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Microstructure and Compressive Strength of Geopolymer Materials Based on Metakaolin with Hematite and Magnetite Gels as Additives

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Abstract: The purpose of this work is to increase the compressive strength and improve the microstructure of geopolymer materials by adding hematite and magnetite gels, as well as their powders, cured at 80 °C. Hematite and magnetite are dissolved in 10 M sodium hydroxide. Dried gels of hematite and magnetite were then ground to produce powders of dissolved hematite and magnetite. For the production of various geopolymer materials, the metakaolin was replaced by 0 and 10 wt. % of each additive and then mixed with the hardener containing the SiO_2/Na_2O molar ratio set at 1.6. The results show that the reference geopolymer has a compressive strength of 51.11 MPa. These values are 50.99 and 47.59 MPa for the geopolymer materials with 10 wt. % of dissolved magnetite gel and the powder of dissolved magnetite cured at 80 °C, respectively. They are 59.52 and 63.23 MPa for those prepared using 10 wt. % of dissolved hematite gel and for the powder of dissolved hematite cured at 80 °C, respectively. Si, Al, Fe, Na and Ti form a homogeneous phase in the geopolymer structures with the exception of a few magnetite particles agglomerated in the geopolymer materials. Compressive strength was found to be improved by the use of hematite gel and dissolved hematite powder cured at 80 °C as additives. A slight reduction in the compressive strength was observed when the dissolved magnetite gel and the powder of the dissolved magnetite cured at 80 °C were used as additives.

Keywords**:** sodium hydroxide, dissolved hematite, dissolved magnetite, metakaolin, geopolymer materials

1. Introduction

Iron is an element that is generally found in the form of a hard metal. The oxidation state of iron is determined by the ore in which it is found. Iron(III) oxide is a chemical compound with the formula Fe_2O_3, where the oxidation state of the iron is +III. It is also known as ferric oxide and iron sesquioxide. It is one of the three main oxides of iron. The other two are iron(II) oxide FeO, which is quite rare, and iron(II, III) Fe_3O_4. Hematite (ferric oxide, α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (triiron tetroxide, Fe_3O_4) are generally the main groups of iron oxides.[1] Among these iron minerals, hematite is the most stable form under ambient conditions.[2] Iron deposits are found all over the world. The most notable in Cameroon is the Bipindi-Grand Zambi iron deposit in the South Region and the Mballam iron deposit in the East Region. These iron oxides occur in a variety of forms known as iron minerals, such as hematite, magnetite, maghemite, goethite, limonite, etc. Research has shown that these minerals are also present at very low

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levels in clay mineral, fly ash and blast-furnace slag (about 10 wt. %) and at high levels in laterite (generally between 30 and 50 wt. %).[3-6] The presence of iron oxide in the aluminosilicate materials used in the synthesis of geopolymer materials can have either a negative or positive effect on the properties of these materials, depending on the oxidation state of the iron present in the raw material.[7] The structure of geopolymer materials with high iron oxide content cannot be investigated using the ^{29}Si and ^{27}Al NMR techniques. The presence of iron oxide is considered by some authors to have a detrimental effect on the process of geopolymerisation. However, recent studies have shown that iron oxides, particularly iron(III) oxide, have a crucial role in the development of the mechanical properties of geopolymer materials.[8] The amorphous Al_2O_3 and SiO_2 present in the raw material is the main oxides that dissolve in the alkaline solution during geopolymerisation to form poly(sialate), poly(sialate-siloxo) or poly(sialate-disiloxo) chains depending on the molar ratio Si/Al contained in the raw material used.[9,10] However, compounds such as CaO or $CaCO_3$ can also react during geopolymerisation to form calcium silicate hydrate or calcium aluminate silicate hydrate in the structure of geopolymer materials, which contributes to the strengthening of the microstructure.[11-13] In addition to these oxides, quartz, a crystalline mineral that acts as a filler, is usually present in the geopolymer network.[14,15] Iron oxide, like hematite powder, has been reported to act as a filler by several authors.[16] Several authors have reported that iron oxide, as well as hematite powder, contained in or added to feedstocks used to synthesise geopolymer materials, acts as a filler. The result is that there is no dissolution of the hematite during the geopolymerisation process. For example, Essaidi et al. investigated the role of hematite in geopolymerisation.[17] They claimed that its presence in the structure of geopolymer material reduces the compressive strength. The effect of hematite on the properties of fly ash-based geopolymers was investigated by Zailani et al. They concluded that the overall properties of geopolymer materials could be improved by increasing the Fe_2O_3 content of the raw material.[18] However, Hairi et al. have provided evidence through the analysis of Mossbauer spectroscopy that the presence of hematite did not interfere with the formation of the geopolymer material.[19] The effect of iron powder on the properties of geopolymer materials subjected to different curing regimes was investigated by Gulmez and Kockal.[20] These authors concluded that the partial replacement of 40 wt. % of fine aggregates with iron powder increased the compressive strength compared to mortars without iron powder. Recently, Ngnintedem et al. investigated the effect of iron oxides such as hematite, magnetite and goethite on the properties of geopolymer materials.[16] They concluded that replacing 10 wt. % of the hematite powder with metakaolin gave maximum strength. The peaks of hematite, magnetite and goethite were found on the X-ray patterns or infrared spectra of each geopolymer material. This is an indication that these iron minerals are not being dissolved during the process of geopolymerisation. The compressive strength of geopolymer materials containing magnetite and goethite as additives decreases, while that of those containing hematite increases. This confirms that hematite acts as a mineral filler. To date, the use of dissolved hematite or magnetite gels and the powders of dissolved hematite or magnetite cured in an oven in geopolymer materials have not been reported. What would be the properties of the geopolymer materials if dissolved hematite or magnetite gels and the powders of dissolved hematite or magnetite cured at 80 °C were used as additives?

The purpose of this work is to increase the compressive strength and improve the microstructure of geopolymer materials by adding hematite and magnetite gels, as well as their powders, cured at 80 °C.

2. Materials and experimental procedures

2.1 *Materials and method*

At the site of Mayouom in the West Region of Cameroon, kaolin of the MY3 type has been collected. After collection, it was air-dried for approximately 12 hours and then broken into smaller pieces. They have been ground in a ball mill for 1 hour. The powders obtained were calcined in an electrically programmable furnace at 700 °C for a period of 4 hours in the firing stage. A rate of 5 °C/min was used for heating and cooling. To obtain the smallest particles of metakaolin, designated MK-MY3, the resulting calcined powder was sieved at 125 μm for 15 minutes using an electric sieve shaker. The silica source for the production of sodium waterglass with a molar ratio of SiO_2/Na_2O of 1.6 was rice husk ash supplied by UNVDA (Upper Nyoung Valley Development Association, located in Ndop, North-West Cameroon). Laboratory grade granules (96% by weight, Sigma Aldrich, Italy) were used for the NaOH pellet. Red and black iron oxides supplied by Serraciments Company (Barcelona, Spain) were used as iron sources. The powders of these reddish and blackish iron oxides were used as additives in the synthesis of metakaolin-based geopolymer materials by Ngnintedem et al. They reported that reddish and blackish iron oxides are hematite and magnetite, respectively.[16] Their X-ray patterns and infrared spectra are shown in Figures 1 and 2, respectively.

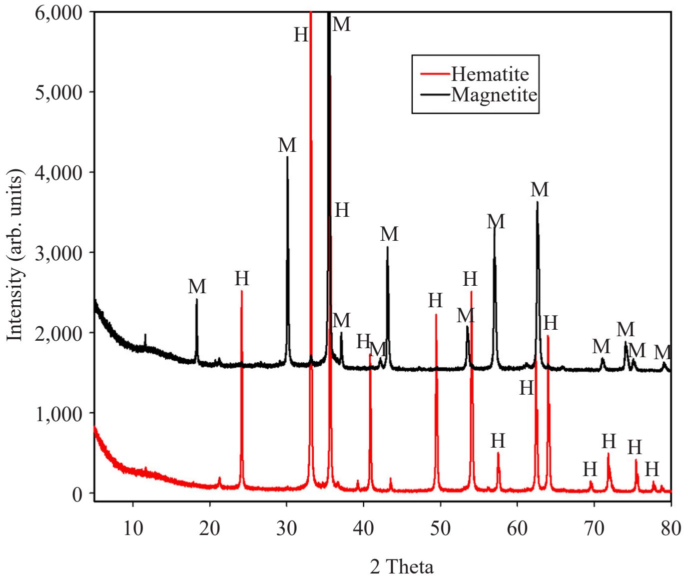


Figure 1. X-ray patterns of hematite and magnetite. M and H denote peaks of magnetite and hematite, respectively

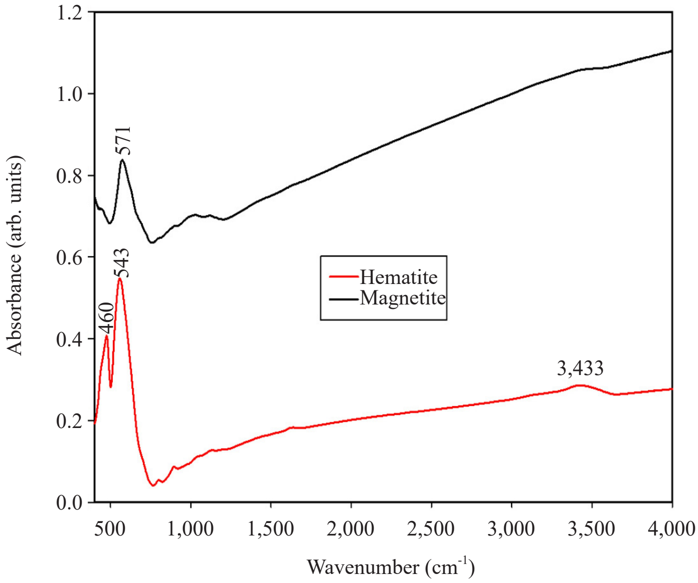


Figure 2. Infrared spectra of hematite and magnetite

The kaolin used in this study was previously used by these authors for the preparation of geopolymer materials. The X-ray pattern and infrared spectrum of metakaolin are shown in Figures 3 and 4. Figures 1 to 4 are described in detail by Ngnintedem et al.[16]

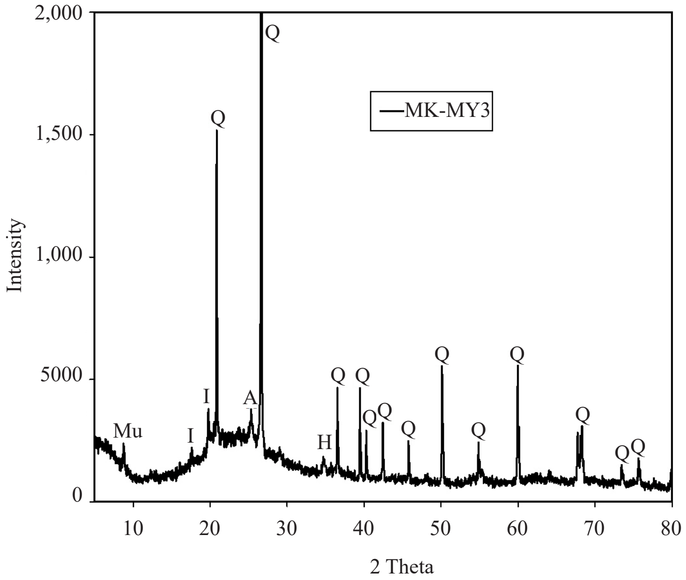


Figure 3. X-ray pattern of metakaolin

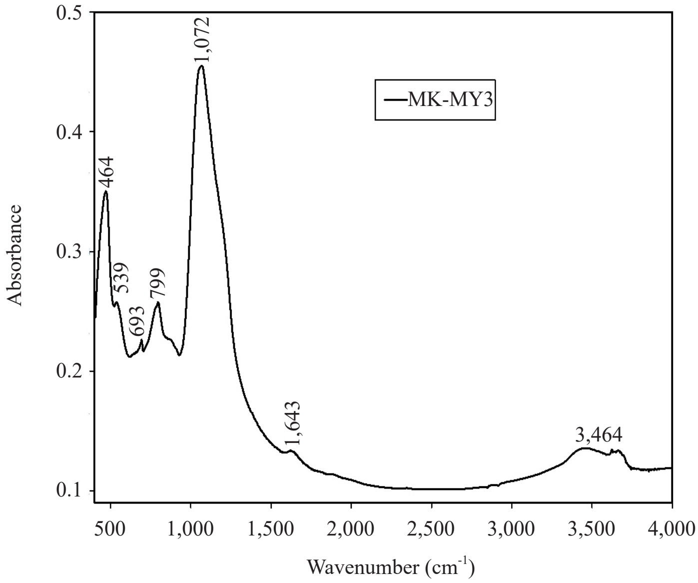


Figure 4. Infrared spectrum of metakaolin

The chemical compositions of kaolin (MY3) and rice husk ash (RHA) are given in Table 1.

Table 1. Chemical compositions of kaolin (MY3) and rice husk ash (RHA), wt. %

Oxides	Samples	
	MY3	RHA
MgO	-	0.28
Al_2O_3	33.29	0.58
SiO_2	46.61	93.20
K_2O	0.94	3.05
CaO	-	0.57
TiO_2	3.96	0.03
SO_2	0.05	-
Fe_2O_3	1.46	2.20
P_2O_5	0.40	-
Others	-	1.78
LOI	13.97	1.2

2.2 *Experimental procedures*

2.2.1 *Preparation of the additives and sodium waterglass*

Hematite and magnetite are the iron minerals used in this work. These are then dissolved separately in a 10 M sodium hydroxide solution. Some of the dissolved gels were used directly as additives. Other gels, made from dissolved hematite and magnetite, were hardened in an oven at a temperature of 80 °C for a period of 24 hours. The hardened materials obtained were separately ground in a ball mill for 30 minutes. The metakaolin was replaced with the resulting powders of each additive.

To produce the white rice husk ash known as RHA, the rice husk was calcined in the company's traditional kiln at a temperature of around 600 °C. A ball mill was then used to grind the white ash from the rice husk for about 30 minutes. The result was a fine powder of rice husk ash. For the preparation of sodium silicate solution, the pellet of sodium hydroxide has been dissolved in water. Sodium waterglass was then obtained by adding it to the resulting rice husk ash powder and mixing at 100 °C for 1 hour with a magnetic stirrer. Prior to use, the sodium waterglass was stored in a sealed container in the laboratory at room temperature for a minimum of 24 hours. In the prepared sodium silicate solution, the SiO_2/Na_2O molar ratio is 1.6. The geopolymer materials prepared in this work have been carried out using the same metakaolin, the same hardener, the same hematite and the same magnetite, prepared under the same conditions as those of Ngnintedem et al.[16]

2.2.2 *Synthesis of geopolymer materials*

The geopolymer materials were prepared by the following processes: Powders of 0 and 10% by weight of dissolved hematite or dissolved magnetite cured at 80 °C were used to replace part of the metakaolin. Other geopolymers were prepared by direct replacement of metakaolin with 10 wt. % dissolved hematite gel or dissolved magnetite gel. With the addition of a sodium silicate solution, each formulation was then mixed in the porcelain mortar for approximately 5 minutes. The mass ratio of liquid to solid was set at 0.83. Fresh geopolymer material was poured into 40 × 40 × 40 mm cube moulds. The moulds were cured for 24 hours at room temperature in the laboratory. Specimens were removed from the mould after 24 hours, sealed in plastic bags and cured at room temperature for 28 days before compressive testing. The geopolymer material without any additives is referred to as G0. GPH and GPM are the names of geopolymer materials containing 10% by weight of the powder of hardened, dissolved hematite and magnetite gels, respectively. The terms GGH and GGM have been used to designate geopolymer materials that contain 10 percent by weight of dissolved hematite and magnetite gels, respectively.

2.2.3 *Methods of the characterisation of geopolymer materials*

The effects of dissolved hematite and magnetite (gels and gels cured at 80 °C) on the structural properties of geopolymer materials were monitored using Fourier Transform Infrared (FTIR) spectroscopy and X-ray diffraction analysis. In addition to the compressive strength measurements and micrographs taken on the fragments, these characterisation methods were carried out on the geopolymer materials.

The compressive strength values of the geopolymer materials were determined after 28 days. The samples were sealed in plastic bags and stored at room temperature in the laboratory in accordance with DIN 1164. The rate of load applied was kept constant at a rate of 0.500 MPa/s. They were measured using an Impact Test Equipment Limited, UK KA20 3LR, Stevenston, United Kingdom, automatic hydraulic press with a capacity of 250 kN. Six samples were tested for each measurement and the mean values for the closest five were determined.

A Bruker D8 Advance X-ray diffractometer equipped with the LynXeye XE T detector, which detects copper Kα1, 2 in the Bragg-Brentano geometry, was used to identify the crystalline and amorphous phases present in the geopolymer materials obtained. The crystalline phases were identified using X'Pert HighScore Plus software, with each X-ray pattern recorded at 40 kV and 40 mA between 3 and 80° (2θ) for approximately 2 h in 0.5° increments. For the determination of the content of amorphous and crystalline phases in the structure of the selected geopolymer materials (G0, GPH and GPM), 30 wt. % corundum was used as the internal standard. The XRD profiles of the selected samples were then analysed using Rietveld refinement and TOPAS 6.0 software (Bruker AXS). The main tasks were the quantification of the phases present and the subsequent calculation of the amorphous fractions. Agate mortar was used to crush all samples. A glass plate was then used to press them into the sample holders. The sample had to be flattened during this preparation. This was done to create a uniform surface. It also minimises the possibility of measurement errors. To avoid contamination, the prepared sample holders were transferred directly to the X-ray powder diffractometer.

Fourier transform infrared spectroscopy analysis has been used to record the functional groups that are present in the structure of the geopolymer materials. A Bruker Vertex 80 v was used to record all spectra. The method used was the KBr method. For this method, approximately 200 mg of KBr was added to approximately 1 mg of each sample. A force of 110 kN was applied to the whole. An ENERPAC P392, USA, was used as the hydraulic press. The spectrum was recorded with a resolution of 2 cm^{-1} using the pellet obtained from each sample. The scan was held at 16.

The micrographs were observed on the fragment of geopolymer materials using a Bruker Jeol XFlash 6160 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) in secondary electron imaging (SEI) mode. The acceleration voltage at 15 kV emission was 56.6 μA, the probe current was 9 and the working distance (WD) was 8.0 mm. Mapping the elements of the geopolymer materials G0, GGH, GPH, GGM and GPM has been studied. Before being photographed, the geopolymer fragments were sputter-coated with a thin layer of gold. This was done to avoid distorting the backscattered images and to allow the electrons accumulated on the examined surface to be discharged.

3. Results and discussion

3.1 *Properties of metakaolin-based geopolymer materials*

3.1.1 *X-ray patterns and phases content in the geopolymer materials G0, GPH and GPM*

The X-ray patterns of the geopolymer materials G0, GPH, GGH, GPM and GGM are displayed in Figure 5.

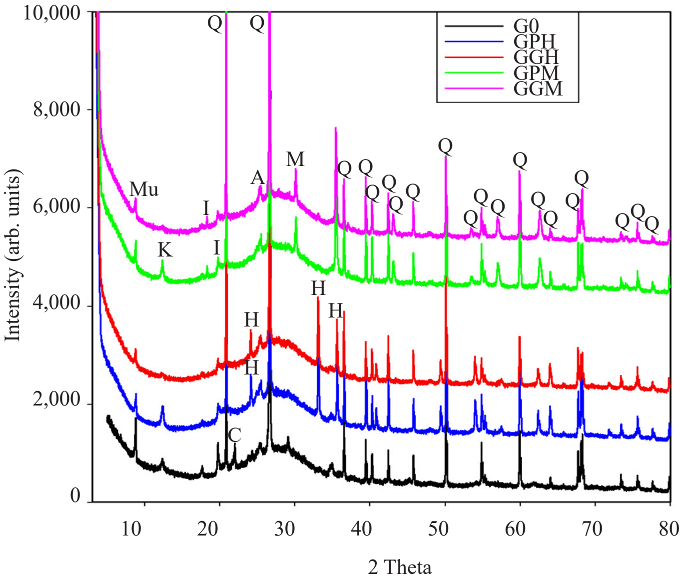


Figure 5. X-ray patterns of geopolymer materials G0, GPH, GGH, GPM and GGM. Mu, K, I, C, Q, A, H and M denote peaks of muscovite, kaolinite, illite, cristobalite, quartz, anatase, hematite and magnetite

The X-ray patterns of all geopolymer materials show peaks of muscovite (JCPDS PDF NO. 07-0042), illite (JCPDS PDF NO. 43-0685), quartz (JCPDS PDF NO. 00-046-1045), anatase (JCPDS PDF NO. 21-1272) and the main peak of kaolinite at about 12.16° (2θ) (JCPDS PDF NO. 00-005-0143). It can be observed that the main peak of kaolinite is too small on the X-ray patterns of geopolymer materials with dissolved magnetite gel (GGM) and dissolved hematite gel (GGH) as additives compared to those containing dissolved hematite powder (GPH) and dissolved magnetite powder (GPM) cured at 80 °C. This may result from the alkaline solution present in the dissolved hematite or magnetite gel reacting with some of the kaolinite. The main peak of cristobalite (JCPDS PDF NO. 39-1425) can be seen on the X-ray pattern of the reference geopolymer G0. X-ray patterns of geopolymer materials (GPH, GGH, GPM and GGM) containing additives do not show this peak. This suggests that after the addition of dissolved hematite and magnetite, cristobalite could react during geopolymerisation. The diffractograms show the hematite (JCPDS PDF NO. 33-0664) peaks in the structure of GPH and GGH, whereas the magnetite (JCPDS PDF NO. 19-0629) peaks are shown in the GPM and GGM diffractograms. This indicates that in the structure of dissolved iron oxides, crystalline minerals such as hematite and magnetite remain. Partial dissolution of hematite and magnetite in 10 M sodium hydroxide may account for this. In addition to these crystalline phases, the X-ray patterns of the geopolymer materials showed a halo diffraction pattern between 18° and 40° (2θ). This is in line with the amorphous fractions that could be part of the binder. On the X-ray pattern of metakaolin, this broad hump structure is observed between 15 and 35 (Figure 3). The change in the microstructure of the metakaolin due to its depolymerisation followed by the polycondensation reaction between the monomers formed is responsible for the shift of the broad hump structure towards higher 2θ. Then, during the curing process, the structure of the materials obtained is reorganised. This leads to the formation of the binder, called the poly(sialate-siloxane) network, known as the amorphous phases. The absence or partial dissolution of magnetite and hematite may explain the absence of ferrisilicate on the X-ray patterns of geopolymer materials. In other words, the free Fe species do not have a role in the formation of a new crystalline mineral phase during geopolymerisation. On the other hand, the formation of fayalite has been observed on the X-ray patterns of geopolymer materials from calcined laterite by Kaze et al.,[21] Kamseu et al.[22] and Nouping et al.[23] The formation of iron silicate ($Fe_7(SiO_4)_4$) was observed by Nouping et al.[23] in addition to fayalite. Amorphous and crystalline phase contents in the selected geopolymers G0, GPH and GPM, previously identified from their X-ray patterns, are summarised in Table 2.

Table 2. Amorphous and crystalline phases content in the selected geopolymer materials

Phases content (wt. %)	G0	GPH	GPM
Amorphous phase	77.54	74.63	76.42
Quartz	15.62	17.52	16.35
Hematite	0.08	3.05	0
Magnetite	0	0	3.38
Muscovite	1.72	0.89	0.95
Cristobalite	0.55	0	0
Anatase	0.89	1.34	0.95
Kaolinite	3.06	2.31	1.74
Illite	0.56	0.23	0.22
Total of fillers content	17.70	22.14	17.52

This table shows that the amorphous phase contents in the G0, GPH and GPM structures are 77.54, 74.63 and 76.42 wt. %, respectively. It can be observed that the amorphous phase content is almost the same as in the control geopolymer material G0 with the addition of 10 wt. % of dissolved magnetite powder cured at 80 °C (GPM). The presence of this mineral in trace amounts is indicated by the low hematite content (0.08% by weight) in the structure of G0. The results in Table 2 justify the absence of cristobalite on the X-ray patterns of the geopolymer materials from the addition of dissolved hematite gel; the powder of dissolved magnetite hardened at 80 °C, the powder of dissolved hematite hardened at 60 °C and the dissolved magnetite gel. Kaolinite content is 3.06% by weight in the reference geopolymer G0. This value seems to decrease after the addition of dissolved hematite and magnetite powders hardened at 80 °C for the geopolymer materials GPH and GPM. These materials contain 2.31 and 1.74 wt. % of kaolinite, respectively. Some minerals act as fillers, such as quartz[14,15] hematite[16], cristobalite,[24] anatase or titanium oxide[25-28] and illite[29] among the minerals present in the geopolymer structures summarised in Table 2. The total content of these minerals in the selected geopolymer materials, G0, GPH and GPM are 17.70, 22.14 and 17.52 wt. %, respectively. It appears that the sum of the fillers in the structure of GPH has a high value. This suggests that this geopolymer material, GPH, may have a more dense structure.

3.1.2 *Infrared spectra*

The infrared spectra of geopolymer materials G0, GPH, GGH, GPM and GGM are displayed in Figure 6.

Absorption bands at 445-439 cm^{-1}, corresponding to Si-O vibrational modes, are found on geopolymers' infrared spectra. Only the infrared spectra of GPH, GGH, GPM and GGM show bands at 565-525 cm^{-1}. The Fe-O vibrational modes of hematite[21,30-33] in GGH and GPH and magnetite in GGM and GPM are responsible for the presence of these bands. On the infrared spectrum of the reference geopolymer G0, the band around 565-525 cm^{-1} is not present. This result is consistent with the structure of G0 shown in Table 2, which has the lowest hematite content (0.08 wt. %). Quartz Si-O-Si vibrational modes are assigned to absorption bands at 684-679 cm^{-1}. On the infrared spectra of the geopolymer materials G0, GPH, GGH, GPM and GGM, the symmetric and asymmetric stretching modes of Si-O-Si and Si-O-Al appear at 1,011 cm^{-1}. These absorption bands are located at 1,072 cm^{-1} on the infrared spectrum of metakaolin (Figure 4). The difference in microstructure between the metakaolin used and the geopolymer materials is responsible for the shift of these absorption bands towards lower wavenumbers on the infrared spectra of the geopolymer materials.

This is achieved by dissolving metakaolin in a sodium silicate solution. The precursors are then polycondensed to form geopolymer binders. For all geopolymer materials, the wavenumbers of the main bands have the same values. This could mean that the iron oxide, such as hematite, does not get incorporated into the geopolymer matrix, but instead reacts as a filler and therefore improves the compressive strength, see below.

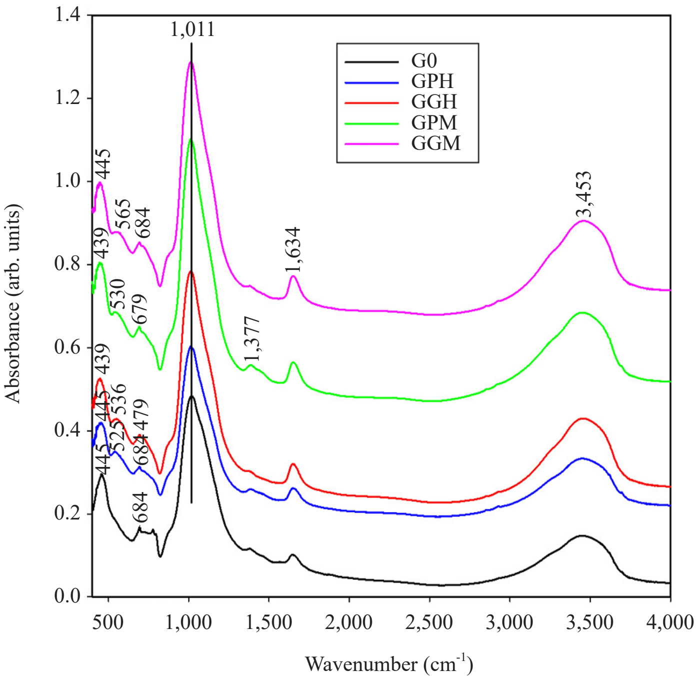


Figure 6. Infrared spectra of geopolymer materials G0, GPH, GGH, GPM and GGM

3.1.3 *Compressive strengths*

The compressive strengths of geopolymer materials G0, GPH, GGH, GPM and GGM are presented in Figure 7.

Compared to these values, the compressive strengths of G0, GPH, GGH, GPM and GGM are 51.11, 63.23, 59.52, 47.59 and 50.99 MPa, respectively. It is therefore clear that the fact that in both cases (dissolved hematite gel and dissolved hematite powder cured at 80 °C) the hematite particles are not modified by the geopolymerisation reaction, resulting in the formation of specific networks other than the geopolymer network, may be responsible for the higher compressive strength values of the geopolymer materials GPH and GGH with dissolved hematite as an additive. By acting as a reinforcing load, these particles improve compressive strength.[34] This may be an indication that the iron(III) from hematite is unlikely to be part of the geopolymerisation process. Zhu et al. reported that the presence of iron(III) binds mainly to hydroxyl groups, which increases the number of nucleation sites and thus the geopolymerisation process, and hence the compressive strength. The low compressive strength of GPM and GGM geopolymers is consistent with the work of Zhu et al. who showed that the presence of iron(II) in magnetite disrupts the long polymer chains, causing fracture. This hypothesis is supported by the lower values for the compressive strength of geopolymer materials in which magnetite is used as an additive, as reported by Davidovits et al. In this work, the values of the compressive strength of geopolymer materials using dissolved magnetite as an additive (GGM made from gel of magnetite and GPM: magnetite gel hardened at 80 °C) are lower than those of GGH and GPH.[35] This may be related to the negative effect of Fe^{2+} in developing geopolymerisation. These interpretations are similar to those of Davidovits,[36] Mustafa et al.,[37] Burduhos-Nergis[38,39] that the presence of hematite in the raw materials is a good indication for the improvement of the properties of geopolymer materials. The compressive strength values of the geopolymer materials obtained after the addition of dissolved magnetite (magnetite gel: GGM and magnetite gel cured at 80 °C: GPM) are slightly lower than those of the reference geopolymer, denoted G0, but remain lower than those obtained after the addition of dissolved hematite. However, the present work confirms the findings of Davidovits and Davidovits that hematite-containing metakaolin-based geopolymers provide greater compressive strength than non-hematite-containing metakaolin-based geopolymers.[35] In addition to the geopolymer networks, an iron-silicate binder could be formed by a chemical reaction between silicate and iron(III), according to Zailani et al.[18] This is in agreement with the findings of Vlasceanu et al. who reported that the addition of magnetite to metakaolin in the range of 5-10 wt. % has no effect on the geopolymerisation reaction.[40] This agrees with the results of Yong et al. who show that Fe_3O_4 ($FeO·Fe_2O_3$) in the raw aluminosilicate does not participate in geopolymerisation. Other authors, e.g. Nyale and others, showed that if the magnetite in the aluminosilicate is soluble, the resulting Fe does not participate in the reaction. Vlasceanu et al. also reported that the addition of magnetite in the preparation of geopolymers slightly increased permeability.[40] The increase in permeability is related to the increase in pore size in the structure of GGM and GPM. This justifies their lower compressive strength values compared to those of the dissolved hematite gel (GGH) and the powder of dissolved hematite hardened at 80 °C (GPH). The higher compressive strength values of GPH and GGH compared to GPM, GGM and G0 are due to the sum of inert particles of quartz, hematite, anatase, muscovite and illite. This is 22.14 wt. % for GPH compared to 17.52 wt. % for GPM and 17.70 wt% for G0. In this way, it was possible to improve the packing density of the GPH geopolymer microstructure. It is as if magnetite does not need to be used for filling. Only quartz (16.35 wt. %), muscovite (0.95 wt. %), anatase (0.95 wt.%) and illite (0.22 wt.%) play the role of filler in GPM. This is due to the fact that the presence of iron(II) destroys the poly(sialate-siloxo) chains compared to 22.14 wt.% in GPH, hence the low compressive strength of GPM and GGM. TiO_2 increases compressive strength through pore filling.[26,27] This finding is also supported by Duan et al. who concluded that increasing the number of titania speeds up the polymerisation process and improves the compressive strength. The compressive strength value of geopolymer materials containing 10 wt. % of the powder of dissolved hematite cured at 80 °C is higher (63.23 MPa) than that of those containing 10 wt. % of dissolved hematite gel (59.52 MPa). This could relate to the fact that the hematite particles in the powder of the dissolved hematite hardened at 80 °C are well distributed in the geopolymer material GPH and therefore fill most of the pores in its network. However, for dissolved magnetite powder cured at 80 °C and dissolved magnetite gel, this trend is in the opposite direction. As a result, the compressive strength of geopolymer material with dissolved magnetite gel (GGM) as an additive is slightly higher than that of dissolved magnetite powder hardened at 80 °C (GPM). This could be due to the agglomeration of magnetite particles[41] in the structure of the powder of dissolved magnetite cured at 80 °C. This helps to create a weak zone in the structure of the GPM. The presence of dissolved Fe_3O_4 (gel or gel cured at 80 °C) in the geopolymer matrix could lead to the formation of local agglomerations of magnetite particles. This could slightly reduce the compressive strength[41] from 51.11 to 47.59 MPa. It is important to mention that Ngnintedem et al. investigated the influence of the undissolved powder of iron oxides such as hematite and magnetite on the compressive strengths and microstructural properties of metakaolin-based geopolymer materials.[16] Significantly, these researchers used the same metakaolin, hematite, magnetite and hardener that we have used here. They reported that the compressive strengths of the metakaolin-based geopolymer materials containing 10 wt. % of the powders of hematite and magnetite were 55.53 and 47.03 MPa, respectively.[16] It can be observed that the compressive strengths of geopolymer materials with dissolved hematite (dissolved hematite gel and the powder of dissolved hematite hardened at 80 °C) are higher compared to those with the incorporation of undissolved hematite powder. The compressive strength of geopolymer materials using the powder of dissolved hematite cured at 80 °C and dissolved hematite gel as additives was increased by 12.18 and 6.7%, respectively. The compressive strengths of the geopolymer materials with the incorporation of dissolved magnetite are almost identical to those obtained with the use of magnetite powder as an additive. In general, it can be seen that the addition of magnetite (dissolved or undissolved) has little effect on the compressive strengths of the geopolymer materials, as they are almost the same value (47.03 MPa for geopolymer material from the incorporation of 10 wt.% magnetite powder,[16] 47.59 MPa for geopolymer material using the powder of dissolved magnetite cured at 80 °C (GPM) and 50.99 MPa for geopolymer material using the dissolved magnetite gel (GGM) and the control geopolymer material (51.11 MPa). The presence of Fe^{2+} in the structure of magnetite could be responsible for the slightly lower compressive strength values of GGM and GPM compared to those of dissolved hematite (GGH and GPH). Because iron(III) is affected by iron(II) and disrupts the geopolymerisation process.[7,42]

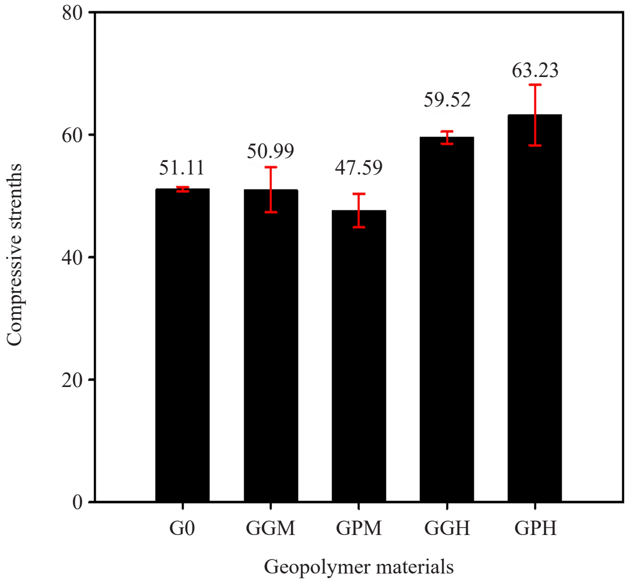


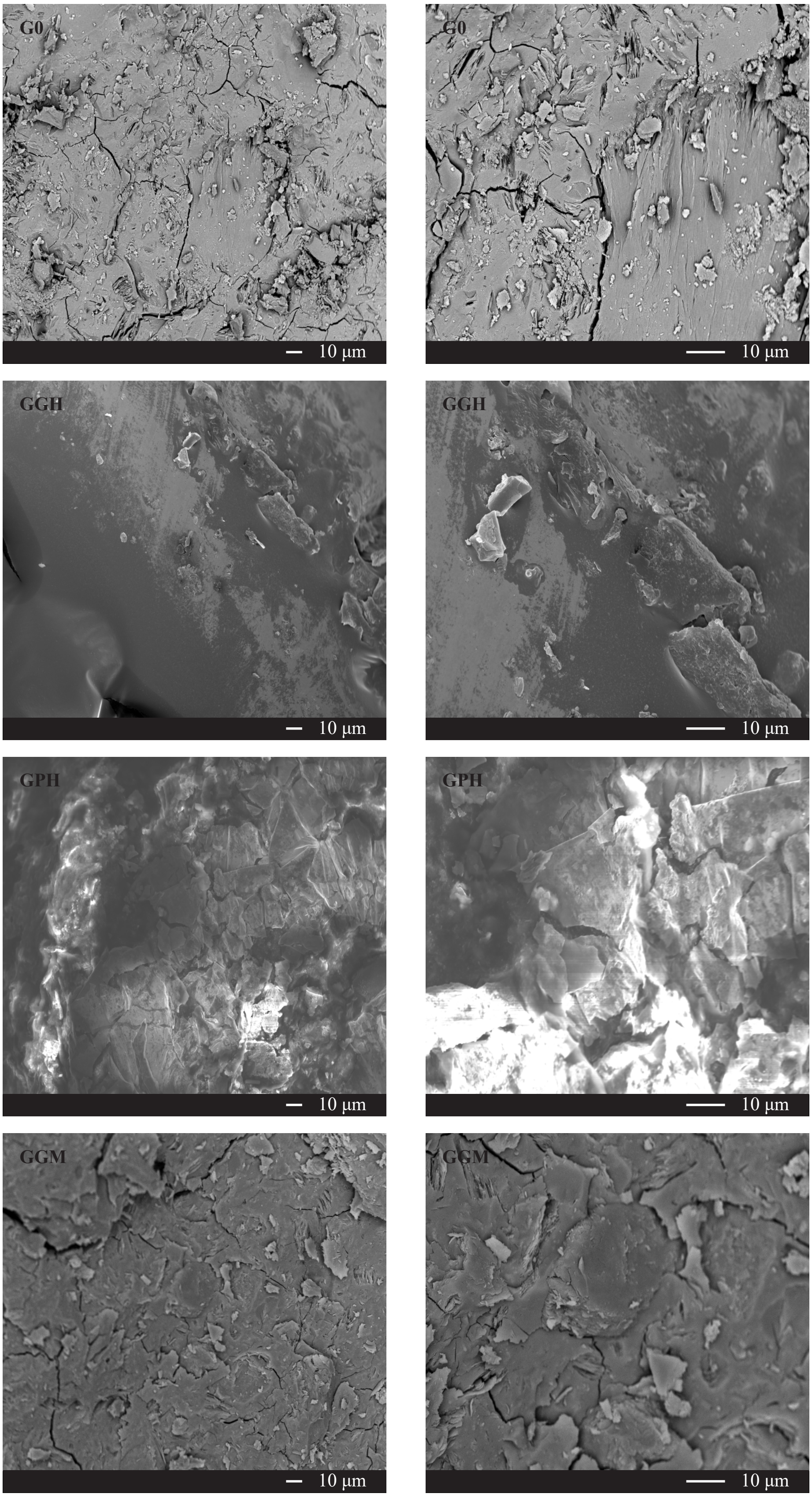
Figure 7. Compressive strengths of geopolymer materials G0, GPH, GGH, GPM and GGM

3.1.4 *Micrograph images and elemental distribution investigations*

The micrographs of geopolymer materials G0, GGH, GPH, GGM and GPM are displayed in Figure 8.

In general, these micrographs of geopolymer materials are compact and homogeneous. They have denser matrices. This matches their compressive strength values (Figure 7). In addition, the micrographs produced by the GGH are smoother in appearance. This is because the structure is more compact. GPH has a coarser microstructure. This explains the higher compressive strength of GGH and GPH compared to GGM, GPM and G0 (Figure 7). The smooth structure of GGH and the coarse microstructure of GPH could be related to the higher filler content reported in Table 2 in the geopolymer materials with dissolved hematite. This contributes to the formation of a denser microstructure. Between the unreacted FeO particles in the magnetite, some capillary pores may have formed. These are visible in the micrographs of the GPM. The results of the work of Lemougna et al.[7] and Li et al.[42] confirm the presence of the unreacted particles of FeO in the magnetite during the geopolymerisation process. The appearance of capillary pores in the geopolymer material GPM is attributed to the magnetite, which increases the permeability, as demonstrated by Vlasceanu et al.[40] and the agglomerated particles of magnetite as demonstrated by Ghazanlou et al.[41] The EDS mapping of the elements Si, Al, Fe, Na and Ti contained in the structure of geopolymer materials G0, GGH, GPH, GGM and GPM are depicted in Figure 9.

The presence of Ti is confirmed by anatase peaks on the X-ray patterns of geopolymer materials. It can be observed that Si, Al, Fe, Na and Ti are well distributed in the structure of the geopolymer materials. This confirms the compact, homogeneous and dense microstructures previously observed in the micrographs (Figure 8). The excellent distribution of Na^+ in the geopolymer networks balances the negative charge caused by the substitution of Si(IV) by Al(III). This does not alter the 3D structure of the geopolymer materials. Agglomerated iron oxide (magnetite) particles are seen in the GPM in some zones. This is associated with the formation of a weak zone.[41] These agglomerated particles are the cause of the formation of capillary pores. Compared to GGM (50.99 MPa), GPH (63.23 MPa), GGH (59.52 MPa) and G0 (51.11 MPa), this is probably due to the lower compressive strength of GPM (47.59 MPa). According to Ullah et al, Transmission Electron Microscopy (TEM) provides important information about the internal composition of the sample. This includes lattice parameters, topography and stressing conditions.[43] This is in contrast to the SEM. The Scanning Electron Microscopy (SEM) provides information about the outer surface and the stoichiometry of the sample.


G0
10 μm
G0
10 μm
GGH
10 μm
GGH
10 μm
GPH
10 μm
GPH
10 μm
GGM
10 μm
GGM
10 μm

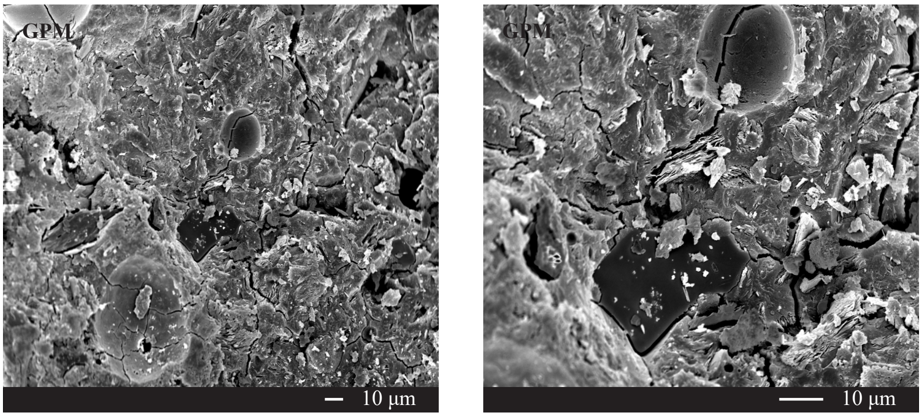
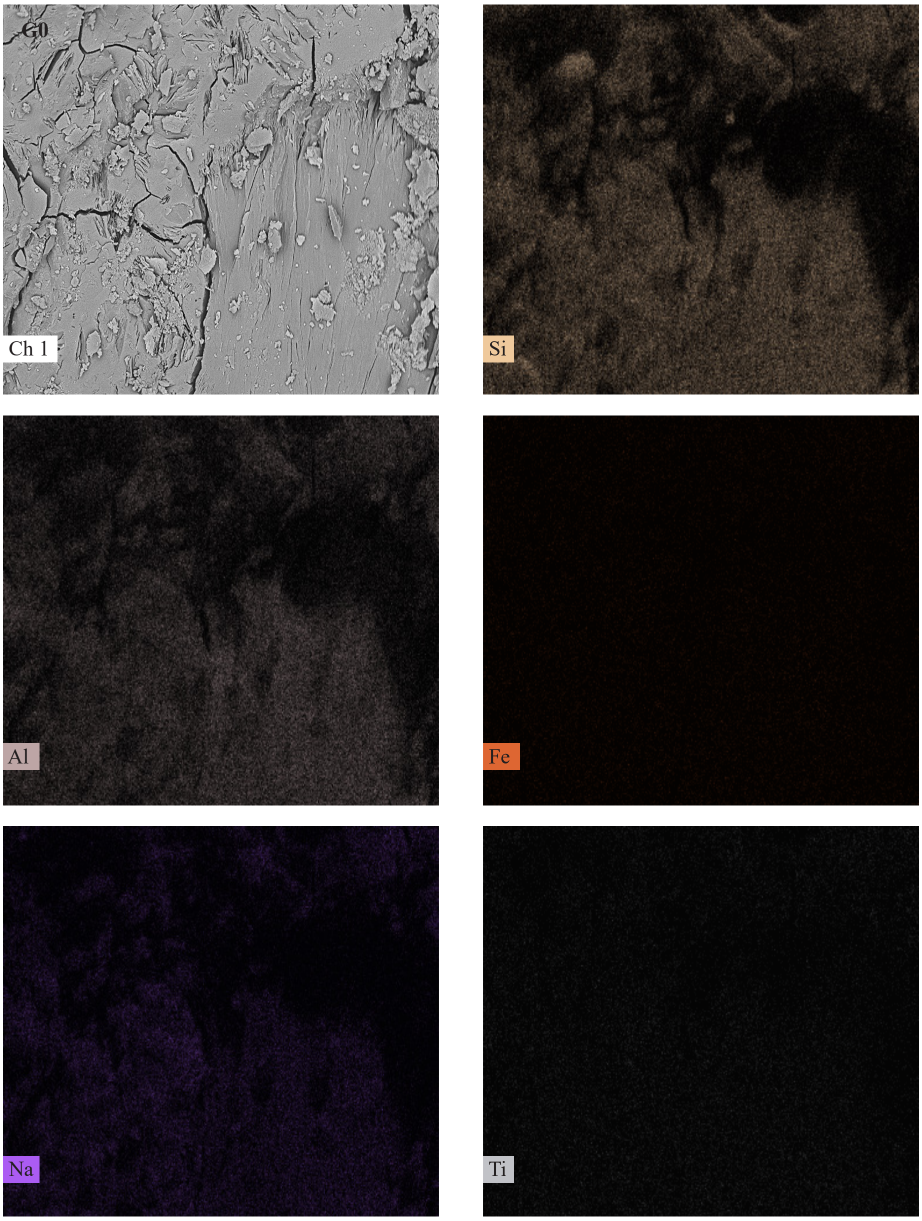
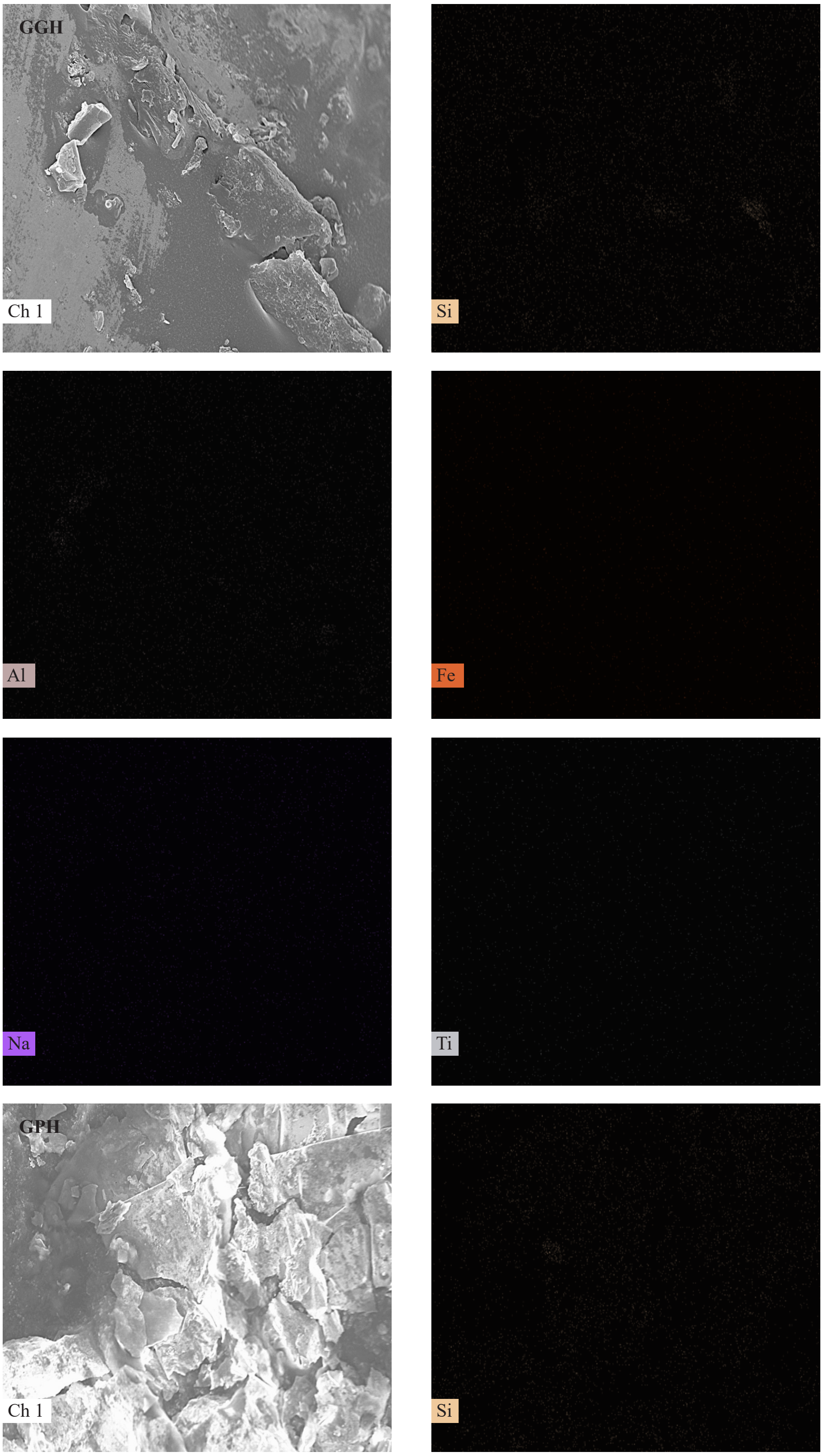
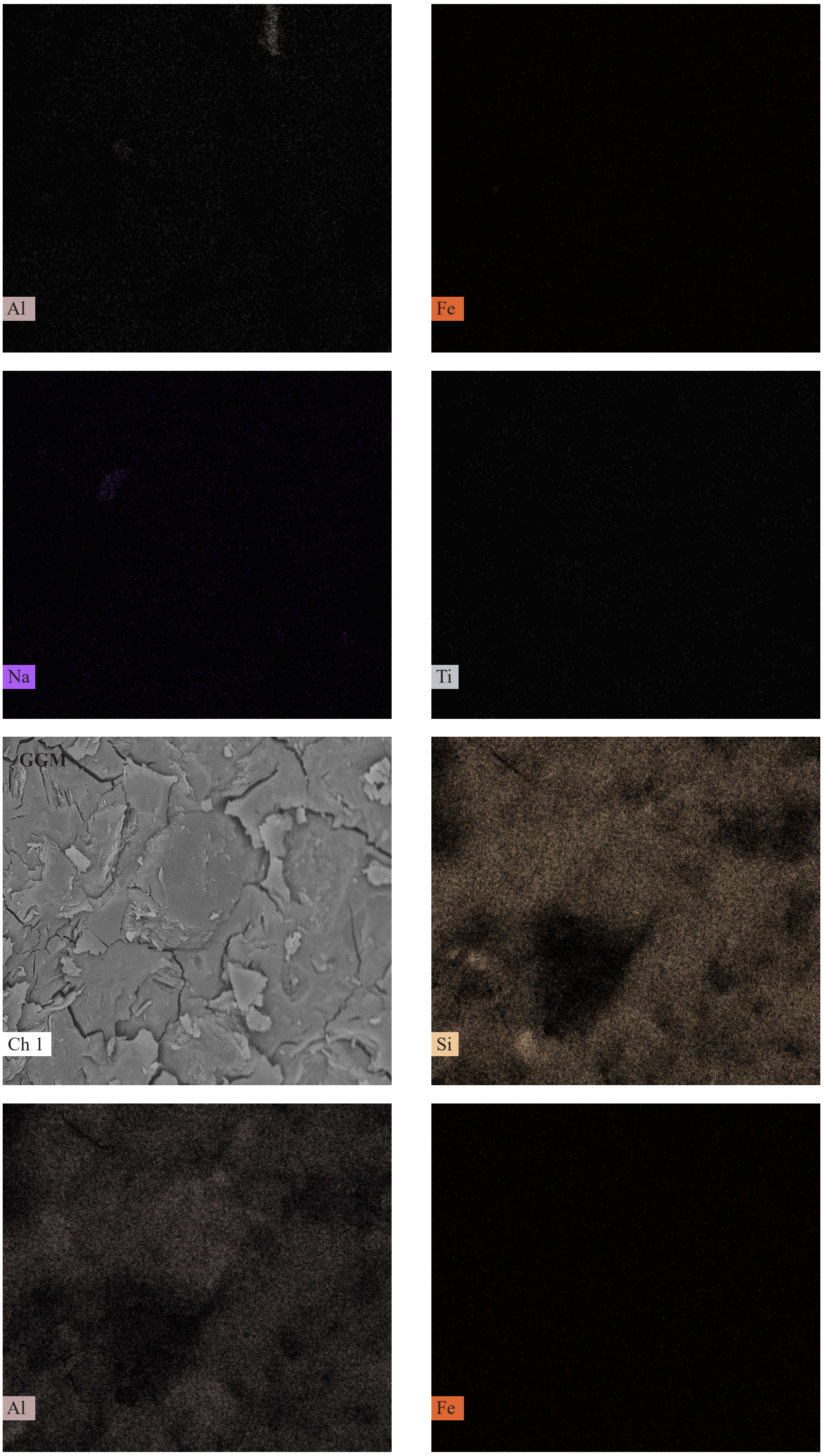


Figure 8. Micrograph images of geopolymer materials




GGH
Ch 1
Si
Al
Fe
Na
Ti
GPH
Ch 1
Si


Al
Fe
Na
Ti
GGM
Ch 1
Si
Al
Fe

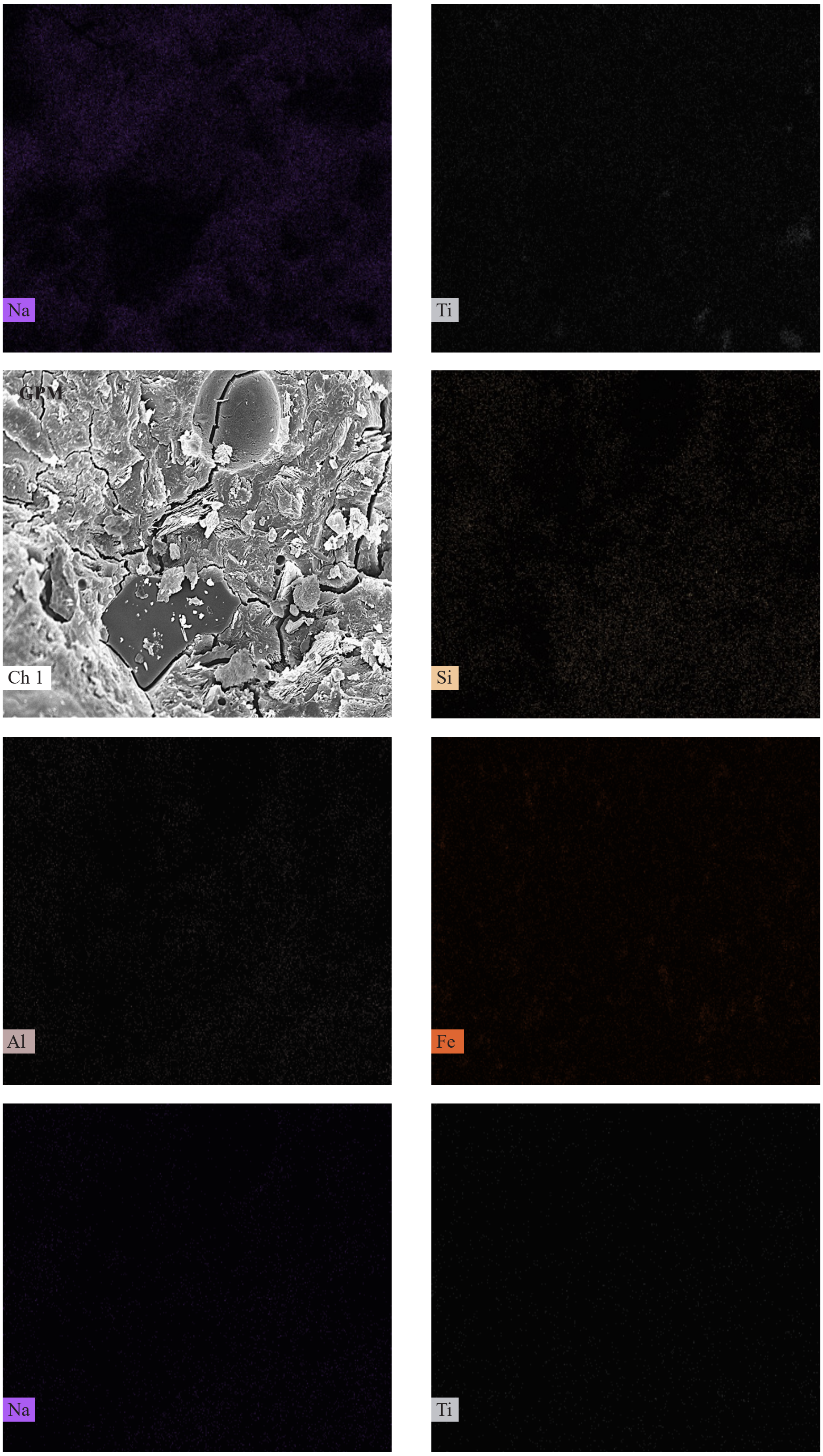


Figure 9. SEM with EDS mapping of Ca, Na, Fe, Si and Al elements in the geopolymer materials, Ch1 is an area of specimen selected for area mapping

4. Conclusion

The magnetite and the haematite were dissolved in a 10 M sodium hydroxide solution. For each of the iron minerals, the gels obtained were then divided into two parts. Some parts of the gels were used directly as additives. Others were hardened in an oven at 80 °C for 24 hours. Those that had been cured in the oven were ground in a ball mill and the powders that were obtained were used as additives. Metakaolin has been replaced to the extent of 10% by weight of each additive. A chemical reagent or hardener was prepared by dissolving rice husk ash in a sodium hydroxide solution. The molar ratio of SiO_2/Na_2O in the prepared hardener was 1.6. The following conclusions are drawn from the reported experimental results:

- The cristobalite peak can be seen on the X-ray pattern of the reference geopolymer material. In the structure of geopolymer materials containing additives, this mineral is not present.
- When the dissolved hematite and magnetite gels have been used as additives, the main peak of kaolinite is reduced.
- The X-ray patterns of geopolymer materials using the dissolved hematite gel and the powder of dissolved hematite hardened in an oven show the peaks of hematite in their structures, whereas the peaks of magnetite appear on the X-ray patterns of the dissolved magnetite gel and dissolved magnetite cured in an oven.
- On the infrared spectra of the geopolymer materials with additives, the Fe-O absorption bands are found between 565 and 525 cm^{-1}. On the spectrum of the geopolymer material used as a reference, this band does not appear.
- The compressive strength of the benchmark geopolymer material was 51.11 MPa. These are 59.52 MPa when using a dissolved hematite gel as an additive and 63.23 MPa when using a powder of dissolved hematite which is cured at 80 °C. In contrast, the values for geopolymer materials using dissolved magnetite gel and powder-dissolved magnetite cured at 80 °C are 50.99 and 47.59 MPa, respectively.
- The micrographs of the geopolymer materials are compact, homogeneous and have a denser matrix.
- In the structure of geopolymer materials, elements such as Si, Al, Fe, Na and Ti are homogeneous in the matrix. Using dissolved magnetite gel and powder of dissolved magnetite cured at 80 °C as additives, some zones show agglomerated iron oxide (magnetite) particles in the structure of geopolymer materials.

Dissolved hematite gel and the powder of dissolved hematite cured at 80 °C have been used as additives to improve compressive strength and the microstructure of geopolymer materials. A slight reduction in compressive strength was observed when dissolved magnetite gel and dissolved magnetite powder cured at 80 °C were used as additives. The compressive strength of geopolymer materials increased when dissolved hematite (hematite gel and hematite gel hardened at 80 °C) were used as additives compared to those of geopolymer materials containing un-dissolved hematite powder. However, the compressive strength of geopolymers containing dissolved magnetite gel and the powder of dissolved magnetite cured at 80 °C was slightly higher than that of geopolymers containing magnetite powder. It can be concluded that hematite gel and its powders cured at 80 °C can be used as additives to improve the compressive strength and microstructure of geopolymer materials. Building materials could be made from the resulting geopolymer materials.

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Conflict of interest

The authors declare no competing financial interest.

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