

Study of the Influence of Na_2CO_3 and H_3PO_4 Activators on the Mechanical and Mineralogical Properties of Geopolymer Based on Coal Waste-fly Ash

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Abstract

This work aims to compare the mechanical and mineralogical properties of coal waste and fly ash based geopolymers obtained in the same conditions using sodium carbonate (Na_2CO_3) and phosphoric acid (H_3PO_4) solutions as diverse activators. Na_2CO_3 solutions with 3.5% and 5% mass ratios were prepared by dissolving Na_2CO_3 powder (99.9%) in deionized water. On the other hand, three H_3PO_4 solutions with molar concentrations of 4, 6, and 8 M were prepared by dilution of the commercial H_3PO_4 (85%) in distilled water. Both types of alkaline and acidic solutions were used to produce geopolymers from the coal waste which is systematically replaced by fly ash (0, 15, 25, and 35 wt.%). The geopolymers were obtained by adding each of the prepared solutions to the blend with a liquid/solid ratio of 0.5 and 0.6 for the alkaline and acid solutions, respectively. The mechanical tests of cubic samples after 28 days of curing showed that the compressive strength of phosphate-based geopolymers is 5.33 MPa while that of alkali-based geopolymers is 5.14 MPa. The strength increases with the increase of the activator concentration. The mineralogical analysis of cured samples after 28 days showed the formation of berlinite (AlPO_4) in the structure of the phosphate-based geopolymer which is dispersed in the matrix and contributes to the strength. For alkali geopolymers, X-ray diffraction results showed the existence of Portlandite crystalline phase and the N-A-S-H gel type.

Keywords

Coal waste, Fly ash, Sodium carbonate, Phosphoric acid, Geopolymer

Introduction

Since ancient times, the use of traditional binders such as cement is still very popular. However, the Portland cement market is shown that the production of each ton of this binder generates approximately one ton of carbon dioxide which makes it responsible for 8 - 10% of global greenhouse gas emissions [1-4]. On the other hand, industrial waste causes many environmental problems that jeopardize the vital needs of all living beings because of serious impacts such as the deterioration of the quality of water and air [5, 6]. To solve this problem, many studies have been carried out in order to use the waste in the construction industry.

In this context, the recycling of mining and industrial waste has become more and more indispensable operation because of its socio-economic benefits. In particular, some recent studies are interested in the recycling of coal waste for ecological and economic reasons. Coal wastes are considered as hazardous materials for the environment. Their accumulations occupy large land field areas for storage and cause a source of contamination of soil, air and water [7, 8]. These coal wastes consist of a mineral part which is extremely important for the reuse

in construction materials [9]. Other studies show that thermal power plants are generating huge quantities of fly ash. This creates a huge burden on solid waste management [10]. Fly ash is an ash separated from the flue gas of a power station burning pulverized coal. It is a fine particulate material deposited from the stack gases of industrial furnaces burning solid fuels such as coal [11, 12]. Coal waste and fly ash are considered as a source of silica and alumina which are the basis of the geopolymer materials [13, 14]. Geopolymers are considered to be the new generation of binders that have attracted a lot of attention in recent years [9]. They are formed when an aluminosilicate precursor (kaolinite [15], metakaolin [16], fly ash [13], slag [17], and coal waste [18], etc.) is activated by an alkaline (NaOH , KOH , Na_2CO_3 , etc) [19] or acid (H_3PO_4 , HCl , etc.) [20] solutions.

These inorganic polymers are essentially chains or networks of amorphous mineral molecules linked together by covalent bonds. These mineral compounds are made from molecular units such as (-Si-O-Si-O-) siloxo, (-Si-O-Al-O-) sialate, (-Si-O-Al-O-Si-O-) sialate-siloxo, (-Si-O-Al-O-Si-O-Si-O-) sialate-disiloxo, (-P-O-P-O-) phosphate, (-P-O-Si-O-P-O-) phospho-siloxo, or (-P-O-Si-O-Al-O-P-O-) phospho-sialate [21, 22]. They are formed by the geopolymerization process at room temperature. In alkali activation, there is a rapid dissolution of the aluminosilicate source with the formation of aluminates and silicates which were then linked to each other to form three-dimensional structures [23]. While, in geopolymers based on H_3PO_4 , the positive charges of the $[\text{PO}_4]$ tetrahedral were balanced by the negative charges of the $[\text{AlO}_4]$ tetrahedra, and therefore the neutrality was maintained [24]. According to various studies, acidic geopolymers had a superior performance with better mechanical, thermal and dielectric properties compared to alkaline geopolymers [25, 26]. The activation with H_3PO_4 of the aluminosilicate precursor can significantly improve the microstructure of the material by densifying its porous system and consequently improve its mechanical and dielectric properties [27, 28].

The present paper investigates the use of coal waste in combination with fly ash as a new aluminosilicate source for the elaboration of geopolymers at the laboratory scale. In this preliminary work, we are interested in the comparison of the mechanical and mineralogical properties of coal waste-fly ash based geopolymers made from Na_2CO_3 and H_3PO_4 solutions as reactive ingredients, which are prepared under the same conditions.

Materials and Method

Materials

All raw materials are local materials; from different regions of Morocco. Coal waste was sampled from the ground of the landfill of the mine of Jerada. The sample was dried in an oven for 24 h at 80 °C to remove the humidity, after which it was ground using a hammer mill to produce a fine powder with d_{50} 45 μm . Fly ash that comes from Jorf Al Asfar thermal power station in El Jadida Province in the form of fine powder (d_{50} 25.13 μm) has been used. Limestone used in this work, to

provide a source of calcium to the formed geopolymer binder, was ground using an agate mortar. Sieving was done using a standardized sieve with a diameter of 0.5 mm, in order to obtain a fine powder (d_{50} 17.36 μm). Table 1 gives the chemical compositions of the raw materials used in this work. The main coal waste chemicals and fly ash are observed to be SiO_2 , Al_2O_3 and Fe_2O_3 with traces of CaO , P_2O_5 and MnO_2 , while limestone is essentially formed from calcium oxide CaO . Materials used are nanoscale.

Table 1: Chemical composition of raw materials.

Oxide (Wt.%)	Coal waste	Fly ash	Limestone
SiO_2	52.18	51.58	13.93
Al_2O_3	21.59	22.60	1.34
Fe_2O_3	4.66	7.23	1.49
CaO	0.56	4.55	45.12
MgO	0.99	2.10	0.78
SO_3	0.97	0.21	0.23
K_2O	2.95	2.89	0.21
TiO_2	-	0.59	0.16
MnO	0.09	0.07	0.07
P_2O_5	0.08	1.20	0.25
Na_2O	-	0.04	0.04
SrO	-	-	0.05
L.O.I	14.22	6.4	35.84

X-ray diffractograms of the raw materials are shown in figure 1. The X-ray patterns showed a highly crystalline structure in the coal waste phases; mainly quartz (silica), clays (muscovite, illite, and clinocllore), and gypsum. For fly ash, the presence of amorphous hump located between 13° - 40° (2 θ), as well as crystalline phases such as quartz and mullite is noted. The two main mineralogical phases of limestone are calcite and quartz.

Methods

H_3PO_4 solutions were prepared by diluting commercial H_3PO_4 (85%) in distilled water to obtain chemical reagents with molar concentrations of 4, 6, and 8 M. The prepared solutions obtained are stored in tightly closed glass bottles and left at room temperature before use in order to completely dissolve the commercial H_3PO_4 and produce H_2PO_4^- ions necessary for the second step of the geopolymerization. Alkaline Na_2CO_3 solutions were prepared by dissolving Na_2CO_3 powder in deionized water until completely dissolved. The Na_2CO_3 content is 3.5% and 5% by weight of the powder mixtures.

After the first step of preparing the raw materials, proportions were proposed to formulate four mixtures. Table 2 shows the proposed proportions.

The two geopolymer materials were prepared by gradually

Table 2: Composition of blended mixtures (Wt.%).

Mixture	Coal waste	Fly ash	Lime
E1	95	-	5
E2	80	15	5
E3	70	25	5
E4	60	35	5

adding each activator to the solid mixture in a porcelain mortar and mechanically mixed for 5 min. The liquid/solid

mass ratio for all samples was kept constant at 0.60 for acidic geopolymers and 0.50 for alkali geopolymers. The binders were poured into cubic molds (5 x 5 x 5 cm). The samples were kept at room temperature for 2 h, and then preserved at 60 °C in an oven for 24 h. The two geopolymer types obtained were unmolded and kept at room temperature for 7 and 28 days before the compressive strength tests.

The comparison of mechanical and mineralogical properties of different binders made from alkaline and acidic activators was evaluated by measuring compressive strength and X-ray diffractometry. Compressive strength was measured using a testing machine Controlab with a compression capacity of 25 kN and a loading rate of 1.6 kN/s. After measuring the compressive strength, the fragments of each specimen were collected. A part of these fragments was finely ground and the powders obtained were used to measure the X-ray diffractometry for the 28-day curing age.

Results and Discussion

Compressive strength

Acid-based geopolymers

The compressive strength of phosphate-based geopolymers as a function of the molar concentration of H_3PO_4 solutions measured at 7 and 28 days is illustrated in figure 2.

In general, the compressive strength increases with increasing curing time from 7 to 28 days and with increasing concentration of H_3PO_4 . At 7 days, the compressive strength increased with the increase in the concentration of the H_3PO_4 solutions from 1.70 to 3.5 MPa for the specimens E1 and E4 prepared with 4 to 8 M, and from 2.53 to 5.33 MPa for the 28-day tests. The low compressive strengths of the specimens observed for the three concentrations could be related to the excess of water in the reaction medium which inhibits the total dissolution reaction of the precursor [29]. This excess of water does not react during the geopolymerization process and remains outside the network, and therefore, escapes during hardening, leaving more pores in the geopolymers and subsequently a decrease in the resistance. This free water

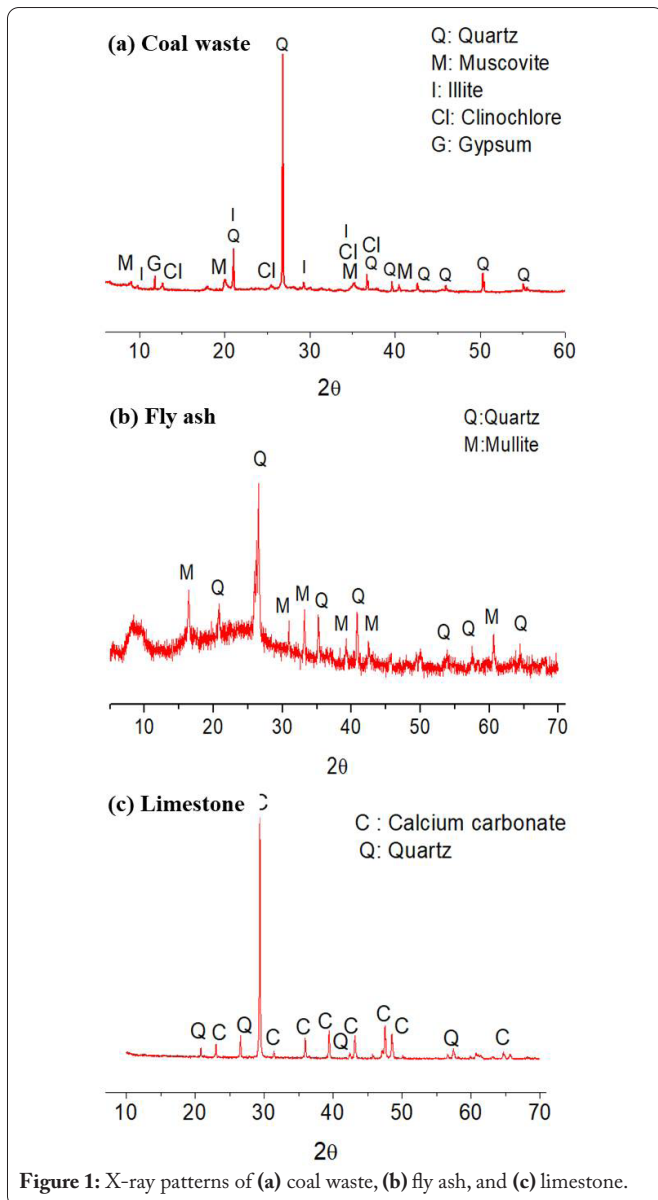


Figure 1: X-ray patterns of (a) coal waste, (b) fly ash, and (c) limestone.

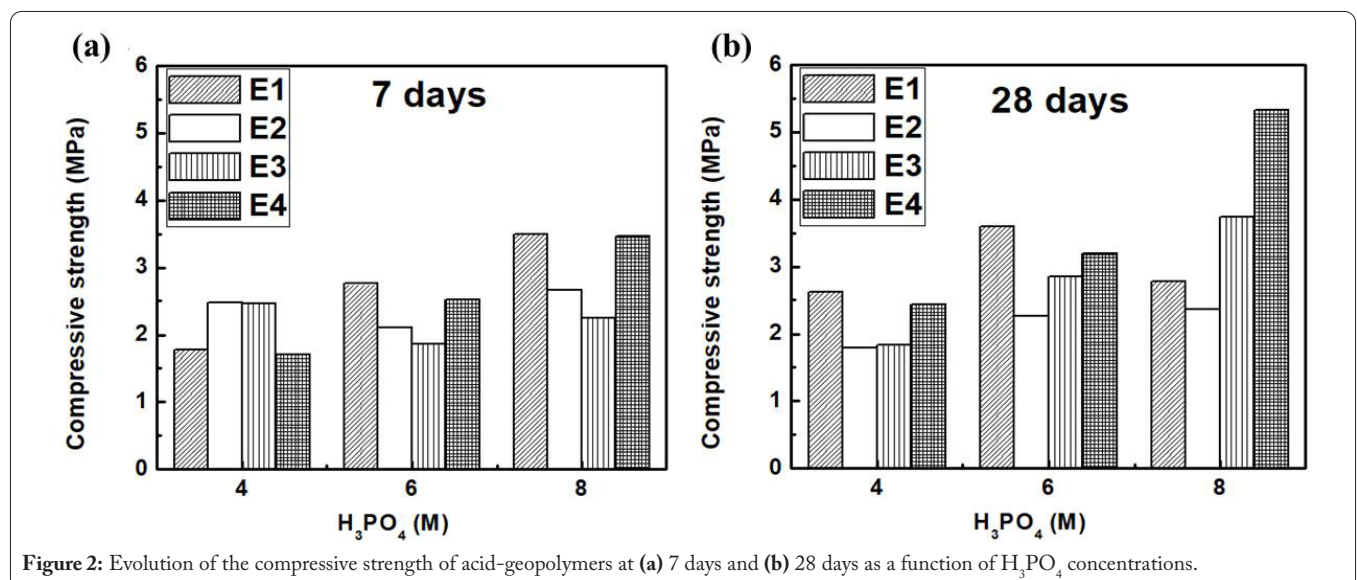


Figure 2: Evolution of the compressive strength of acid-geopolymers at (a) 7 days and (b) 28 days as a function of H_3PO_4 concentrations.

that is not chemically combined with the network implies the low dissolution of raw material suggesting more particles of the unreacted aluminosilicate material in these samples [30]. The difference in compressive strength can be interpreted by the formation of berlinite (AlPO_4) in the structure of the phosphate-based geopolymer, which acts as filler and reinforces the structure, thus improving the compressive strength of the specimen. This is confirmed by the X-ray diffraction results which indicated the presence of a crystalline phase in the form of berlinite. In conclusion, the compressive strength of the geopolymer is related to the porosity and the water content, the latter plays an important role with regard to the pore size. The lower the water content in the suspension, the smaller the final pore size is.

For the 28-day tests as shown in figure 3, it can be seen that for 8 M, the compressive strength increased slightly when the fly ash fraction increases and the coal waste decreases. Contrary to the concentrations of 4 M and 6 M, the compressive strength reached its maximum value for the sample with no fly ash. It can then be concluded that the addition of fly ash improved the compressive strength for high H_3PO_4 concentrations and for a fairly long curing time. The compressive strength reached its maximum at 28 days (about 5.33 MPa) for the sample with fly ash (35 wt.%) and H_3PO_4 (8 M).

Alkali-based geopolymers

Results of the 7 and 28 days compressive strength tests of Na_2CO_3 alkali-activated materials are shown in figure 4. The precursor reactivity is influenced by the Na_2CO_3 . At 7 days, and for a content of 3.5 wt.% Na_2CO_3 , it can be seen that the compressive strength increased slightly when the fraction of fly ash increases and the coal gangue decreases. Unlike for Na_2CO_3 content of 5 wt.%, the compressive strength showed higher values for higher coal waste fraction; values of 3.78 and 3.82 MPa are obtained for the sample with coal gangue alone (E1) and E2 sample containing 15 wt.% fly ash, respectively.

At 28 days, a minimum value of 3.42 MPa can be observed for sample E3 when Na_2CO_3 content of 3.5% was used.

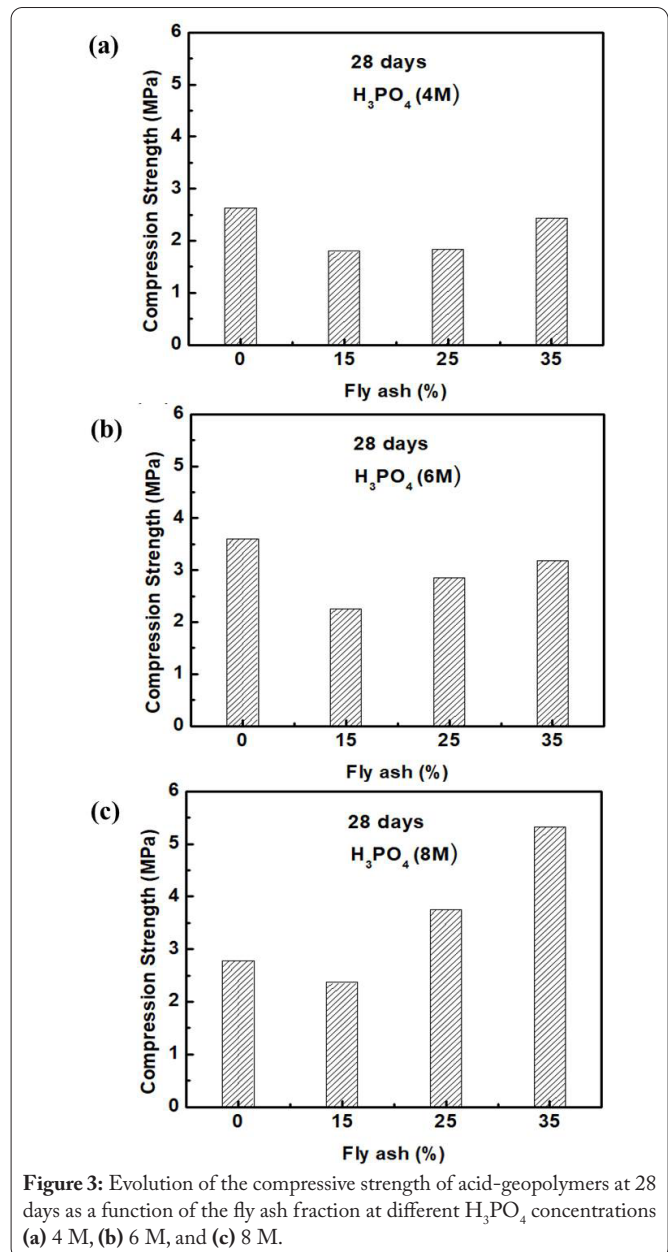


Figure 3: Evolution of the compressive strength of acid-geopolymers at 28 days as a function of the fly ash fraction at different H_3PO_4 concentrations (a) 4 M, (b) 6 M, and (c) 8 M.

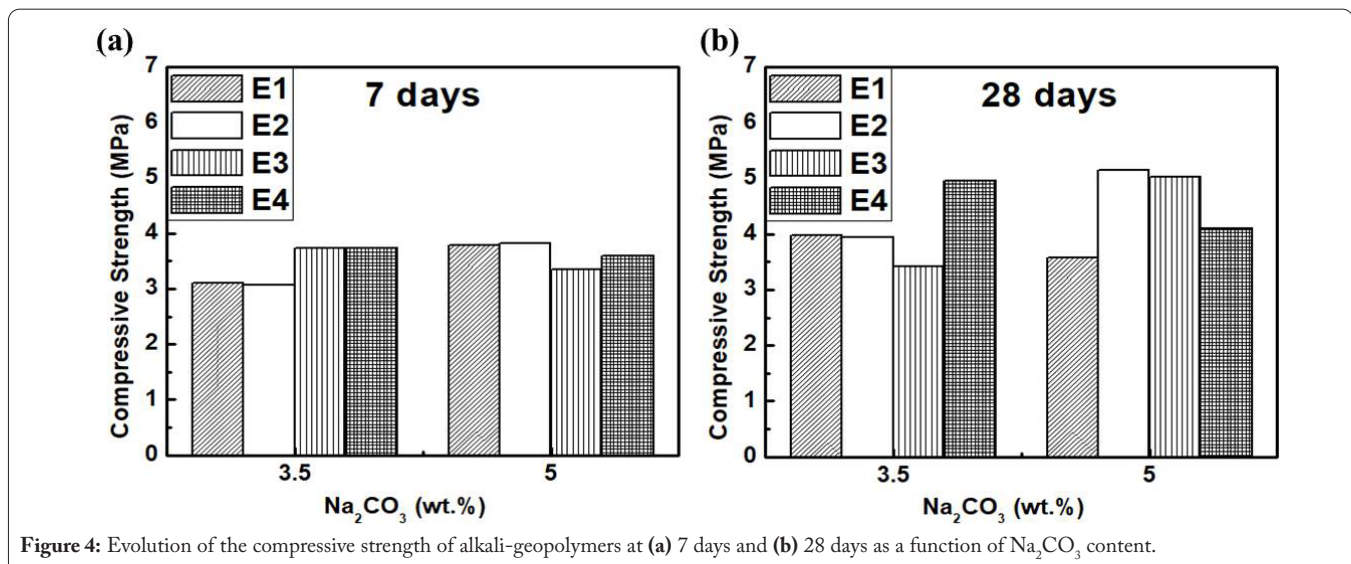


Figure 4: Evolution of the compressive strength of alkali-geopolymers at (a) 7 days and (b) 28 days as a function of Na_2CO_3 content.

Increase of the compressive strength up to 5.02 MPa at 28 days was obtained with Na_2CO_3 content of 5% for the same sample. Sample E2 showed a 28-day compressive strength of 3.94 and 5.14 MPa for Na_2CO_3 contents of 3.5 and 5 wt.%, respectively. This improvement can be due to the increase in the content of Na_2CO_3 in the medium, which accelerate the process of the dissolution and precipitation. On the other hand, the use of coal gangue alone revealed a very low compressive strength; a value of 3.57 MPa is recorded, and this may be due to the absence of the amorphous phase in the coal waste mineralogy. The addition of fly ash has improved the compressive strength. However, an increase in the fly ash fraction weakens this progress; strength of 5.14 MPa is obtained for the sample E2 and 4.09 MPa for the sample E4.

Mineralogical composition

Diffraction patterns of the H_3PO_4 and Na_2CO_3 -based geopolymers are illustrated in figure 5 and figure 6, respectively. After activation, several characteristic peaks remained in the diffraction patterns of the geopolymer samples after 28 days of curing, while new peaks appeared. For both activations, the samples essentially contain quartz and clay minerals such as muscovite, illite, mullite, and clinocllore. These crystalline phases are also observed in the X-ray patterns of the starting materials. This indicates that these minerals are not totally affected during the dissolution process.

From the diffraction patterns, there is the appearance of a hump between 15° and 35° (2θ), indicating the amorphous phase. For geopolymer made with H_3PO_4 solution, the hump is the characteristic reflection of the amorphous semi-crystalline aluminosilicate geopolymers formed during the polycondensation process [22, 31]. The hump is probably attributed to the poly (phospho-siloxo) -Si-O-P-O-Si- [32]. This inorganic polymer is obtained after 28 days of curing in the room temperature. While for alkali geopolymer, the very small hump is probably attributed to N-A-S-H and C-A-S-H type gels [33]. Hydrated sodium aluminosilicate (N-A-S-H) gel is the main reaction product present in the alkali-activation process of calcium-poor precursors (e.g., coal waste and fly

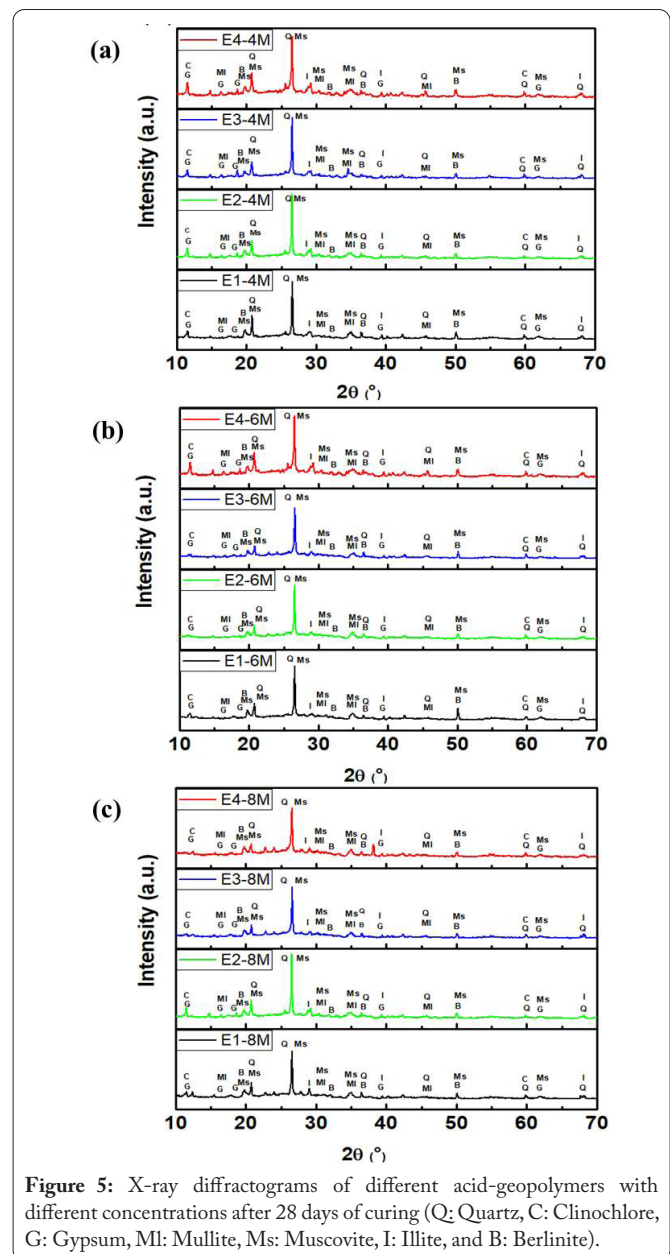


Figure 5: X-ray diffraction patterns of different acid-geopolymers with different concentrations after 28 days of curing (Q: Quartz, C: Clinocllore, G: Gypsum, MI: Mullite, Ms: Muscovite, I: Illite, and B: Berlinite).

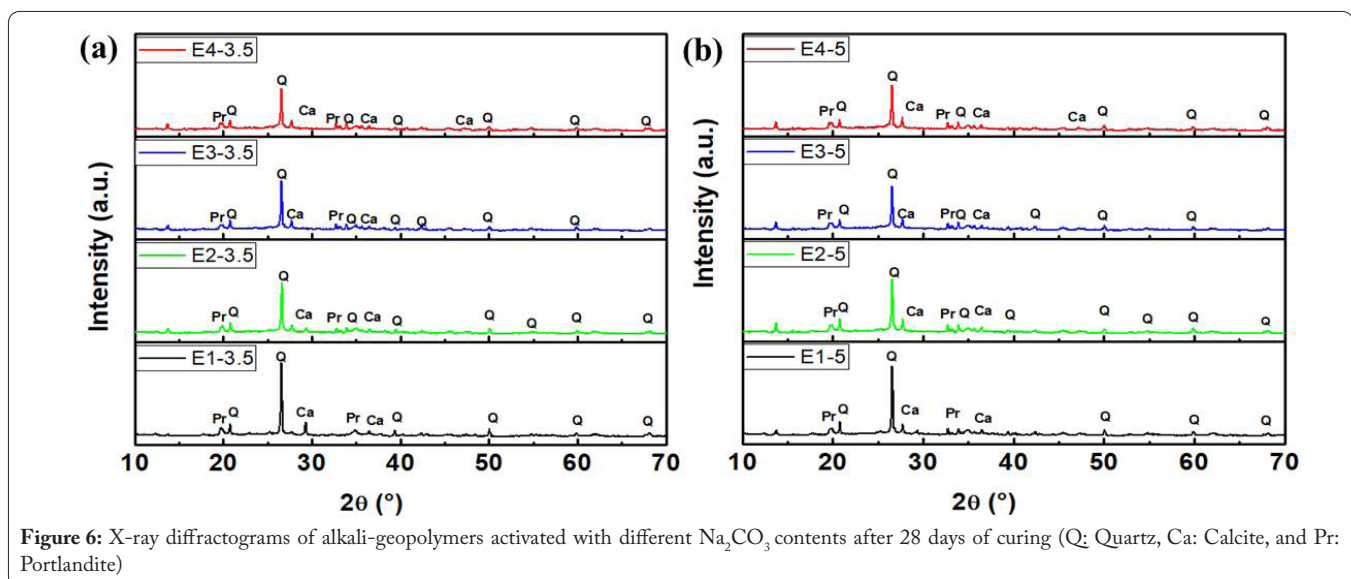


Figure 6: X-ray diffraction patterns of alkali-geopolymers activated with different Na_2CO_3 contents after 28 days of curing (Q: Quartz, Ca: Calcite, and Pr: Portlandite)

ash). Additionally, systems activated with high calcium alkalis (addition of lime) modified the N-A-S-H gels leading to the partial replacement of Na^+ with Ca^{2+} ions to form C-A-S-H gels [34]. It is a hydrated calcium-modified aluminosilicate gel associated with the dissolution and reaction of CaO . However, those phases are formed in very low amounts.

In geopolymers with Na_2CO_3 , peaks associated with Portlandite and calcite was observed. Portlandite is unstable in air with carbon dioxide which is transformed into calcium carbonate, explaining the presence of calcite [35]. Besides, Ca^{2+} ions can be combined with free CO_3^{2-} and give appearance of calcite [36]. Diffractograms of all phosphate-based geopolymers show the formation of a new crystalline phase; berlinite or aluminum phosphate (AlPO_4) which forms during the geopolymerization. This compound forms very quickly even at ambient temperature in the first step of geopolymerization due to the de-alumination of coal waste and fly ash in an acid medium [30]. The formation of this compound can be interpreted by the partial replacement of SiO_4 units by PO_4 units, leading to a modification of the local chemical environment. It involves the incorporation of the PO_4 units into the octahedral AlO_6 units during the process of polycondensation [30].

Conclusion

The effect of the activator types and the variation of the concentrations as well as the proportions of fly ash in coal waste on the mechanical and mineralogical properties of geopolymer materials were studied in this paper. Both acid and alkali-activators were prepared under the same conditions. The mechanical results in this study showed that the maximum compressive strength after 28 days for phosphate-based geopolymer cement was 5.33 MPa while with the alkaline solution was 5.02 MPa. The increase in the content of Na_2CO_3 and H_3PO_4 led to an increase in the mechanical resistance of the materials. Also, an increase in fly ash content in the admixture led to compressive strength development in the case of acid-geopolymers. X-ray analysis after 28 days of acid-geopolymers showed the presence of a hump which can be attributed to the amorphous structure (-Si-O-P-O-Si-). There is also the appearance of peaks associated with the formation of a crystalline phase designated to berlinite or aluminium phosphate (AlPO_4) during geopolymerization. For the alkali activation, the mineralogical results indicated the presence of peaks associated to the crystalline phase of Portlandite, with the existence of a small hump which can be attributed to the C-A-S-H and N-A-S-H type gels. However, those gels are in small amounts. In general, these findings can be explained by the poor amorphous phase present in the coal waste composition which delivers low reactivity in the acid and alkaline media. It is worthy to mention that coal waste contains large inert phases that can prevent geopolymerization reactions. The fly ash addition did not significantly affect the raw coal waste reactivity. In terms of compressive strength, fly ash had no negative effect on strength for higher fraction additions compared to lower fractions. The main challenge is to develop an adequate mix design and explore the possible use of raw coal waste in the manufacture of geopolymers in different media.

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Conflict of interest

The authors declare that they have no conflict of interest.

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