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MICROSTRUCTURAL ANALYSIS OF AMBIENT CURED PHOSPHATE BASED-GEOPOLYMERS WITH COAL-ASH AS PRECURSOR

An alternative for Ordinary Portland cement (OPC) consumption is the production and integration of green cement. In other words, the clinker consumption has to be replaced with new low-carbon binders. A possible solution was introduced by the geopolymerisation technology. However, the alkaline activation of geopolymers offers the possibility of obtaining greener materials with high properties, superior to OPC, but due to the high price of sodium silicate, their industrial use is limited. In the past few years, a new activator has been discovered, namely phosphoric acid. This study approaches the obtaining of coal ash-based geopolymers activated with acid solution cured at room temperature. Accordingly, phosphoric acid, 85% by mass, was diluted in distilled water to obtain a corresponding activation solution for H_3PO_4/Al_2O_3 ratio of 1.0 and two types of geopolymers were ambient cured (22°C ±2°C). Moreover, to evaluate the geopolymerisation potential of this system (coal ash – phosphoric acid), SEM and EDS analysis was performed to investigate their morphologic characteristics.

Keywords: Acid activation; coal ash; microstructural analysis; phosphate based geopolymers

1. Introduction

Currently, the evolution on the industrial scale of geopolymerisation technology is severely limited by the lack of standardization and, more important, high production costs [1,2]. Even, these materials exhibit superior properties to OPC which boost their development and interest for the space industry, automotive manufacturing, medical devices, water treatment applications etc.[3], their main field of application is still limited to civil engineering [4,5]. However, due to their green characteristics and simplicity in manufacturing [6,7], the research interest on this topic is still growing, therefore, multiple projects are focused on standardization development [8], while a considerable number of studies have the main goal to reduce the geopolymers manufacturing cost by replacing the conventional sodium/potassium/lithium silicate with other, cheaper, activators [1,9,10].

According to previous publications, the activator with the highest success is phosphorous acid. H.K. Tchakoute et al. [11] synthesized metakaolin based geopolymers using as hardeners phosphoric acid solution and sodium waterglass. According to their study, the acid-activated geopolymer indicated the formation of a new phase, berlinite ($AlPO_4$), which was dispersed in the matrix positively influencing the mechanical characteristics of the samples. Moreover, both types of hardeners successfully dissolute the metakaolin, resulting in a homogenous and compact matrix. Based on compressive test results, the geopolymers activated with H_2PO_4 solution exhibited a 53% higher value than the alkaline activated one. The increased compressive strength was related to the conversion of oxonium complex in Si-OH and Si-O-PO(OH)$_2$ units due to the $H_2PO_4^-$ presence.

In another study, S. Louati et al. [12], evaluated the microstructural and mechanical characteristics of illito-kaolinitic clay-based geopolymers. Moreover, the influence of the Si/P ratio on compressive strength and structure density was reported. Accordingly, it was found that by increasing the Si/P ratio up to 2.75 (Al/P ratio of 1) better mechanical characteristics can be obtained, besides an increase in the samples crystallinity, i.e. higher contents of amorphous phase are presented in samples with low Si/P ratio. Based on the infrared spectra, the obtained samples contained Si-O-Al-O-P polymeric structure. Additionally, it was observed that the illite addition has a low effect on metakaolin based geopolymers. Hui L. et al. [13], studied the

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reaction mechanism of H_3PO_4 activated metakaolin based geopolymers. According to their publication, compressive strengths up to 120 MPa can be achieved by a two-stage curing process (40°C for 24 h and 60/80°C for 25 h, respectively). Moreover, higher acid concentration and/or curing temperature will accelerate the dealumination of metakaolin and condensation of silicate tetrahedrons, respectively. Therefore, the reaction mechanism consists of dissolution of Si and Al phases, formation of Al-O-P, Si-O-P and Si-O-Si units, upon PO_4^{3-} consumption. Finally, the compact structure will result due to the connection of Si or Al units with $P(OAl)_x(H_2O)_{4-x}$. Accordingly, the empirical formula of alkali-activated geopolymers (eq. 1) is different from the one of acid-activated geopolymers (eq. 2) [14].

$$M^+{}_n[-(SiO_2)_z-AlO_2-]_n \cdot mH_2O \qquad (1)$$

$$[-(Si-O)_z-Al-O-P]_n \cdot mH_2O \qquad (2)$$
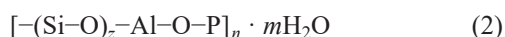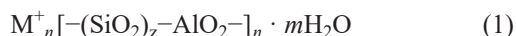
where M is the alkali cation of K^+, Li^+ or Na^+, n is the degree of geopolymerization, z can be 1, 2 or 3 depending on the Si/Al ratio and m is the amount of water [15].

Another important difference between the acid and alkali-activated geopolymers is related to their molecular structure. In those based on acid, structural chains or rings are created as multiple oxyanions of $[PO_4]^{3-}$, $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ joined by sharing edges or corners. Therefore, polyoxyanions, as MO_n polyhedra, will occur in polyphosphates, pyroxenes and other complex structures [16,17]. In other words, the synthesis seems to be based on structures created between P and Si or P and Al, not P, Si and Al. On contrary, those alkali activates consist of N-A-S-H and C-A-S-H gels, which molecules include both Si, Al and the activator in the same structure [18,19].

In summary, multiples researcher focused their efforts on developing new acid based geopolymers with superior mechanical characteristics compared to alkali-activated ones. However, most of them, approach the influence of curing conditions (using temperatures above 60°C) or activator concentration (Al/P ratio) on metakaolin as raw material, while very few approach blended systems (metakaolin mixed with fly ash or another aluminosilicate source). Therefore, considering the environmental aspects (kaoline is a natural material, while elevated curing temperature significantly influences the carbon footprint) a more in-depth analysis of ambient cured geopolymers, especially, those based on wastes is necessary. Accordingly, this study aims to analyse the microstructure and chemical distribution of coal ash-based geopolymers cured at ambient temperature (22°C), compared to those cured at slightly high temperature (70°C).

2. Materials and methods

The obtained geopolymer was manufactured by mixing the raw material with a commercially available acid solution of o-phosphate (H_3PO_4) with 85 wt% solid content. The solid to liquid ratio was optimized to assure an Al/P ratio of 1, for both types of geopolymers (coal ash-based and coal ash mixed with metakaolin based geopolymer).

2.1. Materials

2.1.1. Coal ash

Local Coal ash has been collected from CET II – Holboca, Iasi, Romania [1]. The collected powder was dried and sifted (only particles with a diameter lower than 100 µm have been used) in order to remove the effect of water addition and large impurities, respectively. The drying method has been presented in [20], while the sifting method has been presented in [7].

According to the chemical composition analysis, performed by X-ray fluorescence, the coal ash used as raw material belongs to class F fly ashes. Moreover, as can be seen from the microstructural analysis (Fig. 1), the aluminosilicate waste is a mixture of fly ash and bottom particles, as there can be seen spherical and irregular porous particles, respectively.
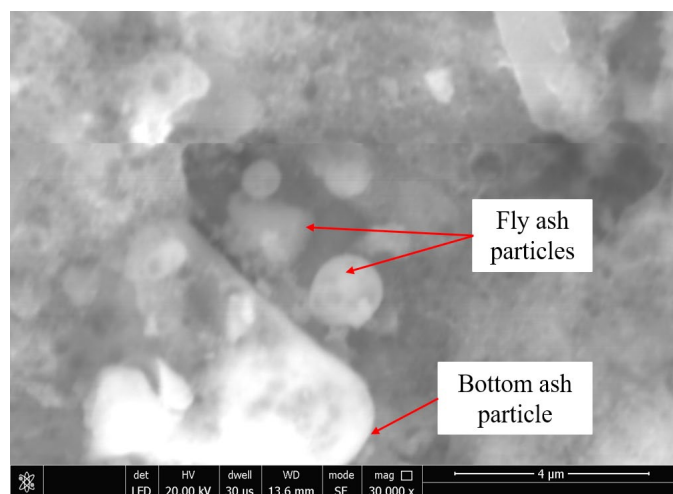

Fig. 1. The morphology of coal ash used in this study shows fly ash and bottom ash presence

Thermal power plant ash is a mineral residue, with small particles, in the range of 0.01 to 300 µm, which results from coal burning in thermal power plants. The oxides with the highest concentrations in their composition are silicon dioxide, aluminium oxide, iron oxide and calcium oxide. However, its chemical composition varies depending on the nature of the coal and the process in the furnace, the degree of separation of particles from the exhaust system. For these reasons, the analysis of its chemical composition is very important, especially, due to its significant influence on the final characteristics of geopolymers.

2.1.2. Metakaolin

The metakaolin used in this study was obtained by low-temperature calcination (heating up to 700°C at 10°C/min rate, and maintaining at 700°C for 30 min.) of commercially available kaolin clay [21], leading to the conversion of the starting material into aluminosilicate source with high pozzolanic activity.

Oxide composition of raw materials, metakaolin (MK) and coal ash (CA)

	Oxide	SiO_2	Al_2O_3	Fe_xO_y	CaO	K_2O	MgO	TiO_2	Na_2O	P_2O_5	Oth.*
MK	%, Wt.	52.8	43.1	1.2	0.7	0.5	0.2	0.9	-	0.2	0.4
CA	%, Wt.	47.8	28.6	10.2	6.4	2.4	2	1.3	0.6	0.4	0.3
Oth.* – oxides in a concentration lower than 0.1% (traces of S, Cl, Cr, Zr, Ni, Sr, Zn and Cu).											

According to the chemical analysis of the metakaolin (TABLE 1), it contains a high concentration of silicon and aluminium oxides.

2.1.3. Activator solution

As an activator, an acid solution of o-phosphate (H_3PO_4) with 85 wt% was diluted in distilled water to obtain a corresponding activation solution for an H_3PO_4/Al_2O_3 ratio of 1.0. According to previous studies [12,13], this ratio exhibits the best performance in terms of the compressive strength of obtained geopolymers.

Using the materials presented above, two types of geopolymers have been synthetized. The geopolymer with coal ash (CA) in 100% of the solid component and the geopolymer with 50% coal ash (by mass) and 50% (by mass) metakaolin (CA_MK) were activated with a phosphorous solution at a solid/liquid ratio of 0.9 (to assure workability). Moreover, to assure better homogeneity, the geopolymer with metakaolin and coal ash was mixed in a dry state for 2 minutes, and for 5 minutes after liquid addition, according to the procedure presented in [18,19].

2.2. Methods

The raw materials were investigated by X-ray fluorescence using an XRF S8 Tiger equipment (Bruker GmbH, Karlsruhe, Germany), to estimate their chemical composition. Their microstructure was analysed using Scanning Electron Microscopy (SEM, FEI Quanta 200, Netherlands), while the elemental distribution on the fracture surface was studied with the energy-dispersive X-ray spectrometer (EDX) equipped on SEM.

3. Results and discussion

The structure of geopolymeric materials can be correlated with their mechanical characteristics [22-23]. Therefore, if the morphological analysis of the samples reveals a compact structure with a high degree of dissolution and a low number of pores, then it is expected that the compressive strength of that sample will be higher than that with low structural homogeneity [24-25]. Among the most important structural parameters, with significant influence on mechanical properties, are porosity, especially large pores, the appearance of cracks and the number of unreacted particles [26-27]. Therefore, the microstructural analysis of the obtained samples focused exactly on the study of these parameters.

At 100× (Fig. 2a), the CA sample exhibit o highly porous matrix, with large pores distributed on its surface. Also, it can be observed that, at room temperature, using coal ash as a precursor, the structure of geopolymers will adopt an understandable structure full of small grains scattered on the surface. At higher magnification (Fig. 2c) these grains seem to have different shapes and dimensions. Moreover, most of them show diameters lower than 100 μm, but there are also, many that have reacted due to the activator presence. Accordingly, the partially reacted zones (Fig. 2e), i.e. the dissolved particles, will result in a geopolymer with low mechanical characteristics and high porosity. Also, at 1000× it can be seen that the morphology specific to the initial coal ash particles has been changed (the porous particles have been converted into glassy grains).

The geopolymer with metakaolin addition exhibited a compact structure with fewer large pores, but smaller in diameter (Fig. 2b), compared with the CA sample, where pores with a diameter close to 300 μm can be observed. Moreover, the sample surface also exhibits few cracks, which can occur due to water evaporation during ageing or sample preparation for fracture analysis. At higher magnification (Fig. 2d), it can be seen that the coal ash particles have been partially embedded by the metakaolin matrix, as there are few visible distinct particles on the analysed surface. However, at 1000× (Fig. 2f) it can be that few coal-ash particles didn't dissolute in the acid environment. Moreover, a higher porous matrix can be observed, with small grains (coal ash particles) bonded in a dissolute metakaolin matrix.

Figure 3 shows the elemental distribution on the surface of the studied samples. As can be seen, the coal ash-based geopolymer exhibits an inhomogeneous chemical distribution. This observation can be correlated with the incomplete dissolution of the raw material, as shown in the microstructural analysis.

Compared to the CA sample, the elemental distribution of the CA_MK sample, exhibit higher homogeneity, accordingly it can be observed that Al and P elements are uniformly distributed on the entire surface. However, by overlapping the Al mapping with P mapping, it can be seen that the highlighted areas of Al (the zones with the higher concentration) are different than those of P. Therefore, the compounds created during activation are Al-O-P and Si-O-P, not common compounds of Si-O-Al-P.
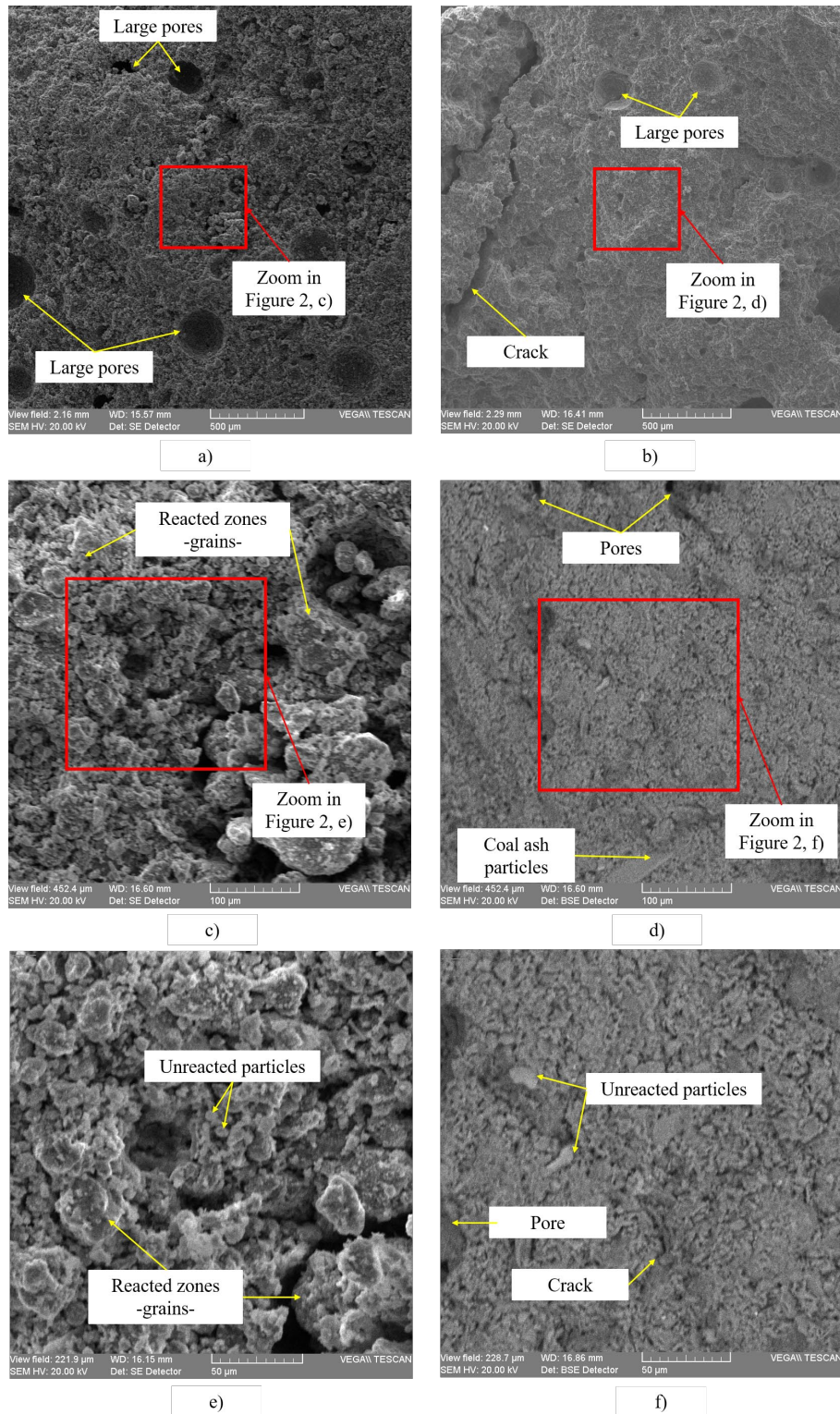
Fig. 2. The micromorphology of acid-based geopolymers at different magnifications: a) CA sample at 100×; b) CA_MK sample at 100×; c) CA sample at 500×; d) CA_MK sample at 500×;e) CA sample at 1000×; f) CA_MK sample at 1000×

4. Conclusions

Two types of geopolymers have been obtained using phosphorous acid as an activator and coal ash or coal ash mixed with metakaolin as an aluminosilicate source.

In the case of acid-based geopolymers, coal ash as a precursor resulted in a highly porous structure, therefore, a geopolymer formed of multiple unreacted coal ash grains wrapped in the geopolymeric matrix. Moreover, due to the phosphorous acid, the porous morphology of the initial particles has been changed to a glassy grains structure.
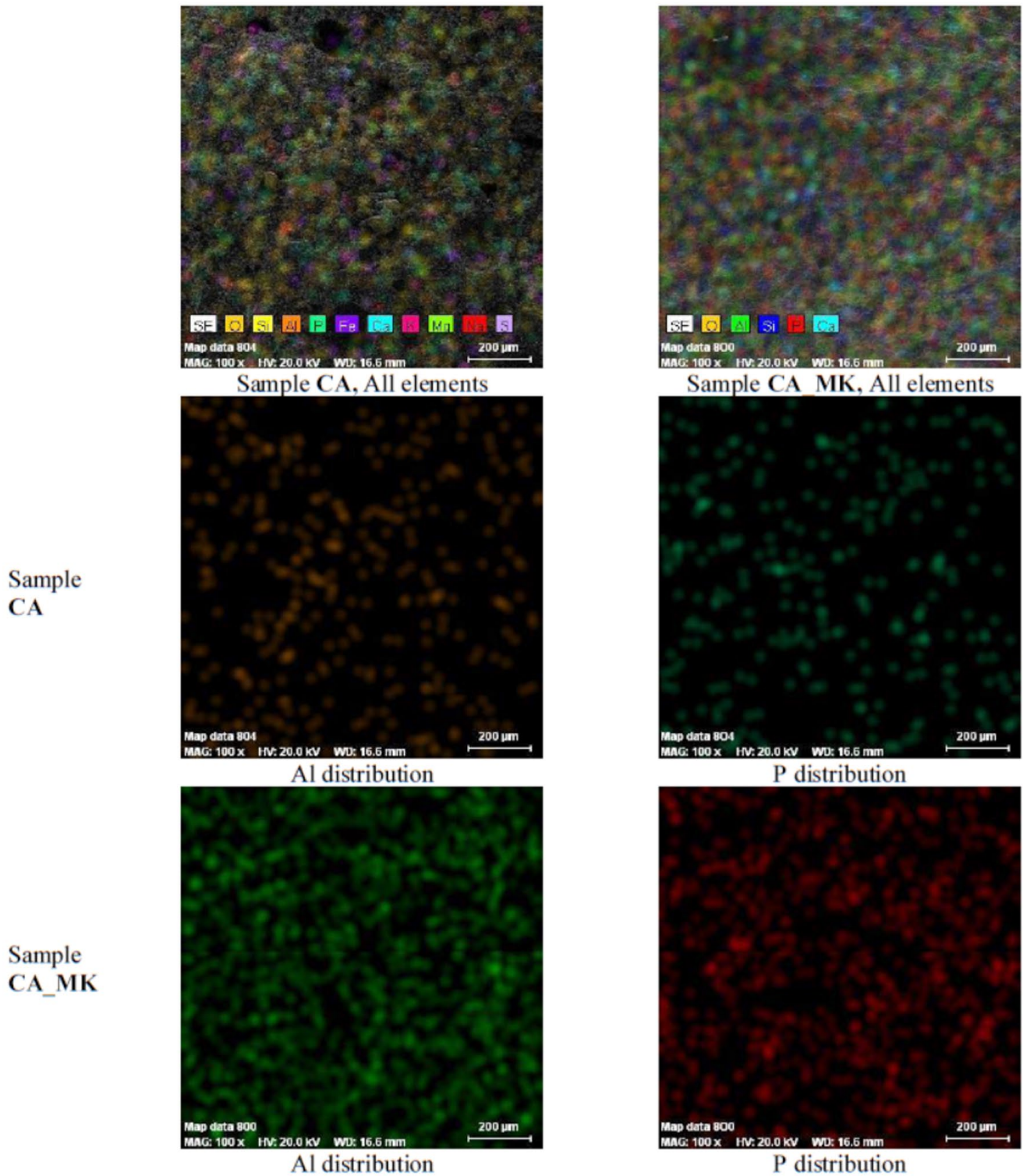
Fig. 3. Elemental distribution on obtained geopolymers surface: Al and P distribution on the surface of CA and CA_MK samples

The geopolymer with coal ash and metakaolin exhibited a denser structure, with fewer pores, smaller in diameter. Also, the metakaolin was better dissolved by the activator embedding the coal ash particle.

Accordingly, future studies should be focused on coal ash processing (mechanical activation), in order to obtain acid-activated geopolymers with compact structures (high dissolution degree and low porosity).

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