# INVESTIGATING SHRINKAGE CHANGES OF NATURAL POZZOLAN BASED GEOPOLYMER CEMENT PASTE

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**Abstract:** Shrinkage behavior of a geopolymer cement paste prepared from pumice-type natural pozzolan was studied by changing parameters of chemical composition including  $SiO_2/Na_2O$  molar ratio of activator and total molar ratios of  $Na_2O/Al_2O_3$ , and  $H_2O/Al_2O_3$ . For investigating the effect of curing conditions on shrinkage, hydrothermal curing was also applied. The obtained results clearly revealed the governing effect of chemical composition on shrinkage. Mixes with different  $Na_2O/Al_2O_3$  molar ratios exhibited different shrinkage behavior due to variations made in  $SiO_2/Na_2O$  molar ratio. Application of hydrothermal curing after a 7-day period of precuring in humid atmosphere also showed strong effect on shrinkage reduction.

Keywords: Geopolymer cement, Shrinkage, Chemical Composition, Curing, Natural Pozzolan

#### **1. INTRODUCTION**

Geopolymer cement refers to any material that uses an alkali activator to initiate a reaction or a series of reactions that will produce a material possessing cementing properties. Alkali activated fly ash, and inorganic polymeric binders based on metakaolin and natural pozzolan [1-4] are all considered to be geopolymer materials exhibiting cementing properties.

The molecular structure of geopolymer cements consists of an aluminosilicate network that is a product of the chemical reaction between aluminosilicate and alkali-polysialate in a relatively high alkaline medium. The aluminosilicate network consists of SiO4 and AlO<sub>4</sub> tetrahedral structural units connected to each other by sharing their oxygen atoms. The presence of positive ions such as Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, and H<sub>3</sub>O<sup>+</sup> is necessary to balance the negative charge of aluminum [3,5].

The molecular structure and hence properties of geopolymer cements depend on some parameters including chemical and mineralogical compositions of raw material and its dissolution properties, composition and dosage of alkaliactivator, and curing conditions. Among which, the chemical composition of both raw material and alkali-activator is very important in determining the molecular structure of the product. The chemical composition of such cementing materials can be studied by considering molar ratios of  $SiO_2/Al_2O_3$ ,  $SiO_2/Na_2O$ ,  $Na_2O/Al_2O_3$ , and  $H_2O/Al_2O_3$  [6-9].

Shrinkage of alkali activated materials (AAM) like geopolymer cements is sensitive to the exposure environment, although there are differences in the reported magnitude [10]. Kutti [11] found that for 70% relative humidity (RH), shrinkage of alkali activated slag concrete was similar to ordinary Portland cement (OPC). However, at 33% RH and 50% RH, the shrinkage was 3.0 and 2.3 times the shrinkage of OPC. Collins and Sanjayan [12,13] studied the cracking tendency, microcracking and strength development of alkali-activated slag concrete. They reported that shrinkage was about two times greater than Portland cement (PC) concrete. A lack of moist curing increased the level of microcracking and reduced compressive strength compared to moist curing.

Atis et al. [14] investigated the influence of activator on the strength and shrinkage of alkaliactivated slag mortar. He claimed that slag mortar made with liquid sodium silicate had a high drying shrinkage, up to six times that of PC

mortar. Similarly, slag mortar made with sodium hydroxide had shrinkage up to three times that of PC mortar. However, slag mortar activated sodium carbonate had a lower or comparable shrinkage to PC mortar. Bakharev et al. [15], studying the effect of elevated curing temperature on properties of alkali-activated slag concrete, concluded that heat treatment considerably accelerates strength development, but at later ages the compressive strength was reduced compared to concrete cured at room temperature. They also concluded that heat curing considerably reduces shrinkage of alkaliactivated slag concrete, making it comparable to PC concrete. Few authors however, have studied shrinkage of geopolymer cement paste based on natural pozzolan in relation with their chemical composition parameters and curing conditions.

Previous studies have shown the potential of suitable natural pozzolanic materials as raw materials in synthesis and production of geopolymer cements [2, 16, 17]. To confirm such a potential, studies must be completed considering all the important properties of geopolymer cements. This work focuses on the relation of chemical composition and total shrinkage of natural pozzolan based geopolymer exhibiting cement. Mixes the highest compressive strength were selected to investigate the effect of hydrothermal curing application on total shrinkage of the material.

## 2. EXPERIMENTAL

## 2.1. Raw Materials

Natural pozzolan used in this work was pumice-type obtained from Taftan mountain, located at the south east of Iran. The obtained pozzolan was firstly characterized for its chemical and mineralogical compositions and also its pozzolanic activity. The results of chemical analysis determined according to ASTM standard C311 are shown in table 1. As seen, this natural pozzolan is a relatively high siliceous one. Figures 1 and 2 show the X-ray diffraction pattern and Fourier transform infrared spectroscopy (FTIR) spectrum of the used pozzolan, respectively. As figure 1 shows, the

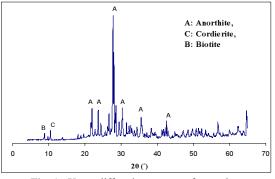


Fig. 1. X-ray diffraction pattern of pozzolan

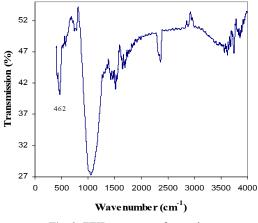


Fig. 2. FTIR spectrum of pozzolan

crystalline mineral phases present in Taftan pozzolan include Feldspar (Anorthite with empirical formula;  $Na_{0.05}Ca_{0.95}Al_{1.95}Si_{2.05}O_8$ ), Amphibole (Cordierite with empirical formula;  $Mg_2Al_4Si_5O_{18}$ ), and Mica (Biotite with empirical formula;  $KMg_{2.5}Fe_2$ +0.5AlSi<sub>3</sub>O<sub>10</sub>(OH)<sub>1.75</sub>F<sub>0.25</sub>).

As seen in figure 2, FTIR spectrum of the pozzolan shows two strong peaks. One at wavenumber about 460 cm<sup>-1</sup> and the other a broad peak at wavenumbers in the range between 1007 to 1050 cm<sup>-1</sup> which are both attributed to asymmetric stretching of Al-O and Si-O bonds of aluminosilicate structure. Some weak peaks are also observed in the wavenumbers between 500 to 800 cm<sup>-1</sup> which are attributed to both tetrahedrally and octahedrally coordinated aluminum.

The pozzolanic activity of Taftan pozzolan was also evaluated by determining its strength

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Composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Cl	LOI
wt %	61.57	18.00	4.93	6.69	2.63	0.10	1.95	1.65	0.04	2.15

Table 1. Chemical composition of pozzolan

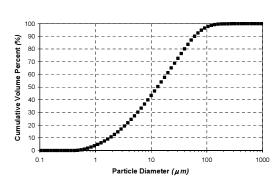


Fig. 3. Particle size distribution of ground pozzolan

activity index with Portland cement at 7 and 28 days in accordance with ASTM C311. The results obtained, i.e. 83.2 and 86.8 percent of control for 7 and 28 days, respectively, show a relatively good pozzolanic activity in accordance with ASTM standard C618. The prepared sample of pozzolan was previously ground in an industrial closed mill to a Blaine specific surface area of 305 m<sup>2</sup>/kg. The particle size distribution of which was determined by a laser particle size analyzer (Mastersizer 2000) and the corresponding curve is presented in figure 3. The mean particle size of the ground natural pozzolan was 23.82 µm. Industrial sodium silicate solution (weight ratio of SiO<sub>2</sub>/Na<sub>2</sub>O=0.92 and SiO<sub>2</sub>=31.36 wt %) and industrial-grade NaOH (99% purity) were used throughout all experiments.

#### 2. 2. Specimens Preparation

A number of mixes were designed in accordance with molar ratios given in table 2. Chemical composition of the mixes has been varied by changing  $SiO_2/Na_2O$  molar ratio (for simplicity, hereafter shown by Si/Na) of activator and total  $Na_2O/Al_2O_3$  molar ratio (hereafter shown by Na/Al) of the material. The corresponding calculated values for total Si/Al molar ratio are also given in table 2. Enough sodium hydroxide was added to sodium silicate

solution and the dosage of activator was so adjusted to prepare geopolymer mixes having molar ratios of Si/Na and Na/Al adjusted at the values given in table 2.

The above mixes were all studied for their shrinkage and compressive strength at a constant total H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> molar ratio (hereafter shown by H/Al) of 8.50. To determine the 28-day compressive strength, the prepared pastes were cast into  $2 \times 2 \times 2$  cm<sup>2</sup> moulds. The moulds were held at an ambient of more than 95% relative humidity (RH) for preventing drying and giving enough time (24 h) to the pastes to set and harden at ambient temperature, i.e. 25 °C. After demoulding, the specimens were cured in an atmosphere of more than 95% relative humidity at 25°C until the testing time. From each measurement, three specimens were used and the average of the three obtained values was reported as the result of compressive strength.

For shrinkage measurement, specimens of the size of  $2 \times 2 \times 10$  cm<sup>2</sup> were prepared. After demoulding, the specimens were cured at an atmosphere of 95% relative humidity at 25°C for a period of 42 days and their shrinkage were measured at the ages of 2, 3, 7, 14, 21, 28, 35, and 42 days using a 0.01 mm accurate caliper.

After 42 days, the specimens were taken out of humid atmosphere and were held at an open air atmosphere to measure their shrinkage at the ages of 56, 63, 70, 77, 84, and 90 days. From each mix, three specimens were used and the average of the three values was reported as the result of shrinkage.

To investigate the effect of total H/Al molar ratio (depending on water-to-dry binder ratio and water content of both sodium silicate and sodium hydroxide) on shrinkage of the material, four mixes exhibiting the highest 28-day compressive strength including mixes P4, P9, P13, and P18 were selected and their shrinkages were studied at five different total H/Al molar ratios of 7.5, 8.0, 8.5, 9.0, and 9.5. Also, 90-day total shrinkages of all the studied mixes were studied.

Mix	Activator Si/Na molar	Total Na/Al molar ratio	Total Si/Al molar		
Name	ratio (adjusted)	(adjusted)	ratio (calculated)		
P1	0.3	0.77	5.58		
P2	0.45	0.77	5.66		
P3	0.6	0.77	5.78		
P4	0.75	0.77	5.92		
P5	0.9	0.77	6.10		
P6	0.3	0.92	5.60		
P7	0.45	0.92	5.70		
P8	0.6	0.92	5.84		
P9	0.75	0.92	6.00		
P10	0.9	0.92	6.22		
P11	0.3	1.08	5.62		
P12	0.45	1.08	5.76		
P13	0.6	1.08	5.90		
P14	0.75	1.08	6.10		
P15	0.9	1.08	6.36		
P16	0.3	1.23	5.66		
P17	0.45	1.23	5.80		
P18	0.6	1.23	5.98		
P19	0.75	1.23	6.20		
P20	0.9	1.23	6.48		

Table 2. Chemical composition of geopolymer mixes (at a constant total H/Al molar ratio of 8.50)

Observation of relatively high amounts of shrinkage for almost all mixes led us to make further investigations. Hydrothermal curing was applied on specimens exhibiting the highest 28-day compressive strength to investigate its effect on shrinkage. The used curing regimes included hydrothermal treatment in steam saturated atmosphere at 85°C for 20 hours after 1 and 7 days of precuring in an atmosphere of 95% relative humidity at 25°C. In the case of hydrothermal curing after 1 day of precuring (HT-curing after 1 day), the moulds were held at an ambient of nearly 95% relative humidity for preventing drying and giving enough time (1 day) to the pastes to set and harden at ambient temperature, i.e. 25 °C. After demoulding, the initial size of the specimens were measured and then cured at 85°C for 20 hours in steam saturated atmosphere. After completing the curing, the specimens were held at an open air and their shrinkage was measured at the ages of 2, 3, 7, and 14 days using a 0.01 mm accurate caliper until achieving constant shrinkage amounts.

In hydrothermal curing after 7 days of precuring (HT-curing after 7 days), after demoulding the specimens were cured at an atmosphere of 95% relative humidity at 25°C for a period of 7 days and their shrinkage were measured at the ages of 2, 3, 7 days. Then, the specimens were cured at 85°C for 20 hours in steam saturated atmosphere. After completing the curing, the specimens were held at an open air and their shrinkage was measured at the ages of 2, 3, 7, 14, and 21 days until achieving constant shrinkage amounts.

#### **3. RESULTS AND DISCUSSION**

#### 3.1. Compressive Strength

Before measuring compressive strength, the

specimens were observed visually for any possible crack. They were quite sound and no macro-crack was seen. The results obtained for 28-day compressive strength and the effects of chemical composition and curing time and temperature on compressive strength behavior were presented and discussed in detail in our previous publications [16,17]. It was concluded that the molar ratio of Si/Na of activator plays an important role in the compressive strength development. Si/Na molar ratio shows a positive effect on compressive strength up to 0.6 for the mixes with Na/Al molar ratios of 1.08 and 1.23 and up to 0.75 for the mixes with Na/Al molar ratios of 0.77 and 0.92. After that, any increase in Si/Na molar ratio of activator resulting from either a decrease in the concentration of sodium oxide or an increase in the concentration of silica causes a significant decrease in 28-day compressive strength.

### 3. 2. Shrinkage

#### 3. 2. 1. Effects of Si/Na and Na/Al Molar Ratios

Figures 4 to 7 show shrinkage of the specimens with different Si/Na molar ratios of activator at Na/Al molar ratios of 0.77, 0.92, 1.08, and 1.23, respectively and at constant H/Al molar ratio of 8.50. As seen, for all the mixes variations of shrinkage generally follow similar trends. In the case of shrinkage in humid atmosphere between 2 to 42 days, two ascending stages can be observed. First stage happens at the early ages between 2 to 7 days and the second happens between 21 to 42 days.

The phenomenon of macroscopic volume reduction of cement paste, mortar and concrete caused by chemical shrinkage is referred to as autogenous shrinkage. Chemical shrinkage is a reduction in volume resulting from the chemical reactions between the natural pozzolan and the activator in the presence of water. Autogenous shrinkage is therefore caused by self-desiccation due to water consumption in geopolymerization reactions.

In the case of inorganic binders other than geopolymers, it is reported that autogenous shrinkage is usually accompanied with formation

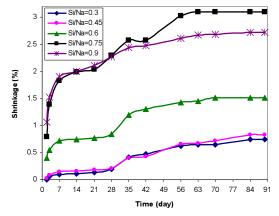


Fig. 4. Variation of shrinkage with time at Na/Al and H/Al total molar ratio of 0.77 and 8.50, respectively.

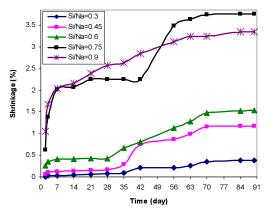


Fig. 5. Variation of shrinkage with time at Na/Al and H/Al total molar ratio of 0.92 and 8.50, respectively.

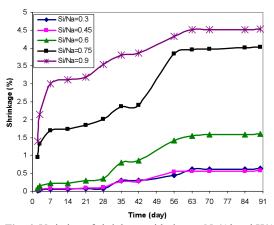


Fig. 6. Variation of shrinkage with time at Na/Al and H/Al total molar ratio of 1.08 and 8.50, respectively.

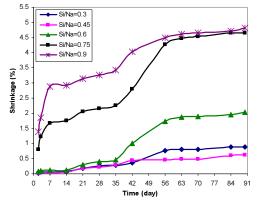


Fig. 7. Variation of shrinkage with time at Na/Al and H/Al total molar ratio of 1.23 and 8.50, respectively.

of fine pores in the microstructure of the cement paste [18]. For geopolymer cements, however, detailed experimental works are necessary to investigate the variations occurring in the pore structure during the course of geopolymerization reactions.

Evaporation of free water from macropores causes the first shrinkage rate peak, occurring immediately after demoulding. Autogenous shrinkage increases rapidly as the geopolymerization reactions becomes more intense [19]. In the case of shrinkage occurred between 42 to 90 days in dry atmosphere, only one ascending stage between 42 to 84 days is observed. After 84 days, total shrinkage gradually becomes constant. Elimination of uncombined water content during the drying process could be the main effective parameter on this shrinkage.

Shrinkage occurred in humid atmosphere is different from the shrinkage in dry atmosphere with regard to the mechanism of humidity decrease in hardened cement body. Shrinkage in dry atmosphere is caused by diffusion of water into the outer environment. Therefore, this shrinkage can be reduced by making the hardened paste denser and preventing the diffusion of water towards the outer environment.

Results obtained show that at a constant Na/Al total molar ratio, shrinkage is relatively low at Si/Na molar ratios less than 0.6. By increasing the Si/Na molar ratio to 0.75 and 0.6, the amount of shrinkage is sharply increased. The Si/Na

molar ratio therefore has a significant effect on shrinkage amounts. In this case, self-desiccation is most likely greater than that found in Portland cement.

### 3. 2. 2. Effect of Total H/Al Molar Ratio

Five different H/Al total molar ratios of 7.5, 8.0, 8.5, 9.0, and 9.5 were used to investigate the effect of this parameter on shrinkage of mixes P4, P9, P13, and P18 exhibiting the highest 28-day compressive strength. The obtained results are presented in figures 8 to 11. As seen, for all the mixes, shrinkage increase as the H/Al molar ratio increases. The variations of shrinkage due to changes made in Na/Al molar ratio, however, are not significant compared to those brought about by changes in H/Al molar ratio.

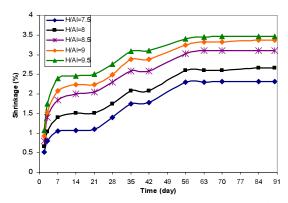


Fig. 8. Variations of shrinkage with time at different H/Al total molar ratios for mix P4.

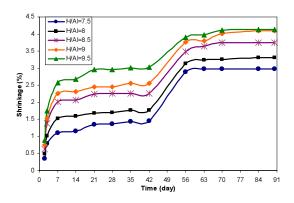
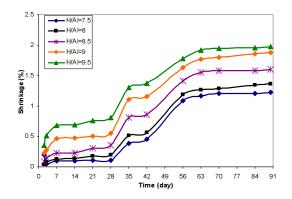


Fig. 9. Variations of shrinkage with time at different H/Al total molar ratios for mix P9.



**Fig. 10.** Variations of shrinkage with time at different H/Al total molar ratios for mix P13.

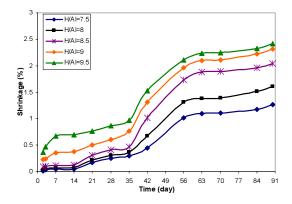


Fig. 11. Variations of shrinkage with time at different H/Al total molar ratios for mix P18.

#### 3. 3. 90-day Total Shrinkage

Figure 12 shows 90-day total shrinkage of the mixes at different Si/Na and Na/Al molar ratios and at constant H/Al molar ratio of 8.5. As seen, variations in total shrinkage versus Si/Na molar ratios follow specific patterns. For mixes with Na/Al molar ratios of 0.77 and 0.92, total shrinkage increases by increasing the amount of Si/Na molar ratio up to 0.75 and after that any increase in Si/Na molar ratios of 1.08 and 1.23, total shrinkage increases continuously by increasing Si/Na molar ratio of activator. It can be observed that some mixes have total shrinkage of less than

1% which is approximately acceptable in order to be industrially applicable. Mixes with total shrinkage of more than 1% are not preferred for industrial applications unless shrinkage reducing methods are used.

Figure 13 shows 90-day total shrinkage of the specimens at different total H/Al molar ratios for mixes P4, P9, P13, P18. As seen, for all mixes, total shrinkage increase as the H/Al molar ratio increases. For the mixes with lower Na/Al molar ratios, i.e. P4 and P9, the amount of total shrinkage is relatively higher than those with higher Na/Al molar ratio, i.e. P13 and P18 so that at highest H/Al molar ratio, the highest total shrinkage is observed for mix P9.

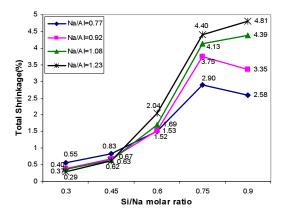


Fig. 12. Variations in total 90-day shrinkage versus Si/Na and Na/Al molar ratios and at constant H/Al molar ratio of 8.5.

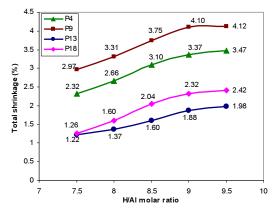


Fig. 13. Variations in total 90-day shrinkage versus H/Al molar ratios for mixes P4, P9, P13, and P18.

#### 3. 4. Effect of HydroThermal Curing

Above mentioned results and high amounts of shrinkage for almost all mixes led us to make further investigations. Hydrothermal curing was therefore applied on specimens exhibiting the highest 28-day compressive strength, i.e. P4, P9, P13, and P18, to investigate its effect on shrinkage.

Figures 14 and 15 show the results of total shrinkage obtained for mixes P4, P9, P13, and P18 cured hydrothermally at 85°C for 20 hours after 1 and 7 days of procuring, respectively. As seen in figure 15, for all the mixes the total

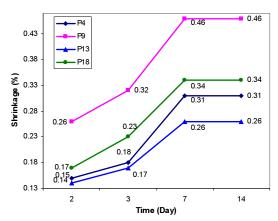


Fig. 14. Time variation of shrinkage of mixes P4, P9, P13, and P18 cured hydrothermally at 85°C for 20 hours after 1 day of precuring.

shrinkage is increased until 7 days after hydrothermal curing and then it becomes constant. Mix P9 shows the highest total shrinkage amount of 0.46% and mix P13 shows the lowest amount of 0.26 after 7 days of applying hydrothermal curing. Results obtained show that after hydrothermal curing all the specimens will have acceptable shrinkage amount and will be industrially applicable.

As seen in figure 15, for all the mixes the total shrinkage amount is increased until 14 days after hydrothermal curing and then become constant. Mixes P4 and P9 with higher Si/Na molar ratio show higher shrinkage values compared to mixes P13 and P18 after hydrothermal curing. The results, however, show that before hydrothermal curing there is an accelerated rate in increment of shrinkage amounts but after hydrothermal curing the rate of increase in shrinkage becomes quite low. As seen, for mix P4 which shows the highest shrinkage amount, before hydrothermal curing the shrinkage value after 7 days is 1.75% so that its value after hydrothermal curing after 21 days becomes 2.02. It means that the specimen has gained more that 85% of its total shrinkage in the first 7 days of curing in humid atmosphere and after hydrothermal curing less than 15% of its remaining shrinkage is achieved. This result is also observable for mix P9.

For mixes with lower amounts of shrinkage, i.e. P13 and P18, it is also seen that before hydrothermal curing the shrinkage values after 7

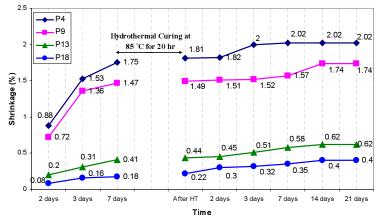


Fig. 15. Time variation of shrinkage of mixes P4, P9, P13, and P18 cured hydrothermally at 85°C for 20 hours after 7 days of precuring.

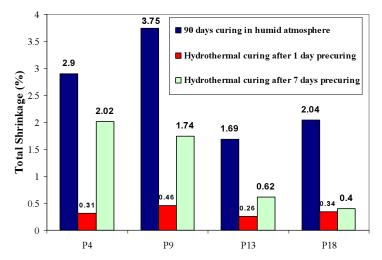


Fig. 16. Total shrinkage measurement for mixes P4, P9, P13, and P18 under different curing regimes.

days are 0.41 and 0.18 which are 66 and 45% of their total shrinkages, respectively.

This behavior could be attributed to the reaction mechanisms and molecular structure development of the studied geopolymer cement at the early ages of curing and the accelerated hydrothermal effect of curing on polycondensation reactions. Previous studies [16] performed by SEM on the microstructure of the hardened pastes of the same mixes cured in humid atmosphere confirmed the presence of a relatively high number of microcracks. The studies also confirmed the positive effect of hydrothermal curing in developing quite sound microstructure with no microcracks. The effect of hydrothermal curing was also studied by X-ray diffractometry. The obtained patterns however were quite the same showing a mainly amorphous material with few crystalline phases, which were originally present in the starting raw material. This indicates that the changes responsible for the differences in compressive strength originate and take place within the amorphous part of the structure and no zeolitic phase is formed during hydrothermal curing. Application of hydrothermal curing, therefore, is not only necessary for eliminating structural microcracks, but also quite beneficial in reducing total shrinkage effectively.

Figure 16 shows a comparison between the amounts of total shrinkages measured for mixes P4, P9, P13, and P18 under different curing

regimes including 90 days curing in humid atmosphere, hydrothermal curing after 1 day of precuring in humid atmosphere and hydrothermal curing after 7 days of precuring in humid atmosphere. As seen, specimens cured 90 days in humid atmosphere show the highest total shrinkage and are not industrially applicable. Application of hydrothermal curing, however, results in quite lower total shrinkage. Application of hydrothermal curing after a 7-day period of precuring causes 30, 53, 63, and 80% reduction in shrinkage for mixes P4, P9, P13, and P18, respectively.

Application of hydrothermal curing after 1 day of precuring however is more effective in shrinkage reduction and causes 90, 87, 84, and 83% reduction in shrinkage amounts for mixes P4, P9, P13, and P18, respectively. The maximum shrinkage reduction occurred in this curing regime for mix P4.

## 4. CONCLUSIONS

- 1. Geopolymerization reactions happening in the studied natural pozzolan based geopolymer binder result in considerable volume contraction or shrinkage.
- 2. The shrinkage behavior of the studied material is strongly influenced by both chemical composition and curing conditions.
- 3. Si/Na molar ratio of the activator is the

most effective parameter of chemical composition on shrinkage of natural pozzolan based geopolymer cement.

4. Hydrothermal curing with short precuring in humid atmosphere could affectively reduce the shrinkage amounts of the studied natural pozzolan based geopolymer cement

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