Research Article

Geopolymers Based on Phosphoric Acid and Illito-Kaolinitic Clay

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New three-dimensional geopolymer materials based on illito-kaolinitic clay and phosphoric acid were synthesized. The effect of Si/P molar ratio on the geopolymers properties was studied. Raw, calcined clay, and geopolymers structures were investigated using XRD, IR spectroscopy, and SEM. The phosphoric acid-based geopolymers mechanical properties were evaluated by measuring the compressive strength. The Si/P molar ratio was found to increase with the increase of the compressive strength of the obtained geopolymers, which attained a maximum value at Si/P equal to 2.75. Beyond this ratio, the mechanical strength decreases. The XRD patterns of these geopolymers samples have proven that when the Si/P molar ratio decreases, the amorphous phase content increases. Besides, the structural analyses have revealed the presence of aluminum phosphate and Si-O-Al-O-P polymeric structure, whatever the Si/P molar ratio is (between 2.25 and 3.5). The obtained results have confirmed that the presence of the associated minerals such as hematite and quartz in the clay does not prevent the geopolymerization reaction, but the presence of illite mineral seems to have a modest contribution in the geopolymerization.

1. Introduction

It is well known that the Portland cement is the most used hydraulic binder in the world. Yet, it is increasingly causing a high degree of carbon dioxide (CO_2) emission leading to global warming. Therefore, many research works have been carried out on the synthesis of new hydraulic binder with less energy consumption and less atmospheric generation in order to safeguard the environment [1, 2]. In 1970, Davidovits has developed a new inorganic polymeric material named "Geopolymer" [3]. This material, with good physical and mechanical properties, has the potential to replace ordinary Portland cement concrete [4]. This new cement is an amorphous, three-dimensional aluminosilicate binder material, whose emission of carbon dioxide is 80 times lower [5].

The geopolymer is obtained by the alkaline attack of aluminosilicate material. Geopolymerization involves an exothermic reaction between the aluminosilicate material (such as metakaolinite (Al_2O_3-$2SiO_2$)) and a strong alkaline solution (KOH, NaOH, etc.) at room temperature or slightly above [6].

Recent studies have shown that geopolymer products could also be obtained by the phosphoric acid attack of the activated aluminosilicate material [7–9]. Compared to alkali-based geopolymer, the phosphoric acid-based geopolymers show superior mechanical properties [10].

According to Cao et al. [9], the basic steps of geopolymerization are the dissociation of aluminosilicate material with phosphoric acid and bonding reaction between the low polymeric P-O tetrahedral units in phosphoric acid solution and the active Al-O structure in metakaolinite granules which adhere to each other, leading to the formation of Al-O-P bonds.

Most of the published research works [7–10] mentioned the use of metakaolin in the synthesis of the phosphoric acid-based geopolymers. But, to the best of our knowledge, no studies have dealt with the synthesis of geopolymers from other aluminosilicate materials. For this reason, the present work considers the synthesis geopolymer from local illito-kaolinitic clay. Indeed, Tunisia is among the countries that have many clay fields. Tunisian clays are mainly used in the ceramic industry [11, 12] and as pozzolanic materials in cement industry [13]. In a previous work [7] local kaolinitic

TABLE 1: Chemical composition of used materials.

	Compositions (mass%)									
	SiO_2	Al_2O	Fe_2O_3	MgO	Na_2O	CaO	K_2O	SO_3	PO_3	LOI
Medenine clay	60.8	16.20	5.87	2.38	0.003	2.15	2.71	0.08	—	9.16
H_3PO_4	—	—	—	—	—	—	—	—	85	—

clay from the region of Tabarka was studied as a precursor for the synthesis of phosphoric acid-based geopolymers. The obtained geopolymers presented good mechanical properties. The aim of the present research is to study the effect of the Si/P molar ratio on the geopolymerization reaction and its effects on the properties of phosphoric acid-based geopolymers obtained from a local illito-kaolinitic clay from the region of Medenine (south of Tunisia) as a geopolymeric precursor.

2. Materials and Experimental Methods

The clay from the South of Tunisia "Medenine" was used as aluminosilicate source. It is characterized by its red color and generally used in ceramic industry. The thermal activation of this clay was performed at 700°C for 5 h in a static bed after sieving at 125 μm according to the procedure established by Essaïdi et al. [14] and quenched by air to ambient temperature. The chemical composition of this clay is presented in Table 1. The phosphoric acid used in this study was a commercial phosphoric acid H_3PO_4 85% provided by CHEMI-PHARMA and distilled water was used as a solvent.

The geopolymer samples were prepared by mixing the calcined clay powder, distilled water, and phosphoric acid for 1 min with ultrasonic waves until the paste was homogenous. The liquid/binder ratio was almost constant equal to 20/80. After mixing, the paste specimens were poured into plastic mold 27 mm in diameter and 54 mm in height then kept at room temperature for 2 hours before curing at 60°C for 24 hours in an oven. The obtained samples were conserved at room temperature for 21 days after demoulding. The obtained phosphoric acid-based geopolymers were examined under different techniques. In order to analyze the geopolymers structure, the samples were immersed in acetone for 24 hours and then dried in an oven at 60°C for 5 hours to stop the reaction of geopolymerization [15].

The identification of the synthesized samples is presented in Table 2. The geopolymer sample is identified as G^x, where x is the Si/P molar ratio.

The chemical composition of the clay was determined by X-ray fluorescence (ARL 8400; XRF 386 software). The mineralogical composition of the clay and the synthesized geopolymers was identified by X-ray diffraction powder (DRX) with a BRUKER-AXS-D8-Advance powder diffractometer using Cu K_α radiations ($\lambda_{k\alpha}$ = 1.5418 Å); the analytical range was between 5 and 60° (2θ) at a rate of 1°/min. Crystallographic phases were identified with the JCPDS cards (Joint Committee Powder Diffraction Standard) and also with the High Score Plus software.

TABLE 2: The formulas of geopolymers samples.

Formulas	$G^{3.5}$	$G^{3.25}$	G^3	$G^{2.75}$	$G^{2.5}$	$G^{2.25}$
Si/P molar ratio	3.5	3.25	3	2.75	2.5	2.25

The infrared spectroscopy was carried out, on mixture added to KBr, to find the different chemical bands in 400–4000 cm^{-1} spectral range. A Perkin Elmer spectrum BX apparatus was used.

The phosphoric acid-based geopolymers samples were mechanically characterized by using LLOYD LR 50K PLUS device which is equipped with compressive test units. The testing rate used is 0.2 mm/min. Tests were performed on cylindrical samples having a diameter of 27 mm. Sample surfaces were previously polished to ensure the best surface quality (parallelism and planarity). All values of the compressive strength reported in this study are mean values over five tests under the same conditions.

3. Results and Discussion

3.1. Raw Materials Characterization. The chemical composition of the Tunisian clay (Medenine clay) used during this study is presented in Table 1. It is clear from these results that the weight percentage of silicon oxides is relatively high (SiO_2 = 60.8 mass%), probably indicating the presence of free silica and/or clay mineral type 2 : 1. In addition, this clay contains a considerable percentage of potassium (K_2O = 2.71 mass%), suggesting the presence of illite mineral. The high percentage of iron oxide (Fe_2O_3 = 5.87 mass%) is responsible for the characteristic red color of the clay. Finally, Medenine clay contains some CaO and MgO, which are probably related to the presence of dolomite [14].

The examination of the X-ray pattern of Medenine clay (Figure 1) indicates the presence of kaolinite and illite minerals, which are associated with nonclayey minerals such as quartz, muscovite, dolomite, gypsum, and hematite. This result is in accordance with those obtained by fluorescence X. Moreover, the comparison between the X-ray patterns of Medenine clay before and after calcination shows that all diffraction peaks related to kaolinite and gypsum disappeared after calcinations at 700°C for 5 hours, which proves the transformation of kaolinite into metakaolinite as well as the dehydration of gypsum. In addition, the peaks related to quartz, muscovite, illite, and hematite persisted after heat treatment. The persistence of illite and hematite has already been reported by He et al. [16] and Hosseini-Zori et al. [17], respectively.

TABLE 3: The principal IR bands and their corresponding species of raw and calcined clay.

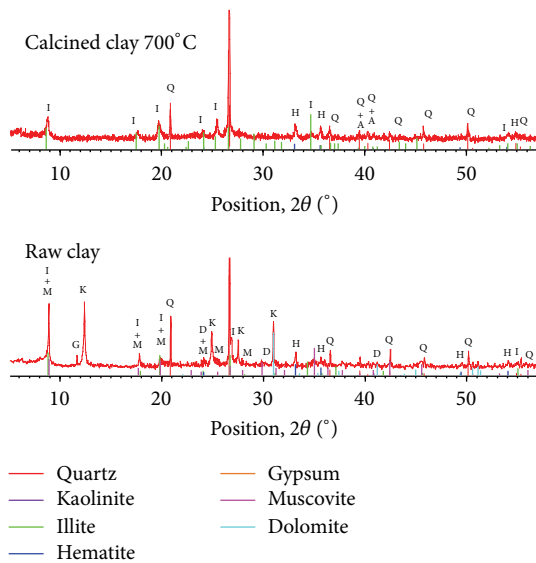| Medenine clay		Calcined Medenine clay	
Wavenumber (cm^{-1})	Corresponding species	Wavenumber (cm^{-1})	Corresponding species
3656, 3698	Hydroxyl groups (OH) of kaolinite	—	—
3624	Hydroxyl groups OH of illite	3624	Al-OH of illite
3434	OH of water	—	—
1648	H-O-H of water	—	—
1000, 1036, 1005	Si-O	1034	Si-O
470	Si-O	480	Si-O
789, 778	Doublet of quartz	789, 778	Doublet of quartz
536, 754	Al^{VI}-OSi, Al^{IV}-OSi of illite and kaolinite	—	—
694	Si-O-Si of quartz	694	Si-O-Si of quartz
912	Al-OH of kaolinite	—	—

FIGURE 1: XRD patterns of raw and calcined Medenine clay at 700°C for 5 hours. Q: quartz (00-046-1045), K: kaolinite (00-001-0527), I: illite (00-024-0495), H: hematite (00-024-0072), G: gypsum (04-009-3817), M: muscovite (00-001-1098), and D: dolomite (01-075-1655).

FIGURE 2: FTIR spectra of raw and calcined clay.

The differential thermal and thermogravimetric analysis (DTA-TG) of Medenine clay were already reported by Essaïdi et al. [14]. The thermograms have shown the appearance of five phenomena, four of which are endothermic and are as follows: the first one is related to the elimination of the free water at $T < 100$°C, the second one, at $T = 115$°C, resulted from the dehydration of gypsum, the third one occurring at approximately 480°C is attributed to the structural dehydroxylation of kaolinite and the formation of the amorphous phase, metakaolinite, and the fourth phenomenon at 700°C is correlated to the decarbonation of dolomite. In addition, an exothermic phenomenon at ~970°C may be attributed to the structural reorganization of metakaolinite.
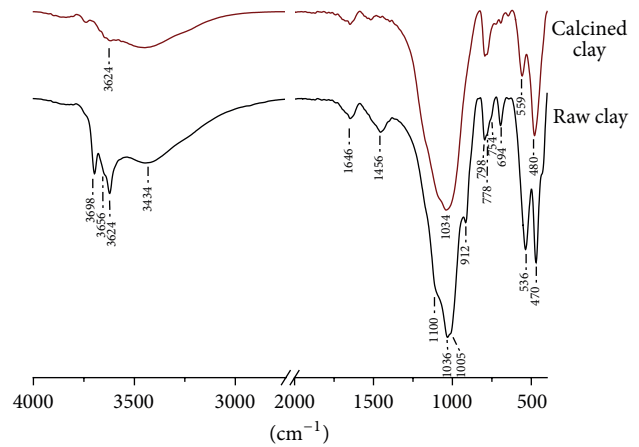
The infrared spectra of the raw and calcined clay are presented in Figure 2. The first spectrum indicates the presence of the characteristic bands of kaolinite and illite. The wavenumber of principal bands and their corresponding species are given in Table 3.

The characteristic bands of 3698, 3656, 3624, and 3434 cm^{-1} correspond to the stretching vibration of the hydroxyl groups (OH) of kaolinite and illite [18]. The other bands at 1005, 1036, 1100, and 470 cm^{-1} are those of Si-O bonds [18, 19]. In addition, the band located at 912 cm^{-1} attributed to the deformation vibration of Al-OH [19], and the bands at 754 and 536 cm^{-1} arise from the deformation vibrations of Al^{IV}-OSi and Al^{VI}-OSi [18, 19]. The presence of a doublet at 798 and 778 cm^{-1} and a single located at 694 cm^{-1} is attributed to the quartz vibrations [20]. This result is in accordance with that of XRD patterns.

The comparison of the clay IR spectra before and after calcination at 700°C in the spectral range between 400 and 4000 cm^{-1} shows the disappearance of O-H bands attributed to kaolinite and the reduction of those of illite (3624 cm^{-1}).
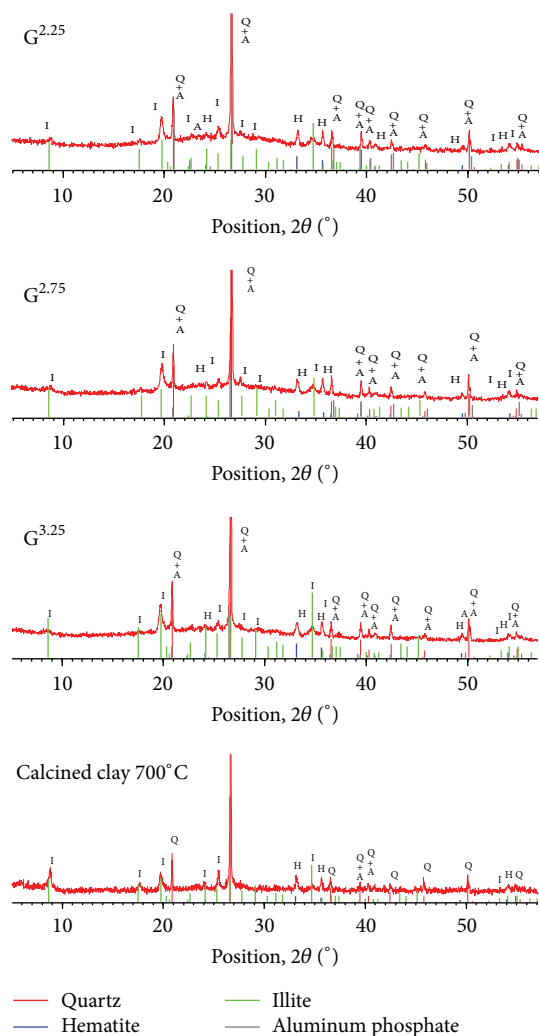
FIGURE 3: X-ray patterns of calcined clay and the obtained geopolymers G^x with different Si/P molar ratios (21 curing ages). Q: quartz (00-046-1045), H: hematite (00-024-0072), I: illite (00-024-0495), and A: aluminum phosphate (00-084-0853).

We also note that, after calcination at 700°C, between 1200 and 800 cm^{-1}, the various bands attributed to illite and kaolinite have been transformed into Q^4 to Q^1 silicates, which are in accordance with the effects of temperature [19]. Thus, we come to the conclusion that the calcination temperature at 700°C is sufficient to transform the kaolinite into metakaolinite, but for the illite, this temperature is not enough to transform this mineral to an amorphous material.

3.2. Geopolymers Characterization.
The mineralogical compositions of geopolymers samples determined by X-ray diffraction are shown in Figure 3. The XRD analysis of all geopolymers samples with different molar ratios proves the presence of quartz, illite, and hematite, which already exist in calcined clay. In addition, the XRD patterns of these geopolymer samples prove the presence of a diffuse halo between 25 and 35° characteristic of an amorphous material. When the Si/P molar ratio decreases, that is, when the amount of phosphoric

TABLE 4: The semiquantitative X-ray diffraction of the crystalline phases in the obtained geopolymers.

Green: illite, red: quartz, blue: hematite, and gray: aluminum phosphate.

acid increases, the halo diffuse intensity increases. This could be explained by the fact that when the amount of phosphoric acid increases, the dissolution step in geopolymerization process increases. Furthermore, the XRD analysis proves also the presence of new crystalline phases such as aluminum phosphate, which is formed during geopolymerization.

The semiquantitative X-ray analysis (Table 4) shows that the iron dioxide percentage (hematite) is the same (% Fe$_2$O$_3$ = 2) whatever the Si/P molar ratio is (2.25, 2.75, or 3.5). This may be explained by the noncontribution of hematite in the geopolymerization. Therefore, the hematite structure is not destroyed by the phosphoric acid and iron does not penetrate into the structure of geopolymers. In addition, the illite amount is relatively reduced (47 > 43 > 40%) when the Si/P molar ratio decreases, which indicates a slight contribution of illite in the geopolymerization reaction. This could be explained by the fact that a calcination temperature of 700°C is not sufficient to transform the illite mineral to an amorphous material, potentially reactive with phosphoric acid. As for the percentage of aluminum phosphate, it increases (22 < 28 < 30%) when the Si/P molar ratio decreases. This indicates the evolution of the dissolution phase during the geopolymerization process.

The infrared spectra of the phosphoric acid, calcined clay, aluminum phosphate, and synthesized geopolymers at different Si/P molar ratios are presented in Figure 4. The infrared spectra of all geopolymers samples indicate (i) the disappearance of the metakaolinite bands (480 and 559 cm^{-1}), (ii) the persistence of illite bands (3624 cm^{-1}), and (iii) the appearance of new bands which are related to other species. The appearance of the bands characteristic of stretching and deformation vibration of O-H and H-O-H groups at 1648 and 3395 cm^{-1}, respectively, indicates the presence of free water molecules. The amount of this water seems to increase when
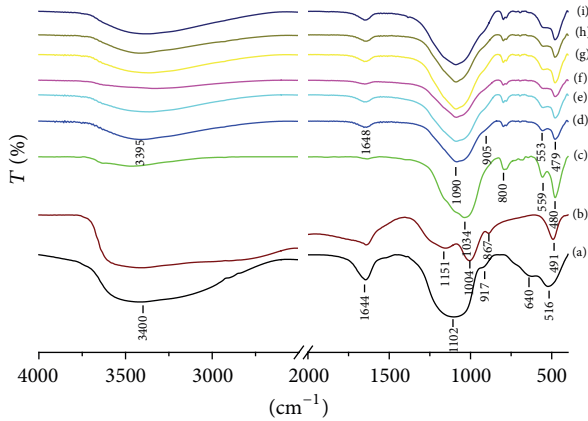
Figure 4: Infrared spectra of calcined Medenine clay at 700°C, phosphoric acid 85%, aluminum phosphate, and geopolymers at different molars ratios Si/P(G^x). (a) AlPO$_4$, (b) AP (85%), (c) calcined clay 700°C, (d) $G^{3.5}$, (e) $G^{3.25}$, (f) G^3, (g) $G^{2.75}$, (h) $G^{2.5}$, and (i) $G^{2.25}$.

Figure 5: Compressive strength evolution of the phosphoric acid-based geopolymers G^x at 21 curing days for different Si/P molar ratio.

the molar ratio Si/P increases. Furthermore, the band at 1034 cm^{-1} in the spectrum of calcined clay is shifted about 56 cm^{-1} to larger wavenumber, after geopolymerization reaction. This result proves that a change in the microstructure occurred during the geopolymerization reaction and led to the formation of new products with a microstructure different from that of calcined clay. According to Figure 4, the large band at 1090 cm^{-1} for geopolymers spectra is the result of the linked bands between Si-O symmetrical vibration, P-O vibration, and Al-O bands. So the obtained products are Si-O-Al-O-P oligomers. Moreover, after the geopolymerization reaction, the band located at 559 cm^{-1} in the spectrum of calcined clay attributed to Si-O-Al shifted to 553 cm^{-1}. It is clear that its intensity increases when the amount of phosphoric acid increases. It is noteworthy that the shift may be the consequence of the partial replacement of SiO$_4$ tetrahedron by PO$_4$ during the process, which suggests a change in the local chemical environment. However, when the molar ratio Si/P decreases, that is, when the amount of phosphoric acid increases, the intensity of the bands located at 479 cm^{-1} in the infrared spectra of geopolymers increases. This would probably be explained by the consumption of Si-O monomers and the formation of oligomers type Si-O-P. In addition, the appearance of a new band at 905 cm^{-1} for all geopolymers samples indicates the incorporation of P-O band in the structure of geopolymers. Finally, a slight modification took place for the intensity of the shoulder of illite located around 830 cm^{-1}. This indicates the modest contribution of the illite present in the starting calcined clay to geopolymerization process. These results are in accordance with those obtained by X-ray diffraction.

The results of the mechanical properties of geopolymers after 21 curing days are presented in Figure 5. The latter shows that when the Si/P molar ratio decreases, the compressive strength increases until a maximum value (37 MPa) when the molar ratio (Si/P) equals 2.75. Beyond this ratio, the mechanical strength decreases. For higher Si/P molar ratios,
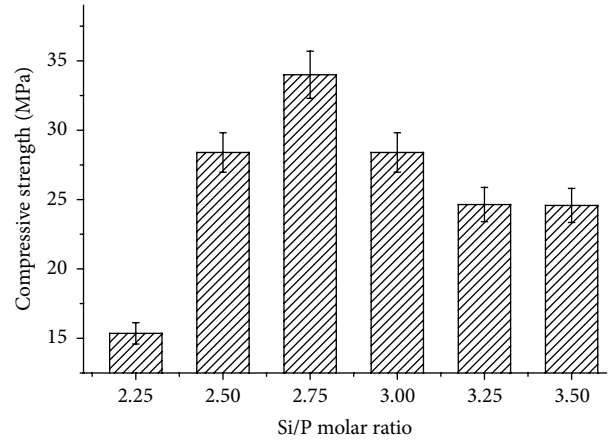
corresponding to relatively small amount of phosphoric acid, the mechanical strength is low because the dissolution phase is not completed. This is due to the deficiency in the amount of the phosphoric acid. For the molar ratio Si/P = 2.75, the compressive strength is maximum, because the amount of phosphoric acid is sufficient enough to complete the dissolution step. For this Si/P ratio, the charge balance is assured because the corresponding numerical ratio AlO$_4$/PO$_4$ = 1 [9]. For lower Si/P molar ratios, the large amounts of phosphoric acid lead to an excess in PO$_4^{3-}$ which improves the dissolution of the geopolymerization process to be more disordered. Consequently, the mechanical properties decrease due to the unbalanced charges [7].

These results are in accordance with those obtained by the SEM (Figure 6) which indicates that the structure of the obtained geopolymers becomes denser, when the Si/P molar ratio decreases from 3.25 to 2.75. For lower Si/P molar ratio, the structure is less dense (Figure 6).

4. Conclusion

The properties of the phosphoric acid-based geopolymers obtained through using calcined illito-kaolinitic clay at 700°C sieved at 125 μm as an aluminosilicate precursor for making geopolymers are affected by the variation of the Si/P molar ratios. The main findings of this study are the following:

(i) When the Si/P molar ratio decreases, the diffuse hallo in the XRD geopolymer spectra, that is, the amorphous phase content, increases.

(ii) In addition to the amorphous phase, geopolymer XRD analyses show the presence of AlPO$_4$ as a product of geopolymerization reaction.

(iii) The infrared spectra of geopolymers samples show that the geopolymerization product has a polymeric Si-O-Al-O-P structure.

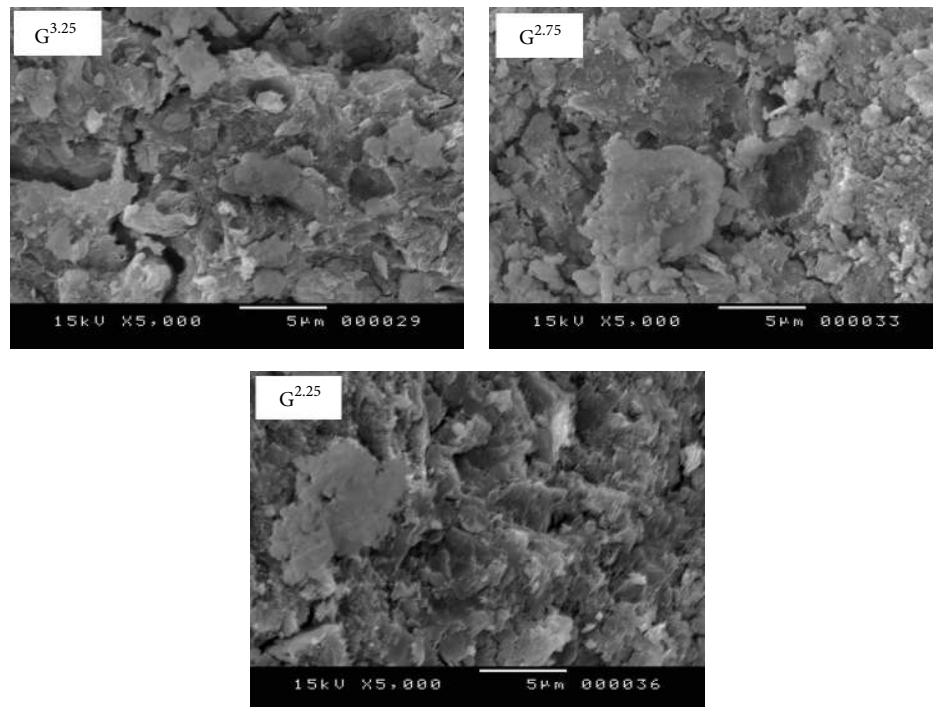(iv) The contribution of illite in the geopolymerization process is relatively low.

FIGURE 6: SEM microcrographs of phosphoric acid-based geopolymers at different Si/P molar ratios.

(v) The mechanical strength of geopolymer attains a maximum (37 MPa) for Si/P molar ratio equal to 2.75, which corresponds to a molar ratio Al/P = 1.
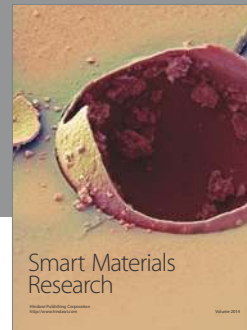
Competing Interests

The authors declare that they have no competing interests.

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