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EFFECT OF NAOH MOLAR CONCENTRATION ON MICROSTRUCTURE
AND COMPRESSIVE STRENGTH OF DOLOMITE/FLY ASH-BASED GEOPOLYMERS

Dolomite can be used as a source of aluminosilicate to produce geopolymers; however, this approach is limited by its low reactivity. This study analyzes the viability of producing geopolymers using dolomite/fly-ash with sodium silicate and NaOH solutions (at multiple concentrations) by determining the resultant geopolymers' compressive strengths. The dolomite/fly-ash-based geopolymers at a NaOH concentration of ~22 M resulted in an optimum compressive strength of 46.38 MPa after being cured for 28 days, and the SEM and FTIR analyses confirmed the denser surface of the geopolymer matrix. The synchrotron micro-XRF analyses confirmed that the Ca concentration exceeded that of Si and Mg, leading to the formation of calcium silicate hydrate, which strengthens the resulting geopolymers.

Keyword: Dolomite/Fly Ash; Geopolymer; NaOH Concentration; Synchrotron Micro-XRF

1. Introduction

Geopolymers, whether in the form of inorganic polymers or alkali-activated binders, have rapidly gained global attention [1]. Geopolymers are produced by mixing aluminosilicate-reactive materials such as fly ash, kaolin/metakaolin, metal slag, or dolomite with alkali solutions [2,3]. Its synthesis was first reported by Davidovits [4,5]. Geopolymers can be amorphous or semi-crystalline and are usually 3-D silica aluminate materials. The alkali solutions commonly used to produce geopolymers include sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate, and potassium silicate.

In geopolymer production, the aluminosilicate source will dissolve and form free SiO_4 along with AlO_4 tetrahedral units and CaO within an alkali environment. The reaction then continues with the removal of water. The SiO_4 and AlO_4 tetrahedra and CaO clusters then combine to form the polymeric precursors by the sharing of the oxygen atoms between two tetrahedra units. Geopolymerisation is dictated by the aluminosilicate chain, which forms the main block of the geopolymer chain, Si-O-Al [6].

Compressive strength is an essential factor in the context of building and construction. A critical factor that dictates geopolymeric strength is the concentration of NaOH. A previous study confirmed this dependence using the fly-ash Class F [7] at NaOH concentrations of 4-16 M. The geopolymer was strongest (compressive strength) when its NaOH concentration was 14 M. When the heat curing temperature was increased to 115°C for 24 hours, a NaOH concentration of 4 M resulted in the lowest compressive strength due to the insufficient Na^+ for aluminosilicate activation. Another study on the effect of NaOH concentration was conducted by comparing the strength of the geopolymer composites based on calcined kaolin at different NaOH molarities [8]. The compressive strength of the calcined kaolin geopolymer was found to have increased in tandem with the concentration of NaOH, and it was concluded that the concentration of NaOH affects the compressive strength of the geopolymers. Geopolymer composites using 5 M NaOH reported low compressive strengths due to the poor leaching ability of the reactive element(s), while geopolymer composites produced at a NaOH concentration of 10 M resulted in the high-

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est compressive strength. The NaOH concentration significantly affected the dissolution of silica and alumina from fly ash, where high molarities increase the dissociation of the active species of raw material, resulting in the formation of a geopolymer gel network [9]. Hafid et al. [10] studied the influence of NaOH concentration (4-14 M) on the properties of cured geopolymers using calcined clay. The NaOH concentration was observed to affect the geopolymer composites' strength significantly. It was also reported that the flexural strength of the composites increased in tandem with molarity increase from 4 M to 11.5 M, which delined when the concentration increased from 11.5 M to 14 M. The high NaOH concentration (14 M) and dissolution resulted in the production of excess of Na^+, which is not desirable in the polycondensation process as it weakens the structure and decrease the overall strength of the geopolymer. Zarina et al. [11] investigated the effect of the addition of dolomite to boiler ash geopolymer properties, while Yip et al. [12] investigated the use of dolomite as a carbonate mineral addition to metakaolin-based geopolymers.

Previous studies concluded that dolomite is a good source of filler and blended material for the production of geopolymers [13,14]. To the best of our knowledge, there are no studies involving the elucidation of the influence of NaOH concentration on dolomite-based geopolymers. The utilization of dolomite as a significant component in a geopolymer system is a new endeavor. There is also a lack of information on dolomite geopolymers in the context of mixing parameters and reactivity. This paper details the investigation into the effect of NaOH concentration on the strength and responsiveness of geopolymer composites based on dolomite/fly ash. The results are expected to be useful for understanding the mechanical properties and use dolomite geopolymers for its strength properties.

2. Experimental method

2.1. Materials

The chemical compositions of the dolomite and fly ash garnered from the X-ray fluorescence (XRF) are tabulated in TABLE 1. The total composition of dolomite and fly ash was 4.02% and 81.1% of SiO_2 and Al_2O_3, respectively. Both raw materials can be used as precursor minerals for the production of geopolymers. Besides its main content of Si and Al, dolomite contains CaO (80.21%), while fly ash contains iron oxide (5%). The dolomite was obtained from the Perlis Dolomite Industries Sdn. Bhd., Perlis, while the fly ash powder was obtained from a coal combustion plant in Manjung, Perak.

TABLE 1

Chemical composition of dolomite and fly ash

Content (wt %)	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	MnO	TiO_2
Dolomite	2.50	1.52	80.21	0.15	15.50	0.01	0.06
Fly Ash	55.3	25.8	2.9	5.5	0.8	0.03	0.88

A solution containing a mixture of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solution was used as the alkaline activator solution. The NaOH flakes (99% in purity, purchased from Formosa Plastic Corporation, Taiwan) were dissolved in distilled water to produce a NaOH solution. The Na_2SiO_3 solution contains 30.1% SiO_2, 9.4% Na_2O, and 60.5% H_2O (SiO_2/Na_2O ratio of 3.20), and was purchased from the South Pacific Chemical Industries Sdn. Bhd., Malaysia. The alkaline activator solution was cooled to room temperature a day before it is used.

2.2. Mixture preparation

The geopolymer samples were fabricated by mixing the dolomite/fly ash powder and the alkali activator solution, as detailed in Fig. 1. The dolomite/fly ash powder was mixed using mechanical stirrer for 5 mins and oven-dried for 24 hours at 105°C. The various NaOH concentrations (16 to 24 M) were prepared by dissolving NaOH flakes in 1 L distilled water.
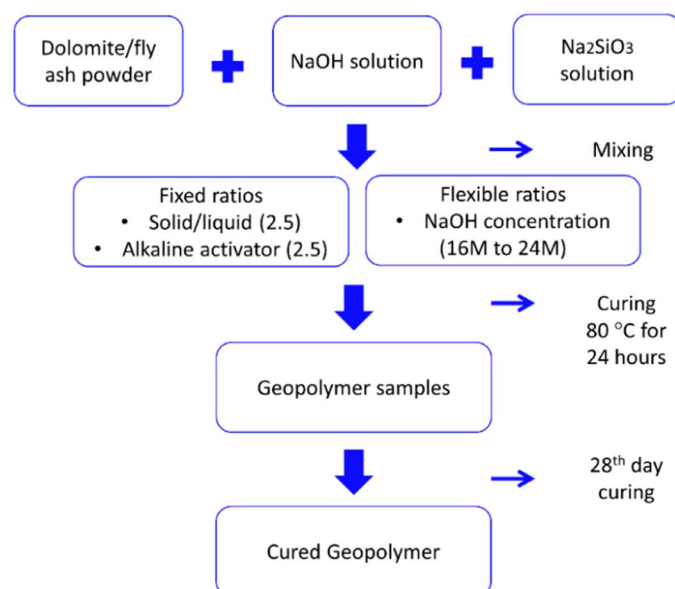

Fig. 1. The process of dolomite/fly ash-based geopolymers

The fixed ratio of dolomite/fly ash (60/40), solid/liquid (2.5), and alkaline activator (2.5) were used in this study. The fresh paste was then rapidly poured into steel molds and compressed in each cube compartment at each layer, as detailed in ASTM C109. The geopolymer samples were oven-cured for 24 hours at ~80°C.

The effect of NaOH concentrations on the dolomite/fly ash-based geopolymers were determined for each design (total of 5 designs). Samples were denoted as DFA x, where x refers to the NaOH concentrations. For instance, DFA20 represents samples manufactured at a NaOH concentration of 20 M on dolomite/fly ash-based geopolymers. The details of the design and the mixture code of the synthesized samples are tabulated in TABLE 2.

TABLE 2

Mixture designs of dolomite/fly ash geopolymers

Mixture code	Dolomite/fly ash ratio	NaOH concentration (M)	Solid/liquid ratio	Alkaline activator ratio
DFA16	60/40	16	2.5	2.5
DFA18	60/40	18	2.5	2.5
DFA20	60/40	20	2.5	2.5
DFA22	60/40	22	2.5	2.5
DFA24	60/40	24	2.5	2.5

2.3. Experimental test and characterization

2.3.1. Compressive strength test

The compressive strength was determined using Instron 5569 Mechanical tester as per ASTM C109/109M-05 [15] for three samples from each NaOH concentration. The loading displacement was set to a rate of 5 mm/min. The maximum load was recorded, and strength calculated by dividing the load applied to the specimen by its cross-sectional area.

2.3.2. Scanning electron microscopy (SEM)

The microstructure of dolomite/fly ash geopolymers was determined using the JSM-6460LA model Scanning Electron Microscope (JEOL) via the application of secondary electron detectors. The dolomite/fly ash geopolymers samples were sliced before its compressive strength tests. The morphological analyses were carried out at an acceleration voltage of 10 kV and a working distance of 10 mm. The samples measured 50 mm × 50 mm × 10 mm, and were coated with palladium.

2.3.3. Synchrotron micro X-ray fluorescence (μ-XRF)

A micro X-ray fluorescence (μ-XRF) machine using a source from synchrotron radiation at beamline 6b (BL6b) of the Synchrotron Light Research Institute (SLRI) was used to determine the chemical composition and elemental distribution of the geopolymer samples. The BL6b exploited the continuous synchrotron radiation emitted from the bending magnet. The specimen was positioned on a motorized stage with three-degree of freedom. The μ-XRF station used the capillary half-lens to focus the X-ray. The optic focused the X-ray beam from 5 × 2 mm at the entrance of the lens down to a diameter of 50 μm measured at a sample positioned 22 mm (lens focal point) downstream of the lens' exit. The experiments were conducted in a helium (He) gas atmosphere, and the exposure time for each point was 30 s. A total scan of 961 points was obtained with a detector time close to 20%, as per [16]. Imaging was set in bilinear interpolation and analyzed using the PyMca software [17].

3. Result and discussion

3.1. Compressive test measurement

Fig. 2 shows the compressive strength of the dolomite/fly ash-based geopolymers at various NaOH concentrations with constant solid/liquid ratios and alkaline activator ratios. The overall results show that the compressive strength increased in tandem with NaOH concentrations. The increment in strength was 5 to 30% at NaOH concentrations of 16 to 22 M. The increase in strength is primarily due to the incorporation of NaOH, which is essential for the dissolution process as it provides Na^+ and OH^- ions to the process. The NaOH concentration significantly influences the dissolution of the silica and alumina species from the raw materials, and it has been shown that increasing the NaOH concentration enhanced the dissociation of the active chemical elements and resulted in the formation of the geopolymer network. Na^+ balanced the negative charges produced as a result of the formation of the geopolymers' main chain (Si-O-Si/Al), while OH^- played a vital role in the hydrolysis process of the dolomite/fly ash aluminosilicate materials. Balancing the free ions during geopolymerization tends to improve the main structure of the resulting geopolymers.
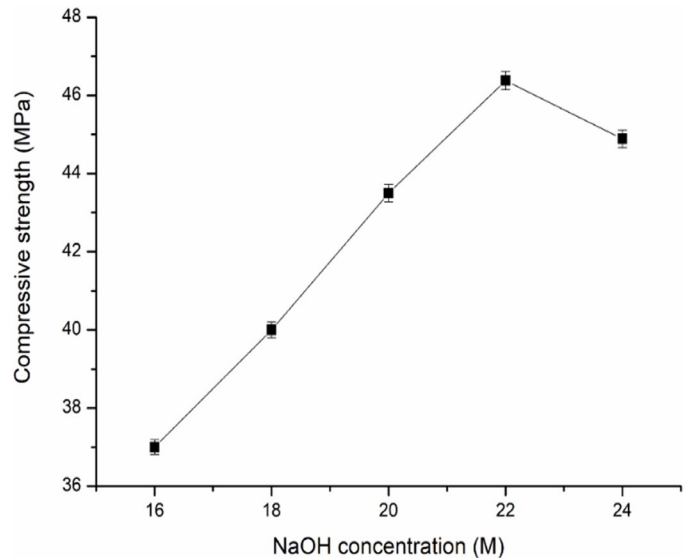

Fig. 2. Compressive strength of resulted dolomite/fly ash geopolymers for various NaOH concentration

The compressive strength increased from NaOH concentrations of 16 M to 22 M, then decreased after being activated at a concentration of 24 M. The dolomite/fly ash-based geopolymers at a NaOH concentration of 22 M (DFA22) reported the highest compressive strength (46.38 MPa). In contrast, the dolomite/fly ash-based geopolymers with 16 M NaOH concentration reported the lowest compressive strength (36.91 MPa). The increment in NaOH concentration enhanced the geopolymerization rate by balancing charges and the aluminosilicate network formation. The rearrangement and exchange process, taking place between the released ions, lead to polycondensation, forming a firm struc-

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ture. The low reactivity of dolomite/fly ash-based geopolymers required higher NaOH concentrations as the alkaline solution boosted the silicon, aluminum, magnesium, iron, and calcium components in the aqueous phase. Contrarily, a higher NaOH concentration of 24 M resulted in excessive Na^+ and OH^- ions in the geopolymer system, prompting the early precipitation of aluminosilicate, which retard the leaching process of Al^{3+} and Si^{4+} ions, decreasing both the geopolymerization rates and compressive strength. The excessive free cation and anions caused the strength degradation of dolomite/fly ash-based geopolymers. Similarly, Somna et al. [18] reported that high concentrations of NaOH hindered the polycondensation process and accelerated the dissolution of the raw materials. The high alkali concentration increased the strength development of the geopolymers, but the excess OH^- concentration contributed to the aluminosilicate gel precipitation earlier, resulting in weaker geopolymers [9].

3.2. Microstructure observation

The SEM images show the morphological feature of the selected strength of dolomite/fly ash at various NaOH concentrations, as displayed in Fig. 3. The selected designs (DFA 16, DFA 22, and DFA 24) were applied to analyze the contribution of NaOH concentrations towards developing and decreasing the compressive strength of dolomite/fly ash-based geopolymers. These images show that the geopolymerization reaction of the dolomite/fly ash-based geopolymers samples activated at various NaOH concentrations resulted in denser microstructures up to 22 M and rough surfaces after being activated at a NaOH concentration of at 24 M. The SEM micrograph of dolomite/fly ash-based geopolymers at various NaOH concentrations are displayed in Fig. 3a (DFA16), Fig. 3b (DFA22), and Fig. 3c (DFA24).

The images shown in Fig. 3a confirms the presence of cracks and unreacted fly-ash material. The use of a low concentration NaOH solution in geopolymerization resulted in a weak chemical reaction, causing the appearance of unreacted fly-ash material. The unreacted fly-ash material was believed to be due to the insufficient Na^+ and OH^- ions retarding the dissolution of Ca, Si, and Al species from the raw materials. The presence of pores and cracks resulted in a less dense and non-homogenous geopolymer matrix, and the subsequent low geopolymer strength.

Sufficient concentrations of NaOH during geopolymerization results in a homogenous geopolymer matrix with a reasonably smooth surface (Fig. 3b). The dolomite/fly-ash material was activated entirely and surrounded by a homogenous geopolymer matrix, which increases its overall strength. Increasing the NaOH concentration to an acceptable level will result in the unreacted fly-ash materials being less abundant and the formation of a denser geopolymer matrix from the better geopolymerization reaction [19]. The microstructure of dolomite/fly ash-based geopolymers at a NaOH concentration of 24 M (DFA24) showed cracks and voids, as per Fig. 3c, due to the presence of excess OH^- during the dissolution process at the initial stage of the geopolymerization reaction. This resulted in decreased strength, as shown in Fig. 2.
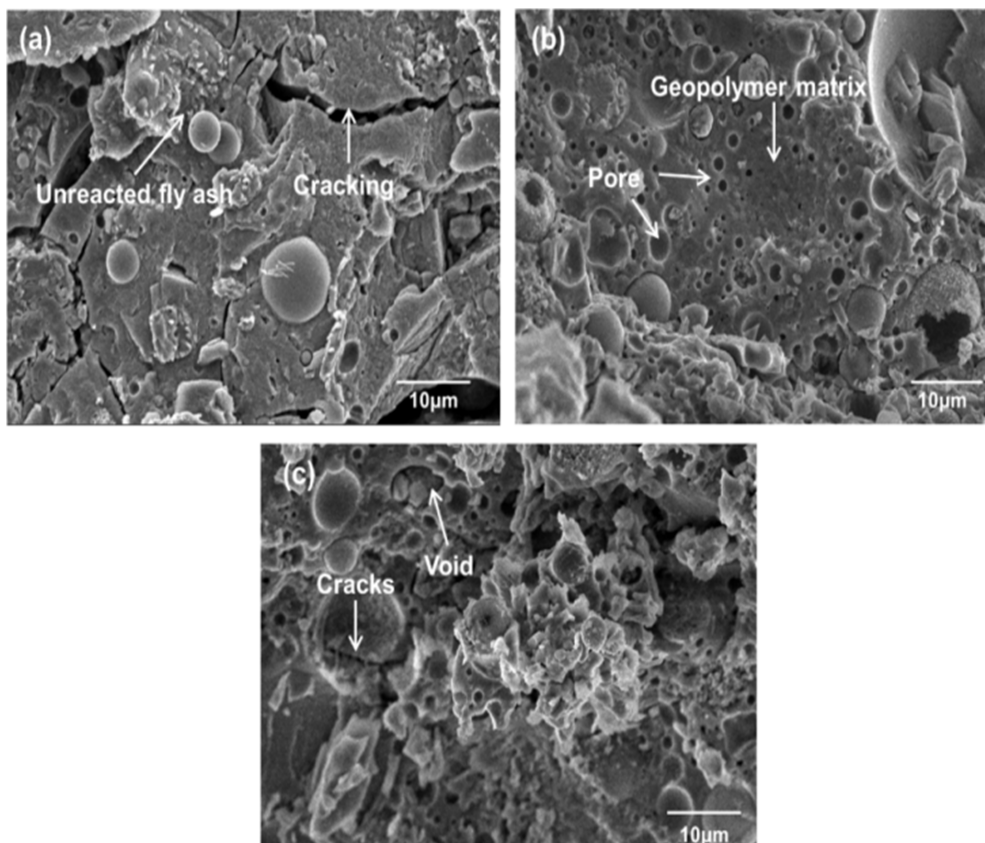

Fig. 3. SEM micrograph of dolomite/fly ash-based geopolymers at various NaOH concentration (a) DFA16, (b) DFA22 and (c) DFA24

3.4. Chemical bonding analysis

The IR spectra of dolomite/fly ash-based geopolymers with various NaOH concentration are presented in Fig. 4. The IR spectrum of dolomite/fly ash geopolymers illustrate the major absorption band at 900-1000 cm^{-1} corresponding to the stretching vibrations of Si-O-Si/Al aluminosilicates and reflected to the geopolymers network formation [20]. The tiny vibration modes at 3300-3600 cm^{-1} were in correspondence to OH^{-} stretching vibration. Meanwhile, the peak obtained at 1420 cm^{-1} to 1520 cm^{-1} was indicates to the carbonate compound production.
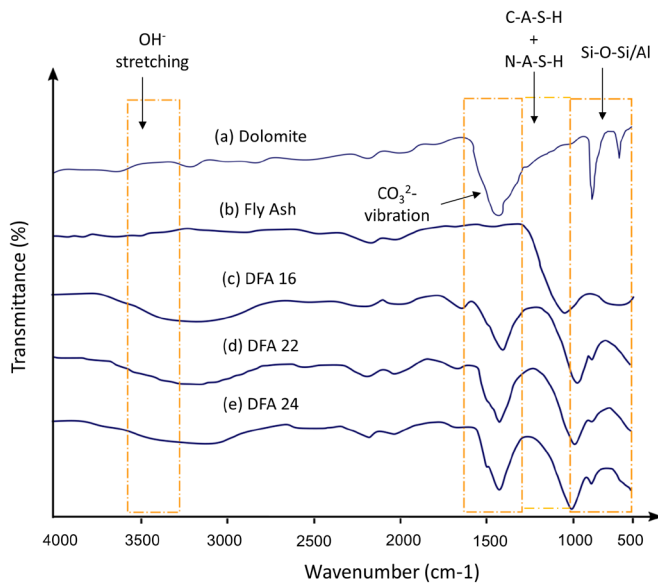

Fig. 4. IR spectra of dolomite/fly ash geopolymers with various NaOH concentration

The shifting of special character with the effect of NaOH concentration can be reffered to Fig. 4c-e. It is revealed that the shifting band from 960 cm^{-1} to 969 cm^{-1} indicates the formation of calcium aluminium silicate hydrate (C-A-S-H) and sodium aluminium silicate hydrate (N-A-S-H) product as the NaOH concentration increased. This finding supported with compressive result in section 3.1. The increased in NaOH concentration enhances the dissolution process of Ca, Al and Si which are dissolved within the binder during geopolymerization.

3.3. Elemental distribution analysis

The dolomite/fly ash-based geopolymers were analyzed using the synchrotron micro-XRF (μ-XRF) maps. Fig. 5 display the localized area and the μ-XRF mapping in Al-Si-Ca-Mg-Fe of dolomite/fly ash-based geopolymers, confirming that the Al, Si, Ca and Mg are located within the geopolymers structure.

The DFA22 sample was selected due to its high compressive strength relative to the other samples. Referring to Fig. 5, the distribution of Si, along with the combination of the Al region, represents the geopolymeric main chain (Si-O-Si/Al). The colors blue, green, and red represent the low, medium, and high intensities for each element distribution in the integrated area, respectively. The homogeneity of the samples can be traced as the Si region represents the medium concentration (green) of Si elements for the dolomite/fly ash-based geopolymers. The red color representing the Si region refers to the quartz grain.

The intermediated concentration of the Ca element is reflected by the formation of the calcium silicate hydrate, while regions with a higher concentration of Ca indicate the presence of
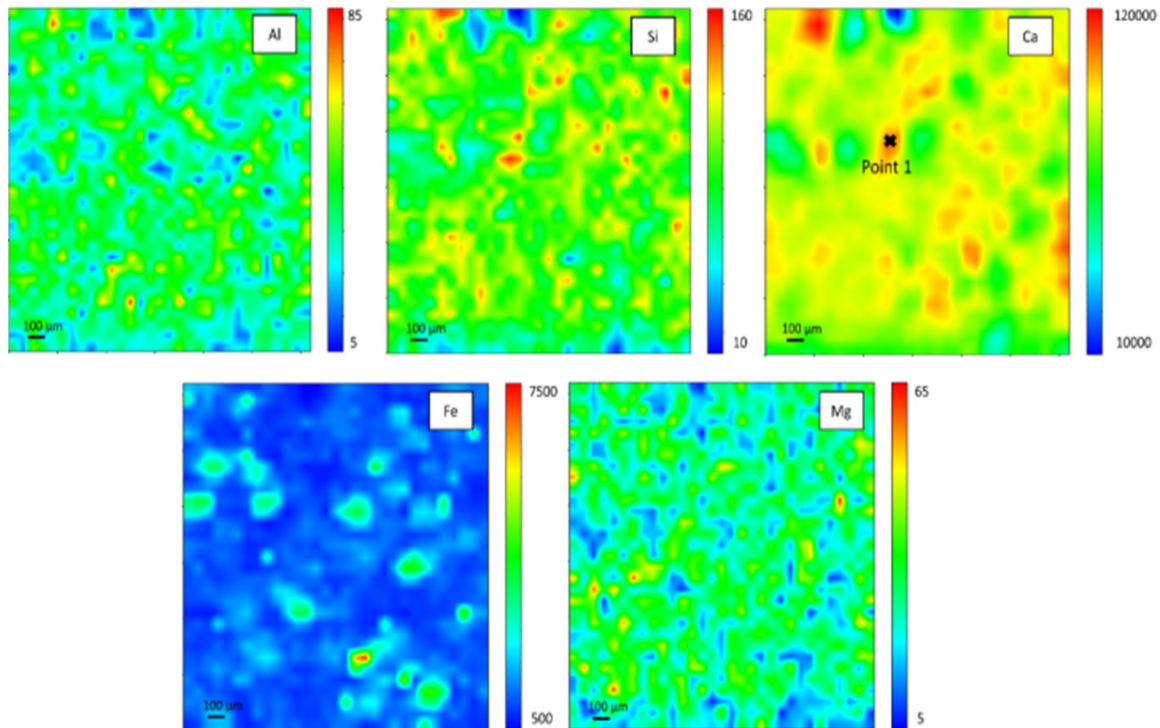

Fig. 5. Micro-XRF elemental distribution of dolomite/fly ash-based geopolymers activated by 22M NaOH concentration

calcite within the geopolymer system. This calcium based-product formed with aluminosilicate firm structure in the dolomite/fly ash-based geopolymers resulted in the best compressive strength, as per Fig. 2. The contribution of calcite in the geopolymer network served as physical filler/micro aggregates, which enhanced the strength of the geopolymer [21]. The combination of Ca and Mg distribution maps represented the formation of dolomite, while Fe is only localized within the main geopolymer structure.

Point elemental analysis of Al, Si, Ca, Mg revealed by the "Point 1 analysis spectrum" is shown in Fig. 6. The highest intense peak was observed at 3.69 keV and 4.01 keV, representing Ca-K alpha and Ca-K beta, respectively. The relatively small intense peak of Si (K-beta, at 1.84 keV), Al (K-beta, at 1.48 keV), Fe (K-alpha at 6.39 keV and K-beta at 7.06), and Mg (K-alpha, at 1.25 keV) were also detected in the dolomite/fly ash-based geopolymers. These peaks confirmed the presence of calcium silicate hydrate, dolomite, and calcite within the main structure.
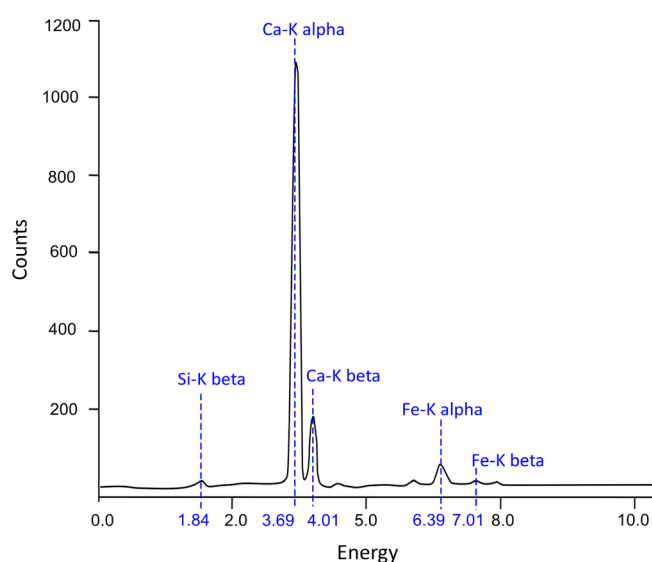

Fig. 6. Point analysis spectrum at Point 1

4. Conclusion

In this work, the dolomite/fly ash-based geopolymers were synthesized at various NaOH concentrations. The geopolymers reported better compressive strength after being cured for 28 days. It can, therefore, be concluded that:

a) The optimal NaOH concentration was 22 M for the dolomite/fly ash-based geopolymers, as it reported the highest compressive strength of 46.38 MPa. The coexistence of the calcium silicate hydrate, calcite, and dolomite components play a crucial role in improving the strength of the geopolymers.

b) The appearance of the denser microstructure was strengthen the dolomite/fly ash-based geopolymers. At lower NaOH concentrations, cracks were detected during the microstructure analysis.

c) The μ-XRF technique is useful in visualizing the distribution of Al, Si, Ca, Fe, and Mg elements in the dolomite/fly ash-based geopolymers.

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