

## Influence of Curing Conditions on the Properties of Geopolymers from Untreated Kaolinite

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**Abstract:** Curing conditions of kaolinite-based geopolymers seems a very efficient process in both dimensional stability and producing quality geopolymer products. Three curing procedures were studied and evaluated in this paper. Experimental results indicated that a dry pre-conditioning before autoclave curing or dry-autoclave curing (C-geopolymers) was very critical for kaolinite geopolymers to achieve desirable strength and high dimensional stability. The strength of geopolymers (C-geopolymers) with dry-autoclave cycle curing was higher to that after conventional dry curing (R-geopolymers). These curing techniques were tested on geopolymers using untreated kaolinite as precursor. The results confirm that the compressive strength increases from 40 MPa to 51MPa with this dry-autoclave curing technique. In addition, the density increases accompanied with decreasing in water absorption as well as curing shrinkage/swelling. Autoclave curing (A-geopolymers) dry pre-conditioning causes sharp decrease in strength, swelling, increase in water absorption and decrease in bulk density of the geopolymers.

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**Key Words:** geopolymers; autoclave curing; shrinkage; strength; kaolinite

### 1. Introduction

Through chemical polymerization, aluminosilicates can be hardened and transformed into aluminosilicate polymers, also known as geopolymers [1-5]. Geopolymers consist of an amorphous, three-dimensional network resulting from the polymerization of aluminosilicate monomers in an alkaline solution [6]. Several studies have been carried out though to identify kinetics and elucidate solution chemistry [7-9]. A reaction pathway for geopolymerization involving polycondensation of hypothetical monomers, i.e. orthosialate ions, has been proposed. As a result of these reactions, solid, hard, and stable materials similar to hydroxysodalite, feldspathoid or zeolite are formed [10-12]. These formed materials, which may be amorphous or microcrystalline, consist of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra linked alternately by sharing all of the oxygen atoms. When aluminum is four coordinated to oxygen atoms, a negative charge is created and therefore the presence of cations such as ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{H}_3\text{O}^+$ ) is essential to balance the negative charge of Al in the four fold coordination [12].

Alkali-activation of untreated kaolinite is an ideal technique to prepare low cost construction materials. This material is produced from a very cheap precursor available in great quantity: clay mineral. This mineral, mixed with alkali solution is compressed then heated in an oven at 80 °C. This material can be compared to geopolymers, but the clay is not thermally activated. As a result the reaction mixture is plastic and cannot be poured but needs to be compressed to obtain dense specimens. Another difference with geopolymers is the lower reactivity of

kaolinite compared to metakaolinite or fly ash and hence alkali solutions need to be used instead of silicate solutions as activator. The resultant material is water stable and has good mechanical properties, comparable to geopolymers. The material will be called here kaolinite-based geopolymer [12].

The mechanism of the geopolymerization of geopolymers from untreated kaolinite is based on exchanging ions such as  $\text{Na}^+$  from alkaline NaOH with the hydrogen ions on the broken edges of the clay. As a result of this ion exchange, repulsion between the  $\text{Na}^+$  ions will dissolve some clay particles into other grains of the soil and bind them together. Although kaolinite-based geopolymers have lots of advantageous properties, it is not as widely used as expected in practice. The major reasons for this are the high amount of the residual alkalis in the products, the low strength, and the high water absorption compared with geopolymers from metakaolin or fly ash .

The purpose of this study is to improve the properties of kaolinite-based geopolymers by optimizing the curing conditions. Three different curing conditions are studied and evaluated: 1) Reference curing (R-geopolymers), 2) Cyclic curing (C-geopolymers) and 3) autoclaving (A-geopolymers). Reference curing is the conventional curing procedure of this type of geopolymers. The R-geopolymers curing procedure is based on drying the sample at 80°C for at least 1 day. The C-geopolymers curing is applied by dry-autoclave cycle curing at 80°C. Finally, the geopolymers are autoclaved (A-geopolymers) at 80°C. The curing conditions are evaluated based on the resultant mechanical and

physical properties, and curing shrinkage. Microstructure changes were identified using SEM, XRD, and TGA.

## 2. Materials and methods

### 2.1 Materials

Geopolymers were synthesized using kaolinite, silica sand and alkaline activator, namely sodium hydroxide. Kaolinite (Merck, Germany, Purity >99%) was used as a source of aluminosilicate. Washed silica sand with grain size varies 100 $\mu$ m and 400 $\mu$ m was used as filler. NaOH solution was used as alkaline activator for the dissolution of aluminosilicate phases. The hydroxide solution with concentration of 14M was prepared using sodium hydroxide (NaOH) flakes of 98% purity (Scharlau) and distilled water.

### 2.2 Fabrication of kaolinite-based geopolymers

The following ratios were used to prepare the kaolinite-based geopolymers: Silica sand (filler)/kaolinite (precursor) mass ratio of 2, and NaOH solution (alkaline activator, 14M)/Kaolinite (precursor) mass ratio of 0.6. The overall mass percent of kaolinite was 28%.

The procedure of specimens' fabrication and tests made on specimens are illustrated in Fig. 1. The aqueous solution of NaOH and H<sub>2</sub>O was mechanically

mixed for 1 min. Silica sand and kaolinite were dry mixed first and then sodium hydroxide solution was added. All reagents were mixed for 15 minutes. The final mixture of each series was divided into eight specimens (60 g each). The mixture was molded immediately after weighing to avoid drying and decrease of the workability of the mixture. This mixture was molded in a stainless steel cylinder (diameter of 25 mm and height of 50 mm) at a pressure of about 15 MPa (Carver hydraulic laboratory press) [12].

### 2.3 Curing procedures

The samples were divided into three series: R-geopolymers, A-geopolymers, and C-geopolymers. Each series composed from 8 specimens with different curing conditions as shown in Fig.1. R-geopolymers or reference specimens were cured by drying at 80 °C for 2 days. A-geopolymers were cured in a modified Veterinary Tabletop Steam Sterilizer (MS-T24), China, at 80°C and under 2 atm. pressure. Finally, the C-geopolymers were dried for one day at 80°C, cured in autoclave (80°C and 2 atm.) for another day at 80°C. All the above mentioned geopolymers with different curing procedures were dried for additional 24h at 80°C as shown in Fig. 1.

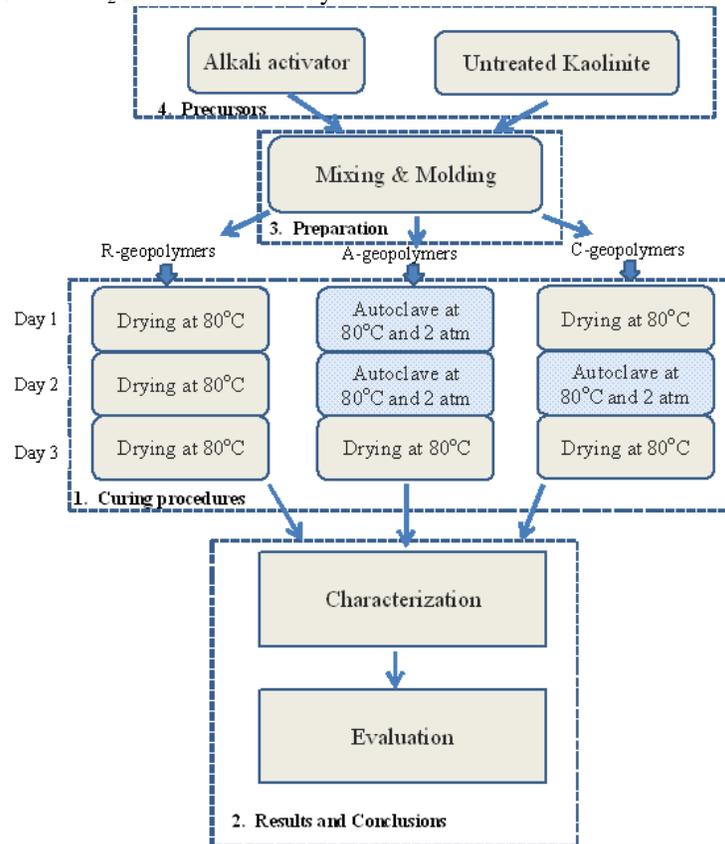


Figure 1: Preparation and curing conditions of the geopolymers

## 2.4 Characterization and evaluation of geopolymer properties

Physical and mechanical properties of the produced geopolymers were investigated and evaluated after different treatments. Eight specimens of each series were divided into three groups. Three specimens (Group-1) were further dried in an oven at 40°C for 7 days. Another three specimens (Group-2) were immersed in tap water at room temperature for 7 days. The remaining two specimens (Group-3) were used for scanning electron microscope (SEM), X-ray diffraction (XRD), and thermal gravimetric analysis (TGA) measurements.

## 2.5 Water absorption, shrinkage and compression tests of geopolymers

Water absorption of the immersed specimens (Group-2) was calculated for each series according to Equation 1.

$$W\% = ((W_w - W_d) / W_d) \times 100\% \quad (1)$$

Where, W % is the percentage of water absorption;  $W_w$  and  $W_d$  are the masses of the immersed specimens and of specimens after drying, respectively.

For dimensional changes measurements after curing, the dimensions of the geopolymers were measured before and after curing using a digital micrometer. Linear shrinkage was calculated for each sample according to equation 2.

$$L\% = ((L_i - L_c) / L_i) \times 100\% \quad (2)$$

Where, L% is the percentage of shrinkage;  $L_i$  and  $L_c$  are the lengths of the specimens before and after curing, respectively.

The compression test was performed using CONTROLS testing machine (Model T106 modified to suit standard testing), where the load was applied and increased by a displacement rate of 2 mm/min. Three dried specimens (Group-1) and three immersed specimens (Group-2) were subjected to compressive strength tests.

## 2.6 Microstructural and phase analyses of geopolymers

The X-ray diffraction (XRD) analysis was carried out on powdered samples to identify major crystalline and potentially newly formed phases using an X-ray diffractometer-6000 (Shimadzu, Japan). The XRD patterns were measured from 5° to 40° 2θ at a scan rate of 2°/min. The crystalline phases were identified by analyzing the positions of the peaks using the software package supplied with the instrument.

The morphology of the specimens was studied using an Inspect F50 Scanning Electron Microscope (Netherlands). The samples were pre-coated with platinum under an argon atmosphere.

The STA 409 thermal analyzer (NETZSCH) was used to measure mass changes of samples as a function of temperature with constant heating rate of 5°/min.

## 3. Results and Discussion

### 3.1 Microstructural characteristics

The XRD patterns of the precursor and the resultant R-geopolymers are shown in Fig. 2. Several strong peaks corresponding to quartz and kaolinite are obvious in kaolinite. Upon geopolymerisation, the intensity of kaolinite related peaks is decreased while peaks corresponding to plagioclase feldspar ( $\text{NaAlSi}_3\text{O}_8$ ) appear. The presence of strong peaks corresponding to kaolinite in the geopolymers indicates the low reactivity of this precursor. This incomplete reaction of kaolinite was proven by SEM analysis as shown in Fig. 3.

From this figure it can be seen the coexistence of geopolymer gel and partially unreacted kaolinite layers in the geopolymers. The unreacted distorted kaolinite is distributed in a random and heterogeneous manner in the microstructure of the geopolymer. This heterogeneity can in part be caused by the evaporation of water during the geopolymerization causing concentration gradients and thus reactivity differences. The fact that the clay particles have different dimensions also plays a role. Larger particles, reacting slower, can remain unreacted due to diffusion control at the end of the reaction [12].

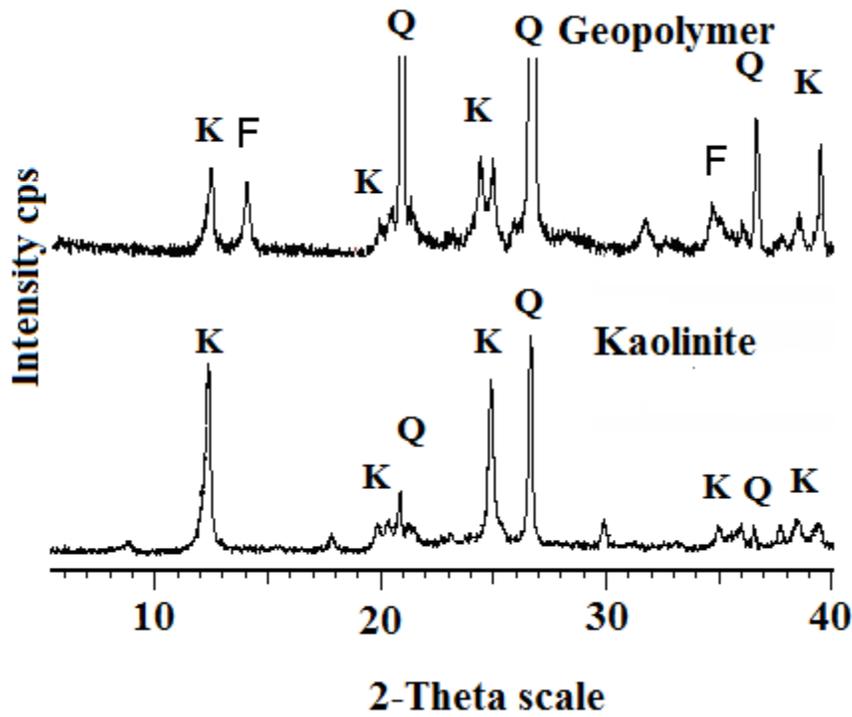


Figure 2: X-ray diffraction spectra of the precursor, and the R-geopolymers; K: Kaolinite, Q: Quartz, F: Feldspar

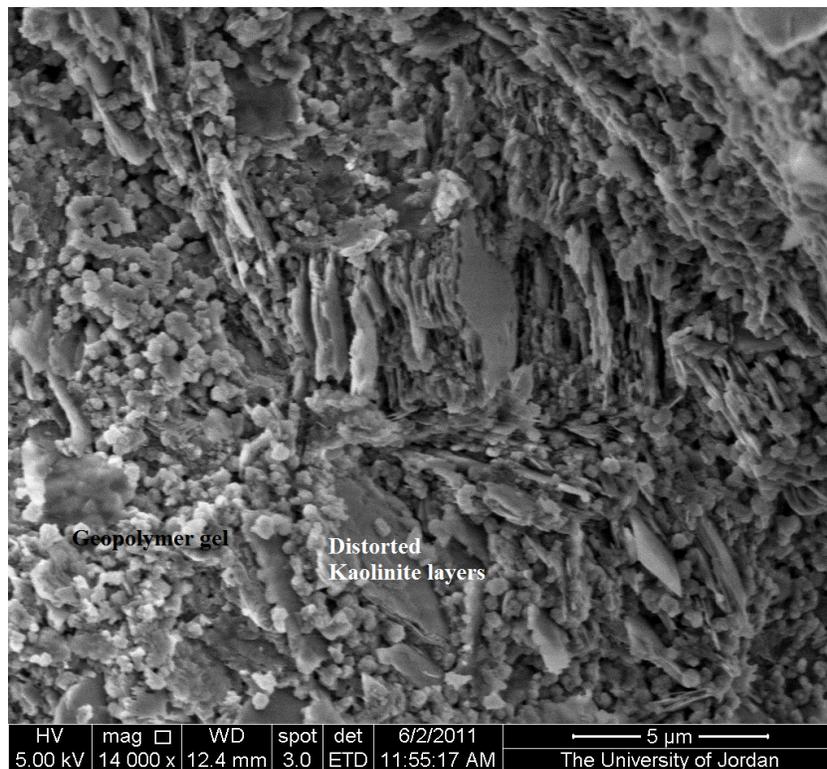
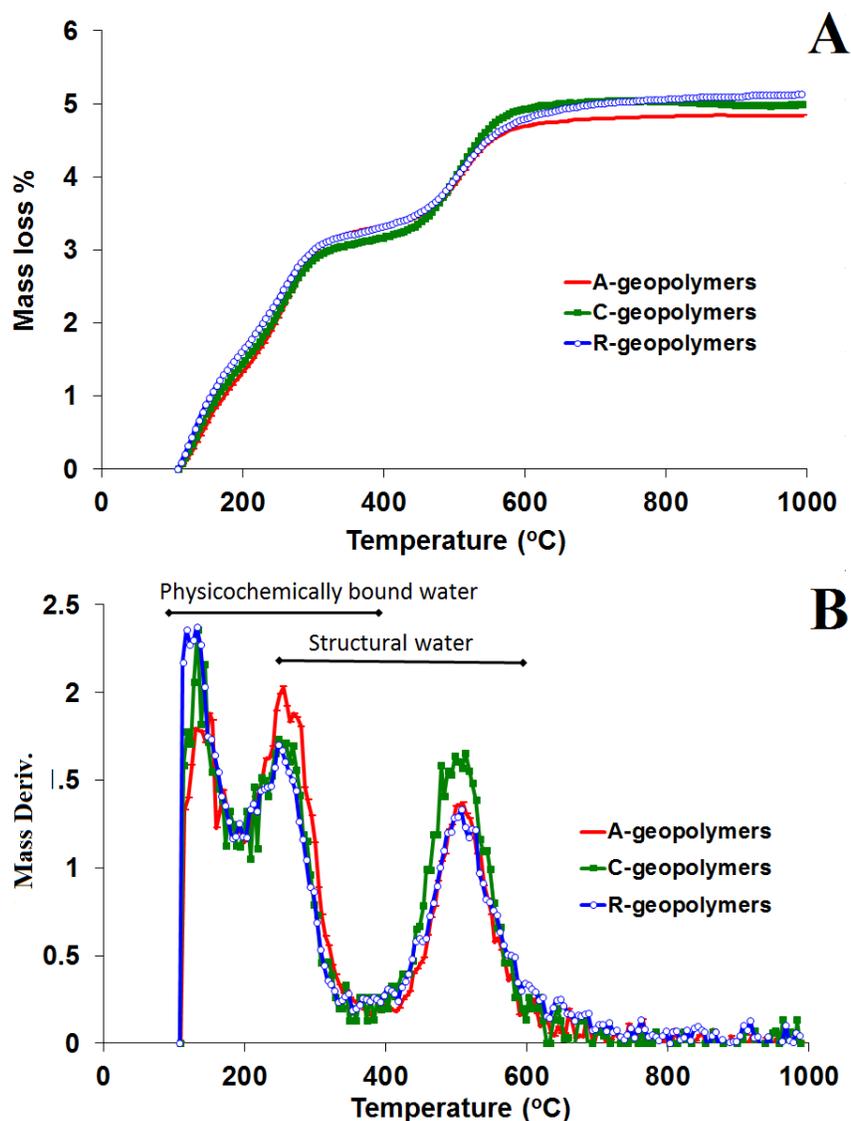


Figure 3: SEM image of R-geopolymers

More detailed information regarding phase composition and the presence of bound water in the geopolymeric structure was provided by TGA. Fig. 4 illustrates the TGA results for of R-geopolymers, A-geopolymers, and C-geopolymers. The overall mass above 100°C loss, as shown in Fig. 4A, results from the loosely bounded water (physico-chemically bounded water) and structural water. These three types of geopolymers exhibit almost the same thermal behaviors.

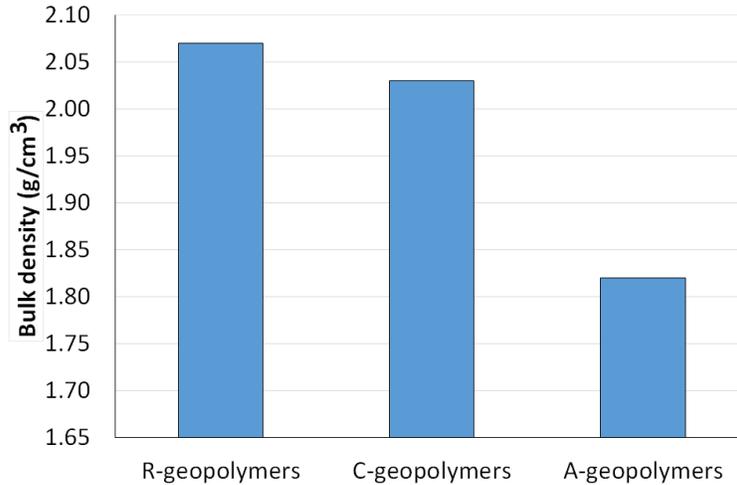


**Figure 4: Thermo gravimetric analysis of A-geopolymers, C-geopolymers, and R-geopolymers**

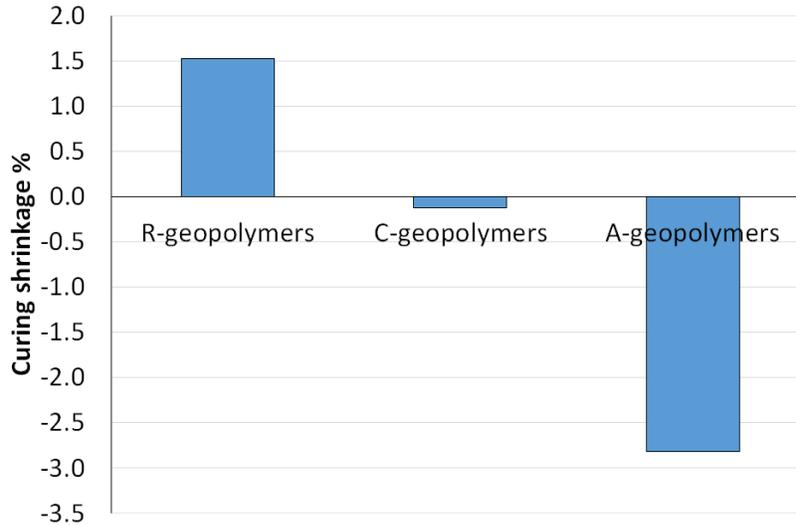
The derivative of the TGA curve reveals that thermal events occur in three temperature ranges, 100 -150°C, 200 - 300°C, and 400 - 620°C respectively, as shown in Fig. 4B. In the first range (100-150°C), the decrease in weight can be attributed to the release of fine-pore moisture. In the second range (200-300°C) the decrease in weight is mainly caused by the combination release of adsorbed and zeolitic water. The dehydroxylation of unreacted kaolinite and the release of strongly bound fine-pore moisture or hydroxyl groups is the major reason of the weight loss in the last range (400–620 °C). R-geopolymers exhibit the maximum percentage of loosely bounded water in the first range (100-150°C). A-geopolymers, and C-geopolymers show more tightly structural water in the temperatures ranges (200-300°C) and (400–620 °C) respectively. This is an indication of formation of large percentage of zeolite or feldspar-like phases in the structure of these two types of geopolymers compared with R-geopolymers.

### 3.2 Mechanical and physical properties

A-geopolymers have lower bulk density ( $1.82 \text{ g/cm}^3$ ) than R-geopolymers and C-geopolymers as shown in Fig. 5. Thus, the autoclave curing (A-geopolymers) decreases the bulk density of the products. This is a strong indication that autoclaving can expand the volume of the material during the curing process if it was not dried in advance as shown in Fig. 6. The A-geopolymers exhibit high swelling during the curing, 2.8%, compared with R-geopolymers (shrinkage 1.5%). With swelling less than 0.12%, C-geopolymers show the best dimensional stability during the curing process.

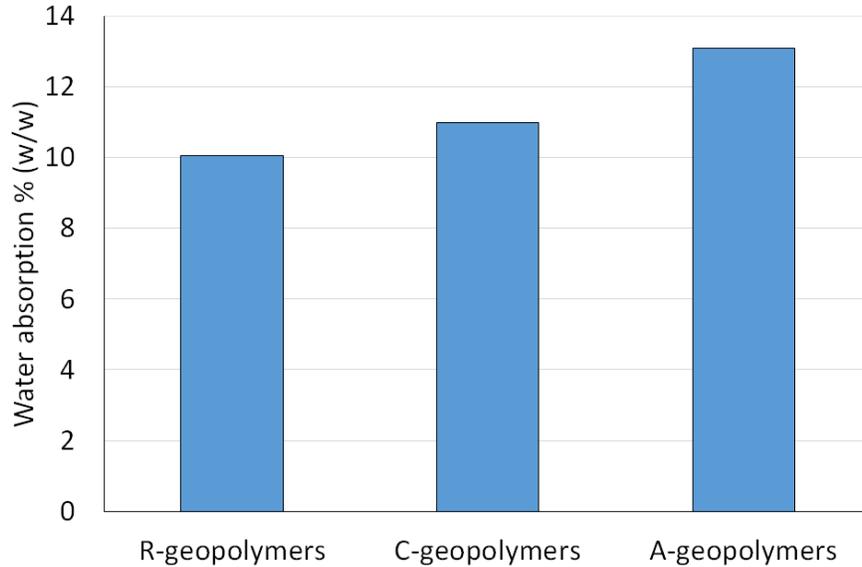


**Figure 5: Bulk density of geopolymers with different curing procedures**



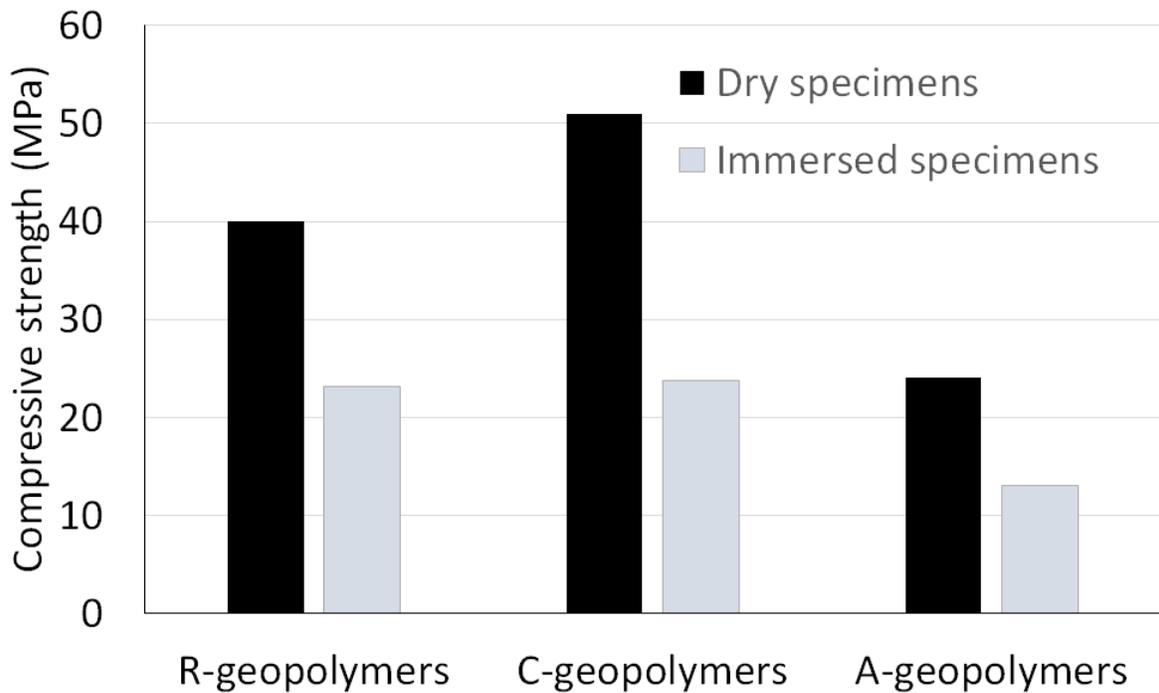
**Figure 6: Curing shrinkage/swelling of the geopolymers with different treatments**

As a result of volume expansion, water absorption is higher in A-geopolymers (14.2%) than in those with reference curing (10.3% in R-geopolymers) or dry-autoclave curing (10.5% in C-geopolymers) as reported in Fig. 7. Again, this behavior is due to the fact that incorporation of autoclave curing (A-geopolymers) into the geopolymer expands the volume and increases the open porosity of the material, which increases the water absorption capability.



**Figure 7: Water absorption of geopolymers with different curing conditions**

Fig. 8 shows the compressive strength of the geopolymer specimens. An increment in strength of dry specimens is observed with cycle curing (C-geopolymers). The compressive strength of geopolymers is doubled with cycle curing compared with autoclave curing. The strength of dry and immersed specimens, 51 MPa and 24 MPa respectively, is obtained (C-geopolymers) as shown in Fig. 8. This strength is much higher than the strength of dry and immersed specimens of R-geopolymers, 40 MPa and 23 MPa respectively. This clearly shows the positive effect of dry-autoclave cycle curing on the development of mechanical strength of the specimens. The fact that only autoclave curing (A-geopolymers) does not lead to good mechanical properties is probably linked to the lower density and high swelling of the material.



**Figure 8: Compressive strength of geopolymers with different curing conditions**

#### 4. Conclusions

The above results show that the drying-autoclave curing cycle based on three phases: drying, autoclave and drying improves the properties of the end geopolymer products. The compressive strength of the geopolymer increases by 25% under dry conditions. The dry-autoclave cycle curing allows the chemical reactions to continue, resulting in increased mechanical properties. However, autoclave curing alone decreases the density of the material and thus the mechanical strength. The dry-autoclave cycle curing periods should be optimized before starting the material production.

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