis of zeolites from FA, using the hydrothermal method. The formation of *zeolite - P* at elevated concentrations of alkali solution, may indicate the geopolymerization of some unreacted FA particles present within the paste.

These FA particles are those which did not react with the activator [53]. The unreacted FA generally consists of an amorphous aluminosilicate phase, mullite, and quartz. The typically smooth surface layer of the spherical FA particles predominantly consists of an amorphous reactive phase, which degrades upon its exposure to a highly alkaline medium. Dissolution of this outer glassy phase of FA particles along with some crystalline quartz, provides the requisite Si and Al for the formation of zeolite products, as observed in Fig. 8 for samples P/1M and P/3M. Meanwhile, mullite in the FA remains stable under exposure to elevated alkali concentrations [54]. Clearly, the quartz peaks seen in the samples P and P/W, disappeared upon storage of the samples in 1M or 3M NaOH solutions, indicating the dissolution of the quartz under exposure to the elevated alkaline media.

The other new crystalline phase which formed in the samples P/1M and P/3M, was *phillipsite*. A different mineral phase, *chabazite* formed only in the paste sample P/3M. It is possible that the deposition of these new crystalline phases i.e. *phillipsite* or *chabazite*, at the surfaces of FA particles could increase the size of the FA sphere [55], thereby contributing to expansion and microcracking in a manner similar to ASR expansion [8].
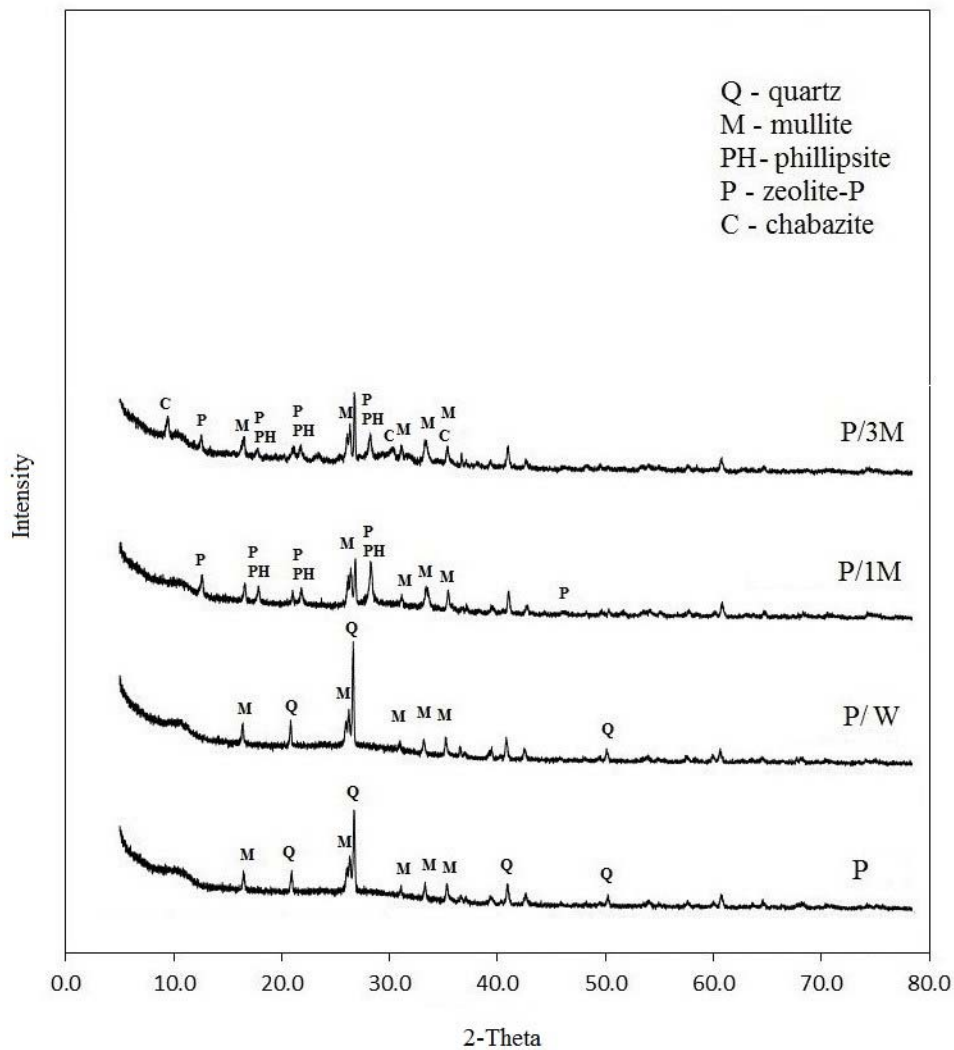
Fig. 8 XRD patterns of fly ash geopolymer pastes after storage in different immersion solutions: P – paste not immersed in any solution, P/W - stored in water, P/3M - stored in 3M NaOH solution.

4.4.2 Scanning electron microscopy

The FA - GPC pastes that were not immersed in any solution, and those that were stored in NaOH solutions were examined by SEM, as given in the micrographs of Figs. 9 to 11. Fig. 9a shows the SEM features of FA - GPC paste sample P, that was not stored in any solution. It can be seen

that there are numerous unreacted, characteristically spherical FA particles surrounded by a dense solidified aluminosilicate matrix. It is evident in Fig. 9a that a relatively large quantity of FA particles may remain unreacted after the geopolymerization reaction. Also seen in the figure is some limited microcracking, which is perhaps related to shrinkage due to loss of free water. Elemental analysis of the paste matrix showed mainly Si, Al and Na elements which indicates a typical silica - rich GPC aluminosilicate composition, as given by the EDS of Fig. 9a. Interestingly, the FA - GPC paste sample P/3M that had been stored in 3M NaOH solution (Fig. 9b), showed no presence of unreacted FA particles unlike the case with sample P in Fig. 9a, where the unreacted FA particles were prevalent. These observations clearly indicate that the unreacted FA particles in the pastes actually dissolved upon exposure to the elevated alkali concentration of 3M NaOH solution.

It can also be seen in Fig. 9b that the pastes that were stored in the 3M NaOH solution exhibited a relatively porous, less dense matrix with severe microcracking distributed throughout the matrix. These features seem to indicate the occurrence of damage within the polymeric structure, perhaps related to breakage of the Si - O - Al bonds under alkali attack. This attack process, which occurs in association with the dissolution of unreacted FA particles present within the paste, could be the main reason for the observed expansion and severe loss of strength for samples that were stored in the 3M NaOH solution (Sections 4.1 and 4.2).

Also seen in Fig. 9b, is a gel - like substance present inside the fine and large map cracks within confined zones of the matrix. The formation of this substance appears to be majorly responsible for the observed expansion of the FA - GPC paste samples stored in the 3M NaOH solution. The elemental composition of this gel - like substance is given in the EDS of Fig. 9b. It mainly comprises Si and Al, possibly emanating from the damaged polymeric structure following alkali attack. Fig. 10 shows a close - up of this gel - like substance inside a pore within the FA - GPC paste. It can be seen that the completely filled void also shows microcracking

radiating into the surrounding paste matrix. It would appear that the pore infilling by the gel is associated with the observed expansion and microcracking of the surrounding paste matrix, as reported in Section 4.2. Again, this gel - like material predominantly contained Si and Al with small traces of Fe and Mg, as shown in the EDS of Fig. 10.

In Section 4.4.1, the new mineral phases that formed in the paste samples P/1M and P/3M which had been respectively stored in 1M and 3M NaOH solutions, were identified using XRD to be *zeolite - P*, *phillipsite* and *chabazite*. Fig. 10 shows features of *phillipsite* that formed at the surface of initially an unreacted FA particle within the FA - GPC paste, stored in 3M NaOH solution. As already mentioned in Section 4.4.1, the possible growth in size of FA spheres due to the formation of such new mineral phases could also contribute additional expansion, further to the main expansion due to the formation of a gel - like substance in confined zones within the matrix. However, the potential contribution of these new mineral phases to expansion could not be verified.
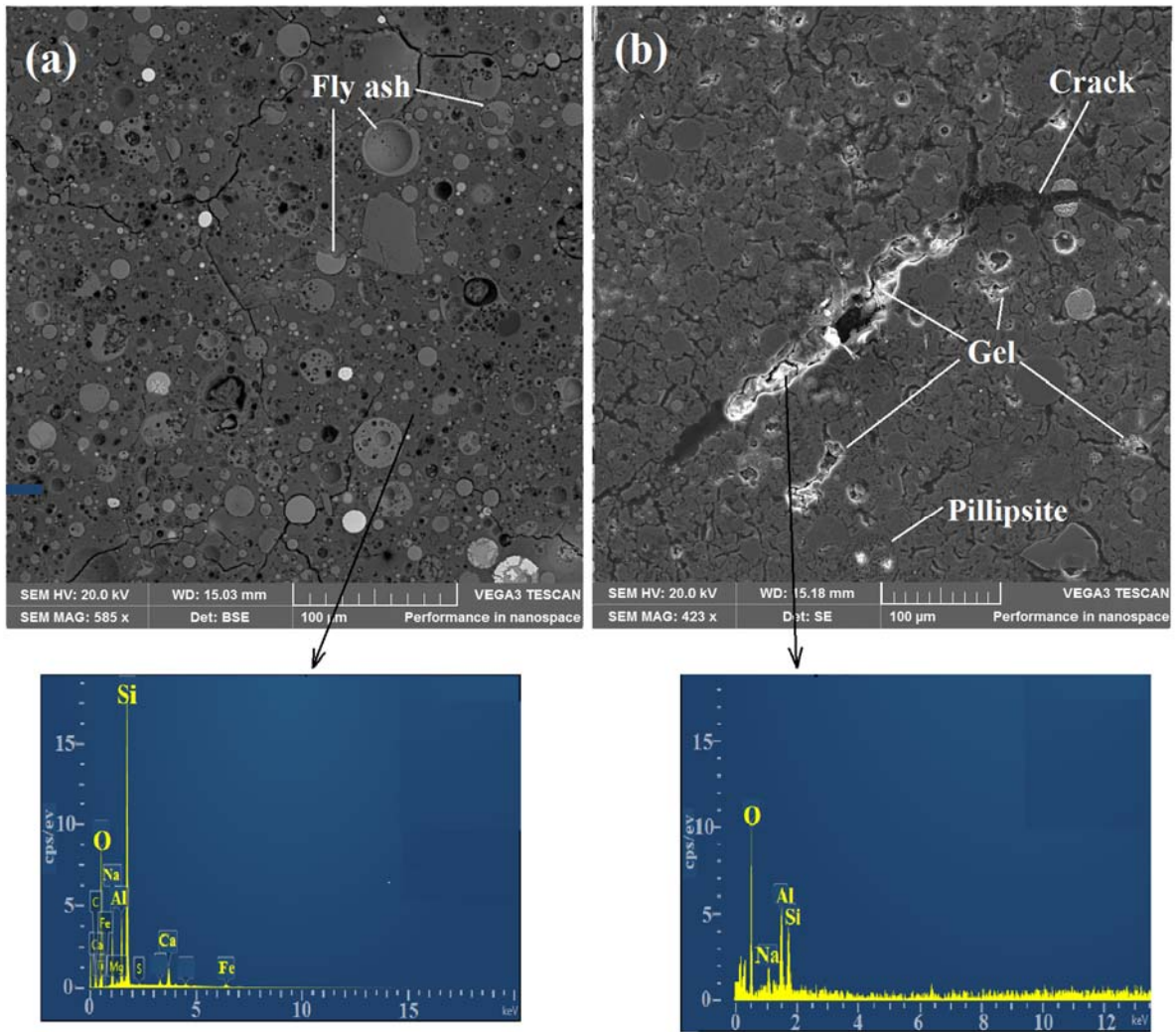
Fig. 9 SEM features of FA - GPC binder pastes: (a) sample P - not immersed in any solution, (b) sample P/3M - stored in 3M NaOH for 28 days.
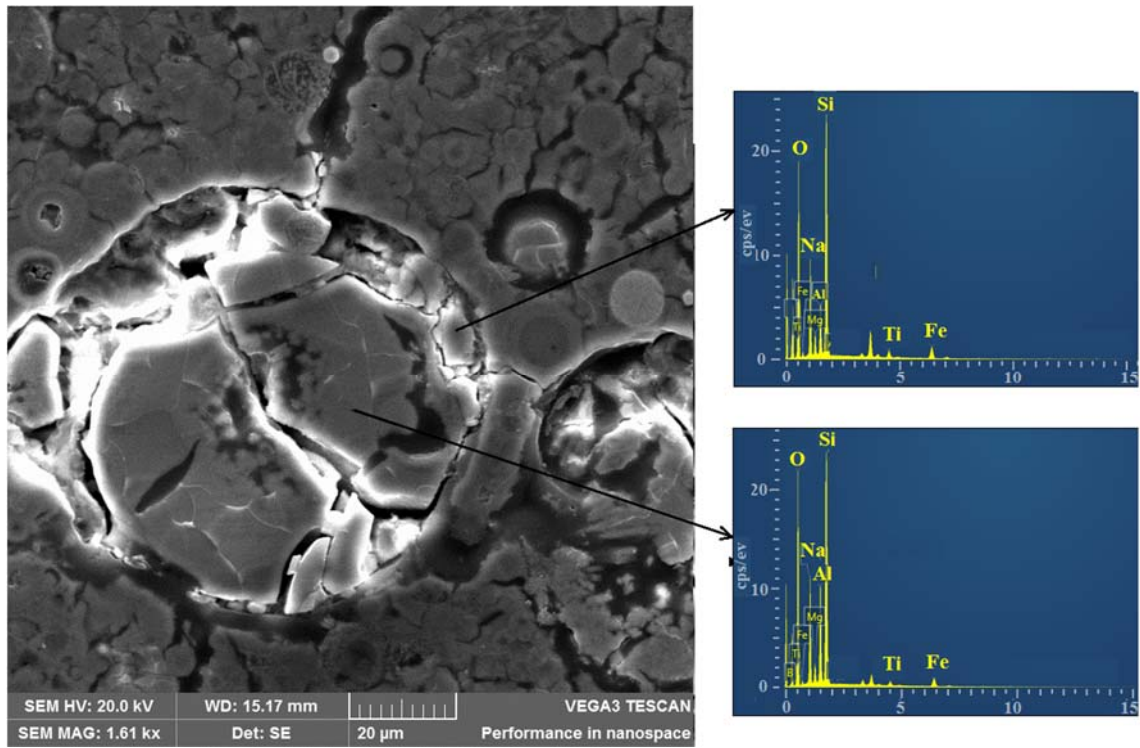
Fig. 10 An infilling of a pore by expansive gel - like substance in FA - GPC paste sample P/3M, stored in 3M NaOH solution.
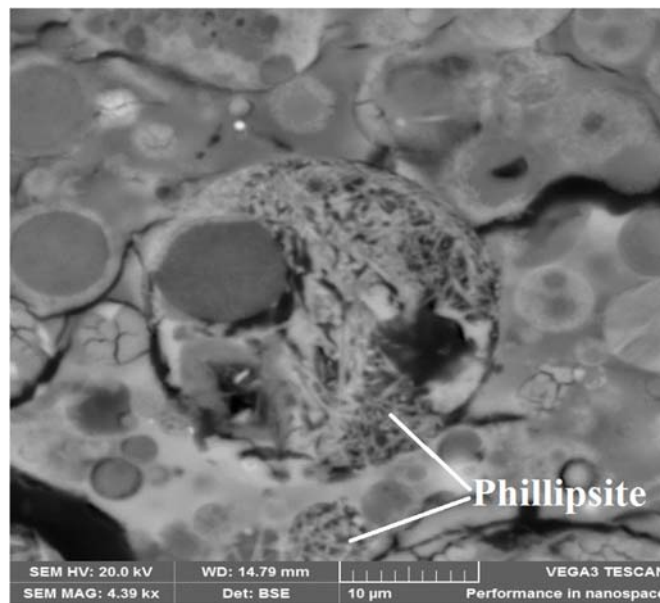

Fig. 11 SEM micrograph showing phase crystallization at the surface of an unreacted fly ash particle in an FA - GPC paste sample P/3M, stored in 3M NaOH solution.

4.4.3 Fourier transform infrared spectroscopy

Fig. 12 shows the FTIR spectra of FA - GPC pastes after storage in water, 1M or 3M NaOH solutions at 80^0C. The bands at 749 and 790 cm^{-1}, which are associated with symmetrical stretching of O - Si - O can be observed in all the samples, regardless of the storage solution [56,57]. These bonds are attributed to the quartz in unreacted FA particles within the FA - GPC binder systems [52]. The bands at 670 and 339 cm^{-1} are related to the Al - O asymmetrical stretching bonds, which could be attributed to the formation of $Al(OH)_4^-$ and $NaAl(OH)_4$ species that are disjointed from aluminosilicate matrix [58]. The bands at 967 to 997 cm^{-1} represent T - O – Si, where T = Si or Al. They show the asymmetric stretching vibrations that are indicative of geopolymerization [59]. There was a shift of bands from 997 cm^{-1} to 974 cm^{-1} then to 967 cm^{-1} corresponding to changes in concentration of the storage solutions from water to 1M to 3M NaOH, respectively. These shifts in bands could be attributed to transformation of the FA glassy phase to crystalline zeolite phases [52].

The stretching vibration band at 3385 cm^{-1} along with the bending vibration band at 1629 cm^{-1}, are associated with H - O - H bonds [26,60]. There is an increase in intensity of the band at 1629 cm^{-1} with increase in concentration of the storage solution from water to 1M to 3M NaOH. This change in intensity could be attributed to the water molecules that may be attached onto FA particles. Deposition of zeolite at the surface of FA particles may increase cation exchange capacity and consequently, the water adsorption of FA particles [61]. The bands at 1413 to 1480 cm^{-1} are associated with O - C - O bonds, indicating the presence of sodium carbonate in the FA - GPC samples [26]. There is an increase in intensity of this band at higher NaOH concentrations, which may be attributed to carbonation of NaOH found within the pores, in a manner similar to that of $Ca(OH)_2$ in OPC mixtures [62,63].
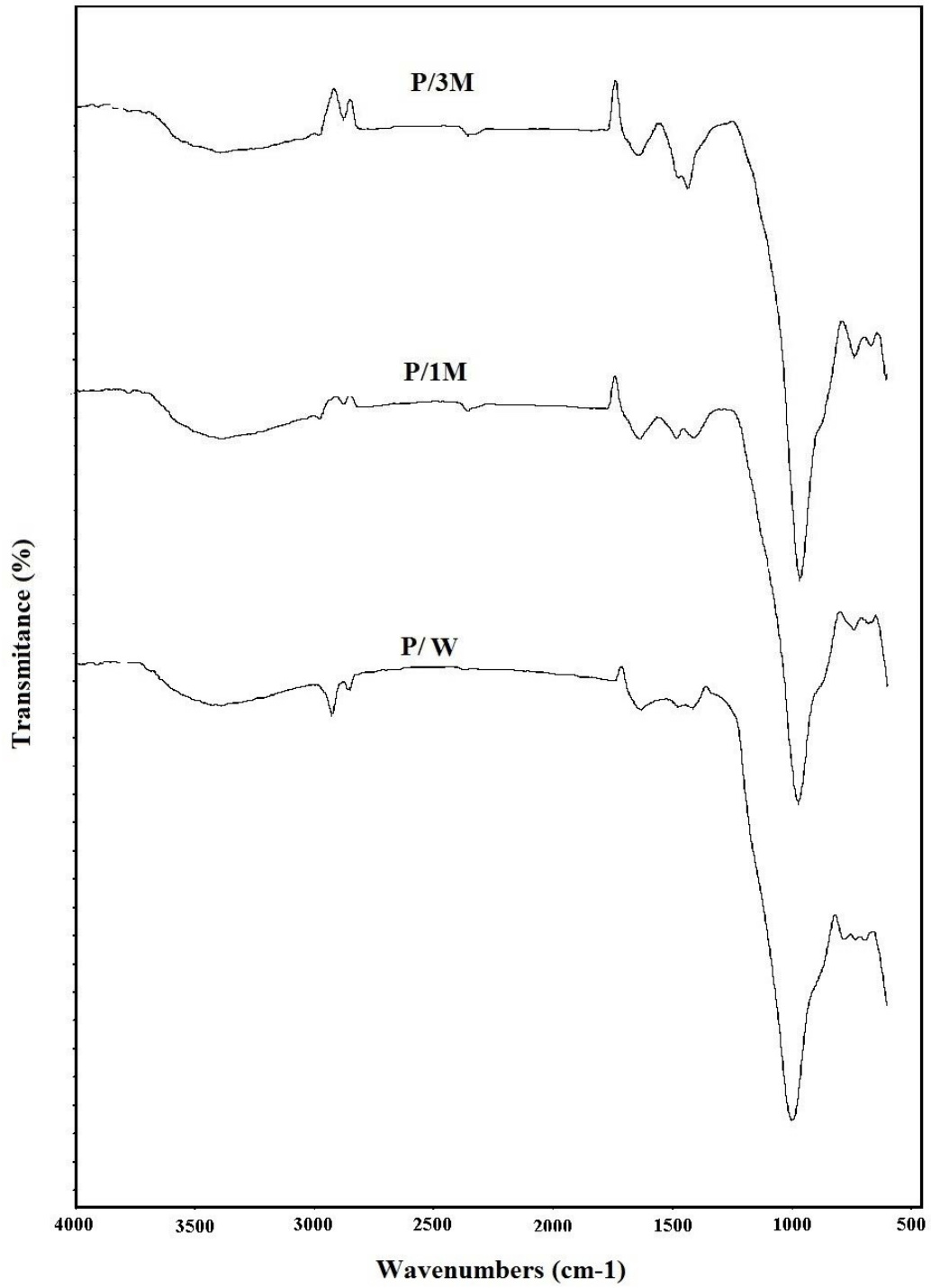
Fig. 12 FTIR spectra of fly ash geopolymer pastes after storage in different immersion solutions: P/W - stored in water, P/1M - stored in 1M NaOH, P/3M - stored in 3M NaOH.

5. Conclusions

The effects of alkaline environment on fly ash geopolymer binder systems were investigated in the present study. Geopolymer pastes and mortars were stored in water, 1M, 2M, or 3M NaOH solutions at the different temperatures of 23, 38 or 80^0C, then evaluated for changes in physico - chemical properties. Microstructural studies were also conducted in an attempt to examine the unfolding mechanism(s) of the alkali attack process.

There was significant to severe loss in compressive strength along with intense expansion, upon exposure of the fly ash geopolymer binders to alkaline solutions exceeding the concentrations of 1M NaOH.

It was found that elevated concentrations of NaOH solutions cause damage to the polymeric structure of the geopolymer binder by breaking the Si - O - Al bonds, leading to liberation of the Si and Al species.

New crystalline phases comprising *phillipsite*, *zeolite - P* and *chabazite* formed in the fly ash geopolymer systems upon storage of the pastes or mortars under elevated NaOH concentrations.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

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