

Characterization, reactivity and rheological behaviour of metakaolin and Meta-halloysite based geopolymer binders

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ABSTRACT

The type of aluminosilicate precursor used in the synthesis of geopolymer binders plays a huge role in the resulting performance. Thus, it is critical to understand the properties of precursors and how they influence the corresponding performance of geopolymer binders. In this study, metakaolin and meta halloysite are used as the aluminosilicate precursor in the synthesis of geopolymer binders. These precursors are obtained locally in order to propel the sustainable development and application of geopolymers. The precursors were characterized and the corresponding influence on the reactivity, rheology and setting times of geopolymers was investigated. In addition to the influence of precursor type on the properties of the geopolymers, the effect of two silica moduli (i.e. 1.3 and 1.5) was also evaluated. The results from this study indicated that increasing the activator silica modulus from 1.3 to 1.5 extended the setting times and increased the stress strain of the geopolymer binders. Characterization of the precursors indicated that metakaolin has a higher amorphous content compared to that of meta halloysite. However, the finer particles of meta halloysite embodied it with the ability to participate in a faster geopolymerization and result in more formation of activation products.

1. Introduction

Geopolymers are sustainable alternatives that can be used as a sustainable to Portland cement as a binder (Duxson et al., 2007; Provis and Bernal, 2014). Geopolymers are synthesized from an aluminosilicate precursor and an activating medium such as alkali (Giogetti et al., 2021; Liu et al., 2020). Extensive studies on the development and applications have been carried out all over the world. However, the majority of such geopolymers are synthesized using fly ash and/or slag as aluminosilicate precursors (Das et al., 2020; Zakka et al., 2021). With the limited availability of these conventional precursors all over the world, it is essential to find alternative locally available materials that can be used in the synthesis of geopolymers.

In certain parts of the world such as Cameroon where clayey materials are available in large quantities, such materials can be utilized in the synthesis of geopolymer in order to promote sustainable construction. Clayey materials such as kaolin and halloysite are some of the

locally available materials that can be calcined to obtain metakaolin (MK) and meta-halloysite (MH), respectively and used in the production of geopolymers. Current studies on the use of clayey materials as a precursor in geopolymers are mostly focused on the laterite (Kaze et al., 2018, 2017). However, there is a need to explore the use of calcinated clayey materials such as kaolin and halloysite in the synthesis of geopolymers. Limited studies exist currently on the use of MK and MH as precursors in geopolymers (Bouna et al., 2020; Nana et al., 2020; Sellami et al., 2019). The majority of the existing studies only focus on the influence of the precursors on hardened properties such as compressive strength. However, understanding the characteristics of these precursors (i.e. MK and MH) and their corresponding influence on the reactivity and fresh properties of geopolymers is limited.

Tchakoute et al. (2020) focussed their study on the mechanical and microstructural properties of the end products made using MK and MH as the precursor. Findings from the studies showed that a compressive

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strength up to 88 MPa can be achieved with the use of MH as the precursor. The higher compressive strength of geopolymer binders made with MH compared to MK was associated with the finer nature of the MH that resulted in higher dissolution and a corresponding higher polycondensation that favoured the formation of dense and strong matrix. However, no information on the reactivity nor the influence on the fresh properties of the geopolymers were provided. The study by Zhang et al. (2012) demonstrated that the presence of halloysite (31%) as a secondary mineral in kaolin improved the reactivity of MK. The isothermal calorimetry conductivity (ICC) assessment carried out in the study showed that the presence of halloysite as a secondary mineral contained in kaolin favoured a high degree of geopolymerization of metakaolin as recorded by the heat released.

Despite these existing studies on the use of MH or MK as a precursor in the synthesis of geopolymers, there is no study where a comparative evaluation of both MH and MK has been carried out. Moreover, there is limited knowledge on the comparative study based on fresh properties of MH and MK used in the synthesis of geopolymers especially in terms of setting time, rheology and kinetic reaction from metakaolin and *meta*-halloysite based geopolymers. Besides, most of the existing studies only focus on the influence of these precursors (i.e. MH and MK) on the properties of geopolymers without an in-depth study on the properties of the precursors and how it influences the corresponding performance of the geopolymers. Thus, this study aims to characterize MH and MK and use these precursors in the synthesis of geopolymers. The effect of silica modulus of 1.3 and 1.5 on the resulting geopolymers synthesized using these precursors (i.e. 1.3 and 1.5) was also investigated. The influence of the precursor type and silica modulus on the properties of geopolymer binders was investigated in terms of the resulting rheological properties, setting times, and heat evolution. It is anticipated that the results presented in this paper would gear more application of locally available clayey materials such as MK and MH in the synthesis of geopolymer binders.

2. Experimental program

2.1. Materials

The MK and MH used in this study were obtained by calcinating kaolin and halloysite, respectively for four hours at a temperature of 700 °C as recommended by a previous study (Kaze et al., 2020). After the calcination of the materials, they were grounded and sieved and only particles passing through the 80 µm were utilized in the synthesis of the geopolymers.

Sodium hydroxide (SH) and sodium silicate (SS) were used as the activating media for the precursors. SH solution was prepared by dissolving solid SH in distilled water to produce a concentration of 8 M. The SH solution was combined with the SS solution to produce the activating solution approximately 24 h before it was used. The SH solution and SS solution were mixed in proportions to produce a silica modulus (SiO₂/Na₂O) of 1.3 and 1.5. The silica moduli (1.3 and 1.5) of alkaline solutions were selected according to previous works.

2.2. Composition and of geopolymer binders

Four geopolymer binders were produced by varying the type of precursor (i.e. MK or MH) and silica modulus (i.e. 1.3 or 1.5). The corresponding mixtures were designated as GPMK1.3, GPMK1.5, GPMH1.3 and GPMH1.5. The mixture ID used represents the type of precursor used in the mixture alongside the silica modulus of the activator. For example, GPMH1.3 represents geopolymer binders made with MH as the solid precursor and activated with a solution having a silica modulus of 1.3. For all mixtures, the liquid to solid ratio was kept at 0.75.

2.3. Methods

2.3.1. Rheological properties

For the rheological measurements of the fresh binders, a stress-controlled rheometer-ARG2 from TA equipment was used. The measuring geometry was made up of a 25 mm upper and lower plate with the temperature regulated with a Peltier. The viscoelastic parameters of the fresh geopolymer binders were investigated through simple shear flow and dynamic oscillatory tests carried out at 20 °C in the linear viscoelastic (LVER) domain. For the rheological measurements, each calcined halloysite and kaolin powders (i.e. MH and MK) was mixed by hand in situ for three minutes and then introduced between the plates of the rheometer. The LVER was carried out by oscillatory strain sweep from 0.002% to 20% at a constant frequency of 1 Hz according to previous studies (Kaze et al., 2020). Herschel-Bulkley law presented in Equation 1 was used to determine the viscoelastic parameters. In Equation 1, τ is the shear stress in Pa, τ_0 is the yield stress in Pa, K is the consistency in Pa.sⁿ, $\dot{\gamma}$ is the shear rate in s⁻¹, and n is the flow index (Lv et al., 2021, 2019). Viscoelastic properties of the geopolymer binders were investigated by oscillatory measurements. The tan(δ) was also calculated by finding the ratio of the loss modulus (G'') to storage modulus (G').

$$\tau = \tau_0 + K\dot{\gamma}^n(1)$$

2.3.2. Setting times

The initial and final setting times of the fresh geopolymer binders were measured by using the Vicat's apparatus. The needle used was 1.00 ± 0.005 mm in diameter. This test was carried out in the laboratory with a relative humidity of 60% room temperature of 20 ± 3 °C. This test was performed according to the EN196-3.

2.3.3. Isothermal conductivity calorimetry

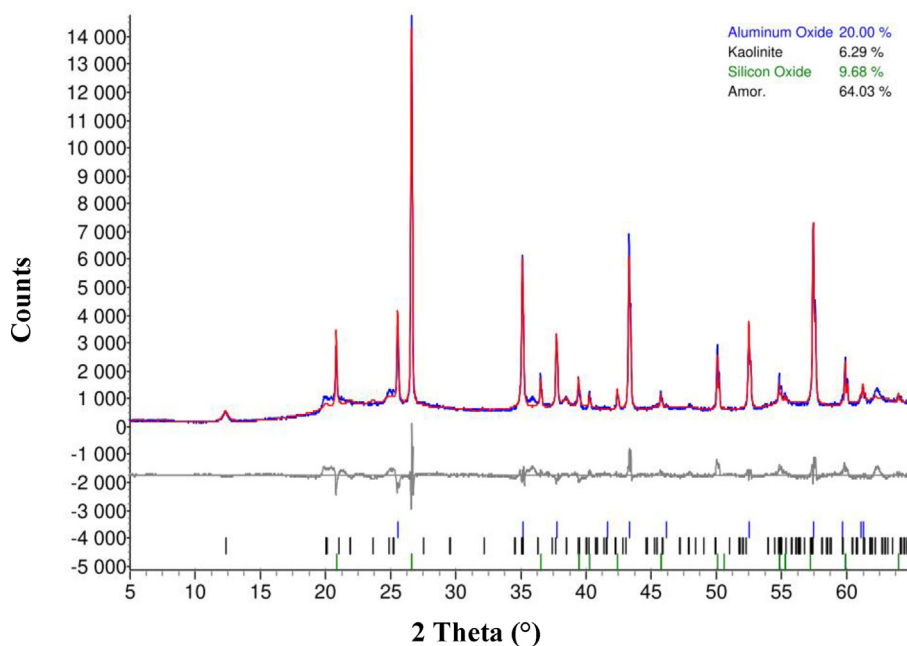
Isothermal conductivity calorimetry (ICC) was used to examine the geopolymerization steps of each geopolymer-based geopolymer pastes at 20 °C using an alkaline solution for 24 h. The measurements were performed in an eight-channel isothermal conduction calorimeter and using an external hand mixing procedure into a calorimeter bottle prior to the start of the test. Approximately 7 g of each calcined precursor (i.e. MH and MK) was individually mixed with both alkaline solutions (i.e. silica modulus of 1.3 and 1.5).

3. Results and discussion

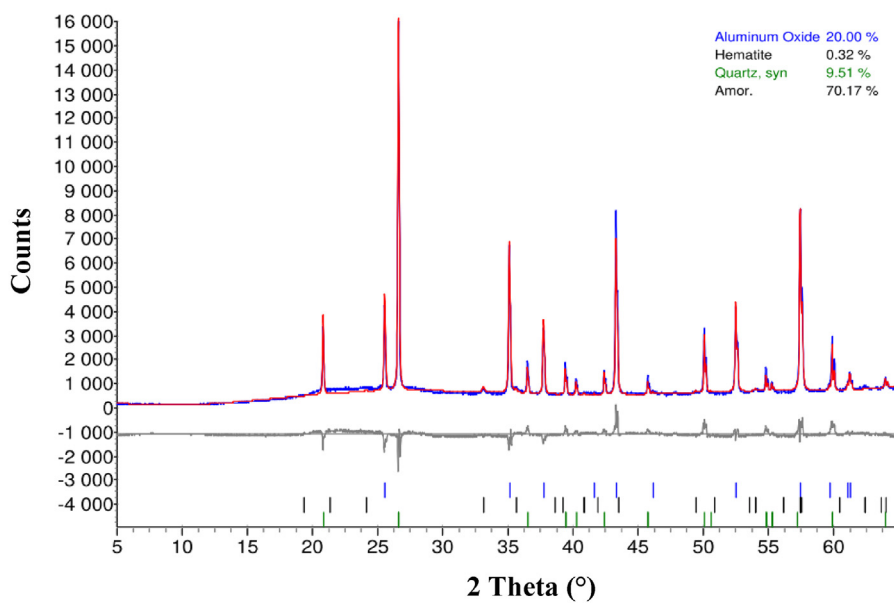
3.1. Characterization of precursors

The amorphous contents in MK and MH quantified by the Rietveld method are presented in Fig. 1. It can be observed from the figure that the amorphous content present was 64% and 72% for MK and MH, respectively. Next to the amorphous phase contents, crystalline phases such as hematite (0.32%), Quartz (9.6%) and Kaolinite (6.29%) were presented in small amounts. The amorphous phases present in the precursors (i.e. MK and MH) indicate their suitability for use in the synthesis of geopolymers. These analyses also show that MH is expected to yield a better geopolymer compared to MK due to the higher amorphous content.

The chemical compositions of MK and MH determined using Fluorescence X-ray analysis are presented in Table 1. It is evident from Table 1 that the precursors are composed of a high content of silicate and aluminate. The silicate content of MK and MH is 46.2% and 50%, respectively while the corresponding aluminate content is 34% and 25.3%, respectively. The high content of these monomers (i.e. silicate and aluminate) in these materials makes them a suitable candidate for the production of geopolymer binders. The silicate to aluminate ratio (Si/Al) has is known to influence the geopolymerization reaction. It



(a)



(b)

Fig. 1. Amorphous phase quantification of (a) MK (b) MH.

Table 1

Chemical compositions of halloysite and kaolin.

Precursors	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	Fe ₂ O ₃	TiO ₂	CaO	MgO	LOI
MKMH	46.250.0	34.035.3	0.5-	0.2-	-2.6	0.80.3	0.2-	0.2-	14.312.0

can be deduced from the results presented in Table 1 that the Si/Al of MK and MH is 1.36 and 1.42, respectively. The lower Si/Al of MK compared to MH could be due to minor traces of minerals such as illite present in the MK. Nonetheless, the Si/Al of the MK and MH are similar and suitable for the synthesis of geopolymers. In addition, both

aluminosilicate materials used as precursors are almost similar in terms of Si/Al ratio which is a determinant factor of geopolymerization reaction.

The XRD diffractogram of MK and MH are presented in Fig. 2. It can be observed that there exists a broad hump between 15 and 35° 2 theta

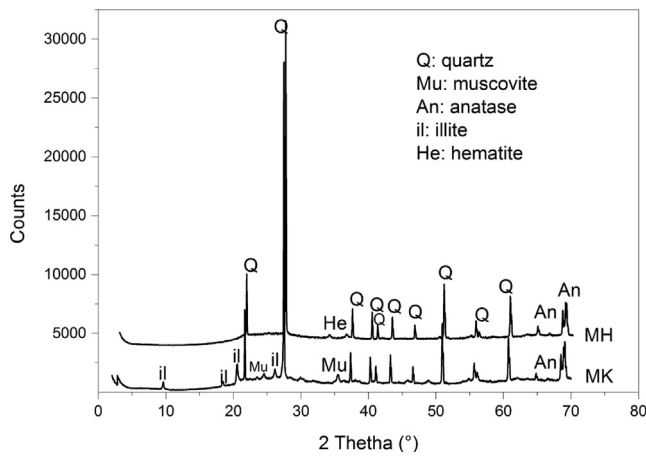


Fig. 2. X-ray spectrum of precursors.

range of both materials indicating the reactive (i.e. amorphous) phase. The presence of crystalline phases such as quartz (SiO_2 , PDF# 00-046-1045); hematite ($\alpha\text{-Fe}_2\text{O}_3$, PDF # 04-003-2900), anatase (TiO_2 , PDF# 00-021-1272) and muscovite ($(\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, PDF #7-32) can also be seen on the diffractograms. The diffractograms also confirm the earlier hypothesis that illite ($(\text{K}, \text{H}_3\text{O}) (\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})]$, PDF# 04-017-0523) is present in MK.

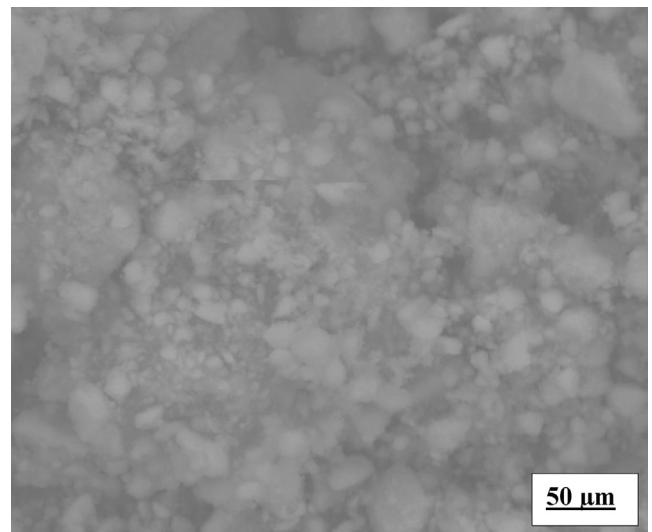
The SEM images of the precursors are presented in Fig. 3. From Fig. 3, it is evident that the MH particles are finer than MK which is dominated by coarse particles. Thus, in alkaline solutions for the synthesis of geopolymer binders, the MH particles are expected to dissolve faster than those of MK. Past studies have shown that the particle size of precursors significantly influences the reactivity, compressive strength and microstructure of the resulting products during the synthesis (Assi et al., 2018). The average particles determined by laser granulometry at $d_{0.1}$, $d_{0.5}$ and $d_{0.9}$ of MK is 8.9 μm , 53.4 μm and 102 μm , respectively while that of MH is 1.60 μm , 5.90 μm and 45.83 μm , respectively.

Fig. 4 presents the infrared spectra of MK and MH. Observing Fig. 4, the broad absorption bands appearing at 1025 cm^{-1} and 1043 cm^{-1} on the spectra of MK and MH, respectively can be attributed to the stretching and bending of Si-O-Al bonds (Bouna et al., 2020; Mohamed et al., 2020; Youmoue et al., 2020). The less pronounced bands located at 775 cm^{-1} and 688 cm^{-1} on the spectra of MK and MH, respectively can be linked to the vibration modes of Al(VI)-O and Si-O bonds (Nemaleu et al., 2020; Tchakouté et al., 2020).

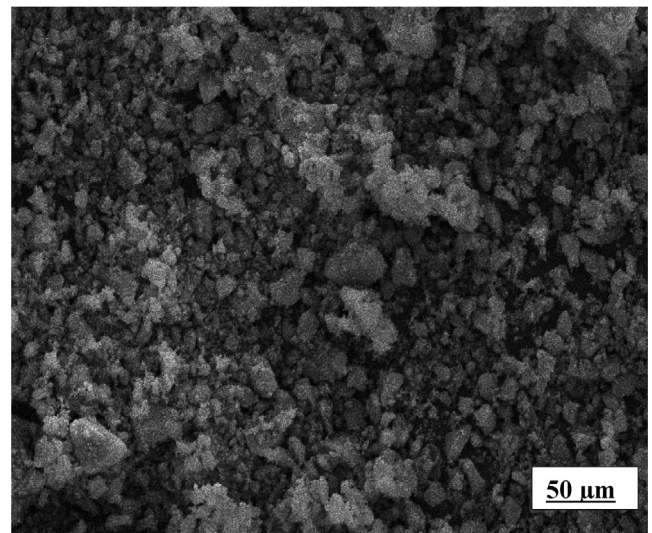
3.2. Setting times

The setting time of the fresh geopolymer binders is shown in Fig. 5. The initial and final setting times of the geopolymer binders activated with a solution having a silica modulus of 1.3 are in the range of 126 min to 175 min and 180 min to 223 min, respectively. On the other hand, geopolymers synthesized with a solution having a silica modulus of 1.5 exhibited initial and final setting times in the range of 216 min to 245 min and 302 min to 354 min, respectively. It can be observed from the results that geopolymer binders synthesized with an activator possessing a silica modulus of 1.5 exhibited higher setting times compared to those made with a silica modulus of 1.3. The final set times of GPMK1.5 and GPMH1.5 are 67.8% and 58.7%, respectively higher than the corresponding geopolymer binder activated with a silica modulus of 1.3 (i.e. GPMK1.3 and GPMH1.3).

The extension in the setting time at higher silica modulus can be ascribed to the lower alkalinity which resulted in a slower rate of geopolymerization. The longer setting recorded on geopolymer binders activated with a silica modulus of 1.5 would be due to the



(a)



(b)

Fig. 3. SEM of (a) MK (b) MH at 50 μm .

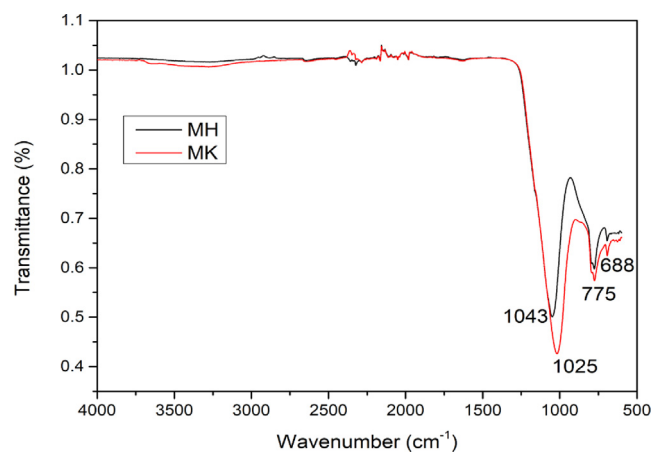


Fig. 4. Infrared spectra of precursors.

formation Si-O-Si rich binder type during the polycondensation which prolonged the setting (Lo et al., 2017). A similar observation was made

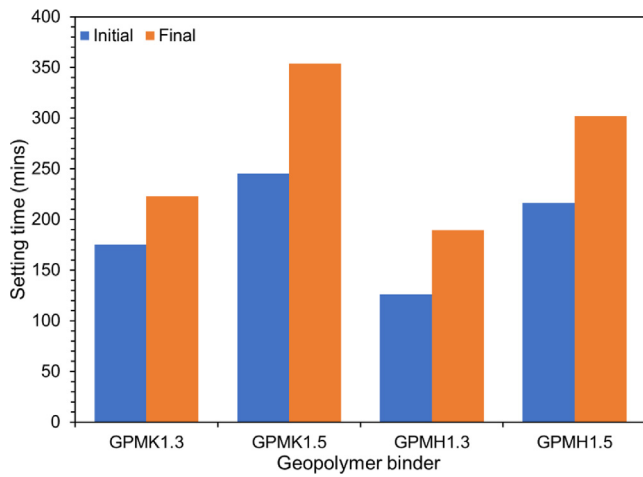


Fig. 5. Setting times of fresh geopolymer binders.

by Baenla et al. (2019) during the synthesis of geopolymer binder from volcanic ash cured at room temperature. These observations are also consistent with other studies where it has been found out that increasing the silica modulus of the activator would result in an extension of the setting times due to the decrease in the alkalinity (Bernal et al., 2010; LI and LI, 2018).

It can also be observed from Fig. 5 that geopolymer binders synthesized with MH as the binder exhibited shorter setting times compared to those made with MK. The results indicate higher dissolution of the MH particles in the alkali solution resulting in the formation of geopolymerization products. The higher dissolution of MH compared to MK particles can be ascribed to its composition which is made up of higher amorphous content as observed in the Rietveld quantification presented in Fig. 1. Also, the finer particle size of MH compared to that of MK would result in a more and faster dissolution of the particles in an alkali solution resulting in shorter setting times.

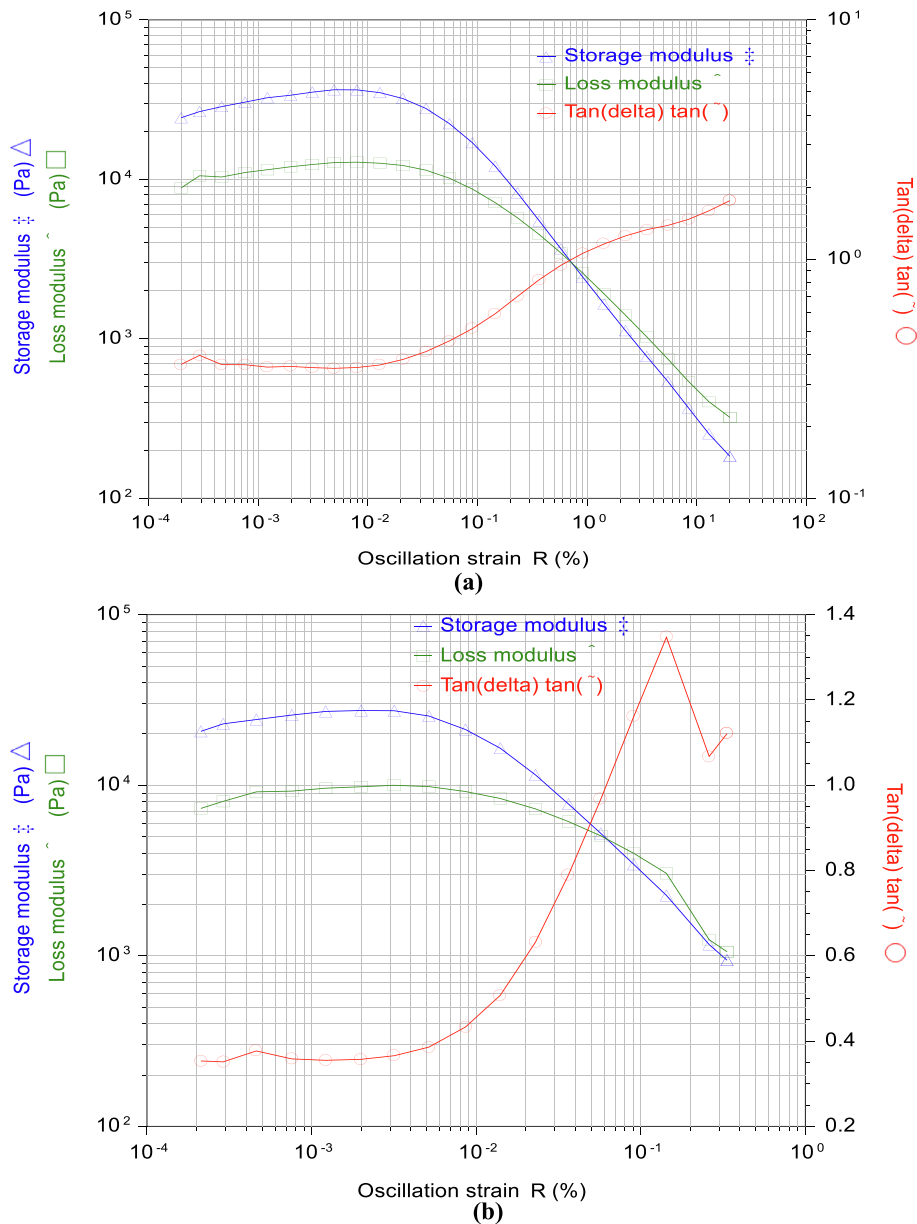


Fig. 6. Oscillatory strain sweep at 1 Hz of MK based geopolymer binders (a) GPMK1.3 (b) GPMK1.5.

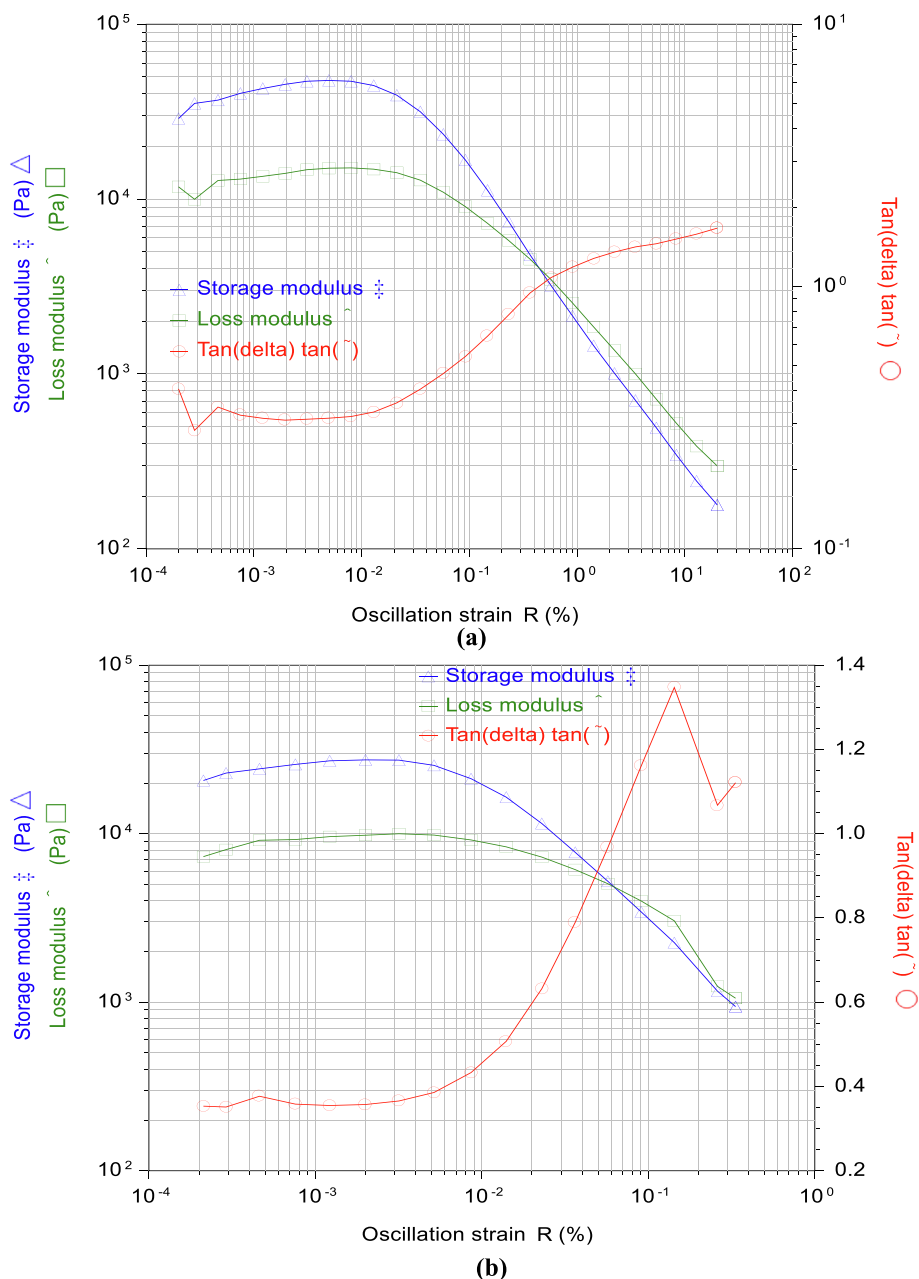


Fig. 7. Oscillatory strain sweep at 1 Hz of MH based geopolymer binders (a) GPMH1.3 (b) GPMH1.5.

3.3. Rheological properties

Fig. 6 and Fig. 7 presents the oscillatory strain sweep of geopolymer binders that are MK-based (i.e. GPMK1.3 and GPMK1.5) and MH-based (i.e. GPMH1.3 and GPMH1.5), respectively. It can be observed from the figures that the linear viscoelastic region (LVER) also known as the gel point corresponding to $G' = G''$ that the storage modulus (G') is higher than the loss modulus (G'') for silica modulus increase from 1.3 to 1.5. This phenomenon is responsible for the solid-like behaviour of fresh geopolymer binders activated with the alkaline solution (Rifaai et al., 2019). According to Poulesquen et al. (Poulesquen et al., 2011), the point where to $G' = G''$ corresponds to the existence of interactions between the constituents and the predominance of the solid properties of the materials even before setting.

At the gel point ($G' = G''$), the stress–strain increases from 0.15% to 0.72% when the silica modulus of the activator used in the synthesis of MH increased from 1.3 to 1.5 (Fig. 7). Similarly, the increase in the silica modulus of the activator used in the synthesis of MK from 1.3 to 1.5 resulted in an increase in the stress–strain from 0.10% to 0.62% (Fig. 6). The increase in the stress strain at a higher silica modulus of 1.5 can be ascribed to the lower interactions between different constituents compared to when an activator with a silica modulus of 1.3 was used. These observations correspond to the setting time results (Fig. 5) where higher silica modulus was found to extend the setting times. However, it is observed that when G'' passed over G' at gel point, the $\text{Tan}(\delta)$ increased in both geopolymer samples activated with a silica modulus of 1.5 and reached a peak at 13% of strain before decreasing as shown in Fig. 6 and Fig. 7. This phenomenon

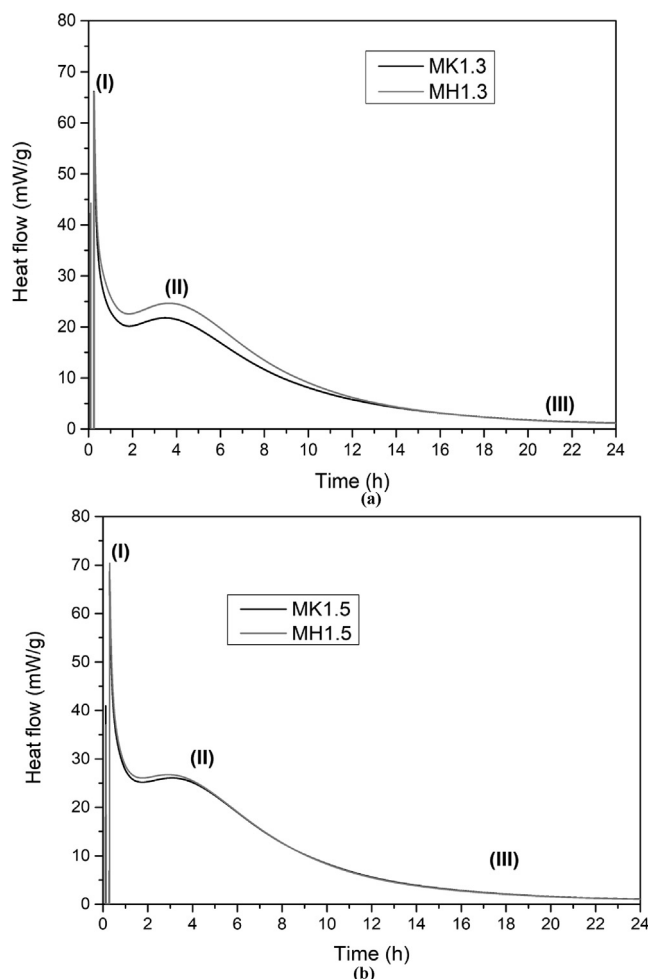


Fig. 8. Heat flow in geopolymer binders (a) GPMK (b) GPMH.

corresponds to the gradual gelation of the geopolymer microstructure pastes as reported by previous studies (Kaze et al., 2020). Conversely, the $\tan(\delta)$ increased in geopolymer samples activated with a silica modulus of 1.3 suggesting that the geopolymerization is slower with silica modulus of 1.5 but with much stronger interactions between constituents.

The yield stress values are obtained by calculating the average values of the onset points and the maximum of the oscillatory stress versus strain curves. For MK-based geopolymer binders, the yield stress increased from 6.3 Pa to 13.8 Pa when the silica modulus was increased from 1.3 to 1.5. On the other hand, an increase from 9.8 Pa to 16.0 Pa in yield stress was observed when the silica modulus of the activator used for MH-based geopolymers was increased from 1.3 to 1.5. The higher stress of geopolymer binders made with a silica modulus of 1.5 (i.e. GPMK1.5 and GPMH1.5) can be justified by the high deformations undergone by the binders as a result of the high viscosity and interactions between Si-oligomer species and other constituents. These results also explained why the geopolymer binders synthesized with a silica modulus of 1.5 exhibited higher setting times compared to those synthesized with a silica modulus of 1.3 (Fig. 5).

3.4. Heat evolution

The reactivity of the geopolymer binders was assessed based on the heat evolution over a period of 24 h after mixing. The heat flow in the geopolymer binders is presented in Fig. 8 while Fig. 9 showed the heat released during geopolymerization in the binders. It can be observed

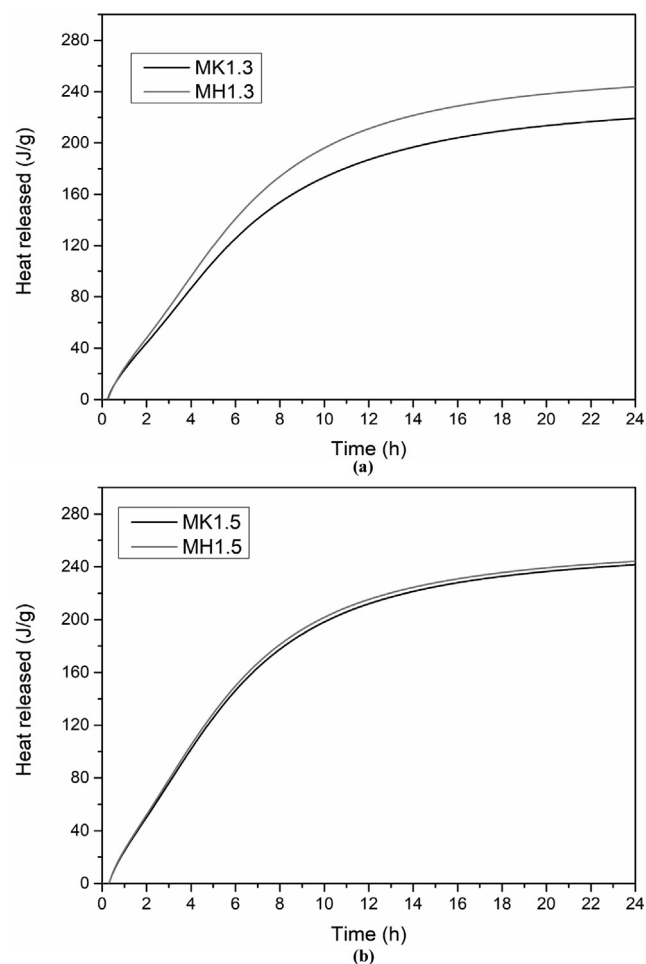


Fig. 9. Heat released in geopolymer binders (a) GPMK (b) GPMH.

from Fig. 8 that during the 24 h, there exist three major peaks of heat evolution. The first exothermic peak I which appeared almost immediately on calorimetric curves when the reaction started is due to the dissolution of the reactive or amorphous phases present in the precursors (i.e. MK and MH) (Nath et al., 2017).

The intensity peaks are almost the same for precursors activated with the activator composed of the same silica modulus. However, when a silica modulus of 1.3 is used; geopolymer binders synthesized with MH as the precursor exhibited a higher heat flow compared to that of MK (Fig. 8a). This difference in the heat flow of geopolymer synthesized with a silica modulus of 1.3 is more evident at the deceleration steps of peaks II and III. These results are consistent with other studies (Najafi Kani et al., 2017; Ogundiran and Kumar, 2015; Zhang et al., 2013). According to Kani et al. (2017), the first and second peaks of heat flow correspond to the instant sorption of activation solution on the surface of raw material particles and the corresponding dissolution of the solid aluminosilicate and aluminate precursors. While the second and third peaks are attributed to polymerization of the dissolved aluminate and silicate species (Provis et al., 2005; Zhang et al., 2012). When a silica modulus of 1.5 was used, the heat flow behaviour is similar for geopolymer binders made with MK and MH as the precursor. These observations are similar to other studies where it has been demonstrated that an increase in the silica modulus improves the reactivity of the precursors and favour their corresponding dissolution in the alkali solution (LI and LI, 2018; Zhang et al., 2013).

Observing the amount of heat released in the geopolymer binders presented in Fig. 9, MH-based geopolymer binders released a higher

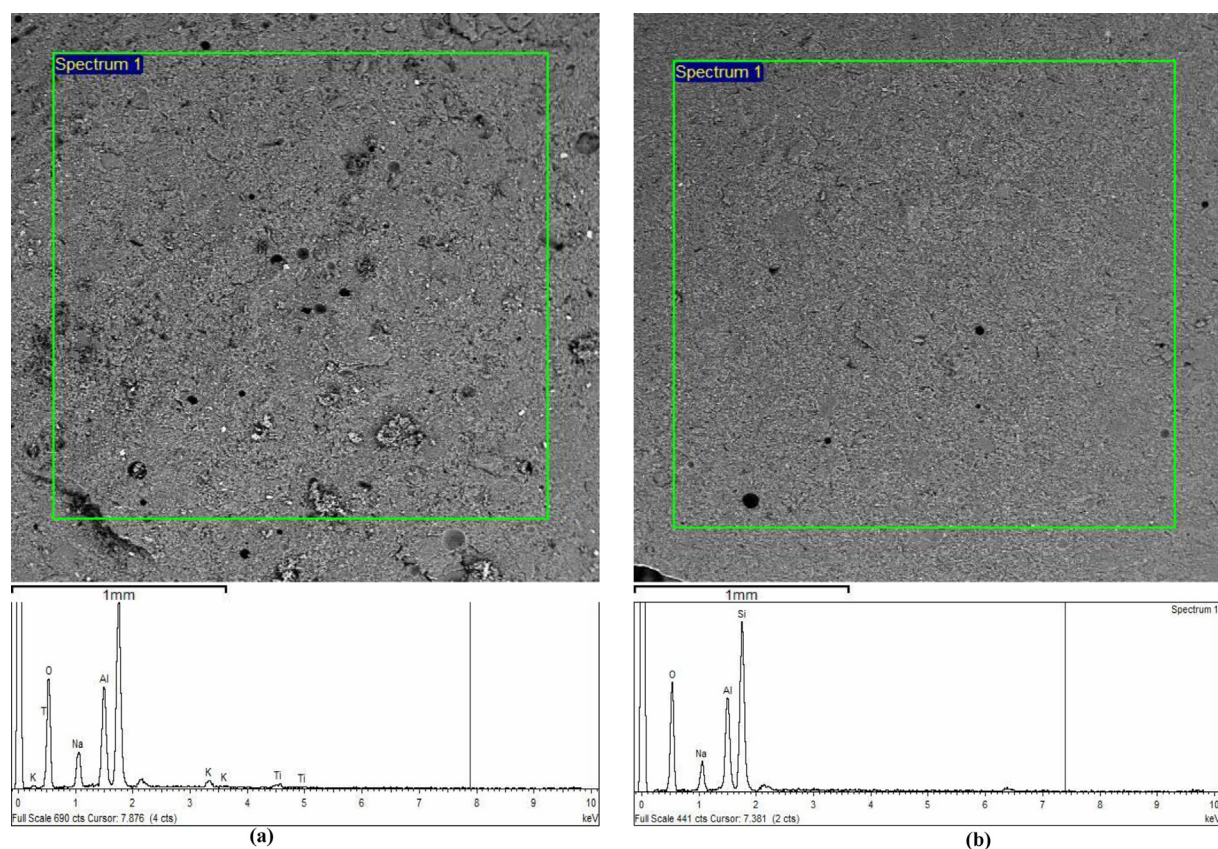


Fig. 10. SEM images and EDS of (a) GPMK1.5 (b) GPMH1.5.

amount of it compared to the MK-based geopolymer binders. The heat released after 24 h in geopolymer binders made with MH as precursors and activated with a solution having silica modulus of 1.3 and 1.5 is 4 J/g and 2 J/g, respectively higher compared to when MK was used as the precursor. The high heat evolution in MH-based geopolymer binders can be linked to the higher reactive or amorphous phase contained in MH which aids the more dissolution of the MH particles in the alkali solutions resulting in good polymerization/polycondensation of the oligomer species. The finer particle size of MH mentioned earlier is also expected to contribute to their higher dissolution in the alkali solution which results in higher heat evolution. Thus, it can be confirmed that the shorter setting time of MH-based geopolymer binders compared to MK is due to their higher dissolution in the alkali solution resulting in a more and faster formation of geopolymerization products.

3.5. Microstructural properties

A scanning electron microscopic image and energy dispersive spectrum of the hardened geopolymer binders activated using an alkali solution with a silica modulus of 1.5 (i.e. GPMK1.5 and GPMH1.5) is presented in Fig. 10. It is evident from the SEM images in Fig. 10 that there is better connectivity between the components in the hardened geopolymer binders. This better connectivity can be ascribed to the formation of polysialate, poly(siloxo-sialate) -Si-O-Al- and -Si-O-Si-O-Al- networks justifying the homogeneity and compact structure of the matrixes. The formation of these networks can be confirmed by the elemental composition of the geopolymer binders shown in the EDS spectrum indicating the dominance of elements such as Al, O, Si and Na across the different matrixes. A similar observation was noticed on both geopolymer samples activated with a silica modulus of 1.3 as shown in Fig. 11. Both geopolymer microstructures are mainly domi-

nated by Al, O, Si, Na and K recorded from the EDS spectrums which also ascribing the existence of elements integrating the geopolymer network.

Conclusions

Geopolymer binders were developed in this study by using calcined kaolin (MK) and calcined halloysite (MH) as the aluminosilicate precursor and activated with solutions having silica modulus of 1.3 and 1.5. The characterization of the precursors (i.e. MK and MH) showed that MH possesses more amorphous content than MK and thus would perform better in terms of alkali activation. The amorphous content of MK and MH obtained by the Rietveld method is 70.2% and 64%, respectively. The XRD results also indicate that the precursors are mainly dominated by crystalline phases such as quartz, hematite, anatase and muscovite.

The setting times of the geopolymer binders were extended when the silica modulus of the activator was increased from 1.3 to 1.5. This extension of the setting times at higher silica modulus (i.e. 1.5) can be linked to the possible formation of Si-O-Si rich bonds during the polycondensation. However, the use of MH as the precursor resulted in a decrease in the setting times compared to when MK was used due to the higher reactivity and fineness of the MH. The setting times results were consistent with the heat evolution in the geopolymer binders where the use of MH as the precursor resulted in a higher heat release rate compared to when MK was used. The fresh geopolymer binders exhibited a solid-like behaviour regardless of the precursor or silica modulus used. However, the increase in the silica modulus from 1.3 to 1.5 resulted in an increase in the stress-strain of the geopolymer binders which is also evident in its high viscosity. Similarly, it was also found out that the yield stress of the fresh geopolymer binders

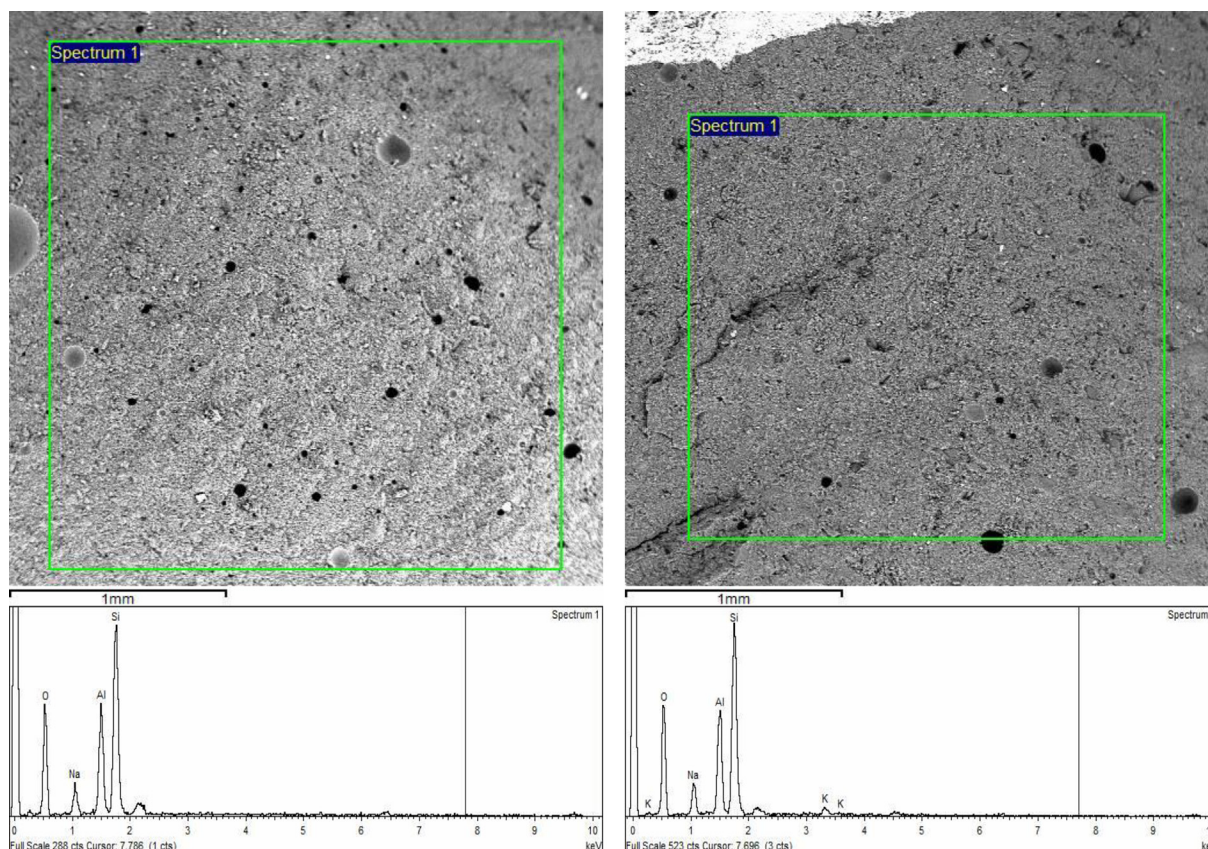


Fig. 11. SEM images and EDS of (a) GPMK1.3 (b) GPMH1.3.

increased with higher silica modulus due to the interactions between Si-oligomer species and other constituents in the geopolymer network.

Declaration of Competing Interest

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

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