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Research Article

Mechanical strength variation of zeolite-fly ash geopolymer mortars with different activator concentrations

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ABSTRACT

Zeolite is of a significance for geopolymers as it is a natural precursor and does not require additional heat treatment for activation. However, aluminosilicates sourced from natural sources require additional handling for the best use of exploitation. In this study, geopolymers were synthesized by binary use of zeolite and fly ash as main binding material and sodium silicate and sodium hydroxide as alkaline activator. The influence of alkaline activator ratios and sodium hydroxide concentrations on the compressive strength and flexural strength of the zeolite-fly ash based geopolymers were studied. In this research, zeolite-fly ash based geopolymer mortars were produced by using 50% of natural zeolite (clinoptilolite) and 50% of C-type fly ash. Four different activator ratios ($Na_2SiO_3/NaOH$: 1, 1.5, 2 and 2.5) and two sodium hydroxide molarities (10M and 12M) was utilized to activate zeolite and fly ash in order to determine the effect of these parameters on the mechanical strengths of the produced geopolymer mortars. The results indicated that as the alkaline activator ratio and NH molarity were increased the compressive strength of the zeolite-fly ash based geopolymers also increased. The maximum compressive and flexural strength values obtained after 28 days of curing were 20.1 MPa and 5.3 MPa respectively and corresponds when used activator ratio of 2.5 and sodium hydroxide concentration of 12 molarity. The obtained results indicated that both the alkaline activator ratio and sodium hydroxide concentration affected the compressive and flexural strengths of zeolite-fly ash based geopolymer mortar specimens.

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1. Introduction

Geopolymer binder materials are amorphous to semi-crystalline materials that have similar structure to certain zeolitic materials which have an excellent characteristic like high strength, high fire resistance, high erosion resistance and good capability of immobilizing nuclear waste products (Van Jaarsved et al., 1999). Apart from metakaolin, some industrial waste materials like fly ash can be utilized for the production of the geopolymer materials. In the side environmental advantages, large benefits are derived by producing a new binder material with resources obtained from residue. Geopolymers which are based on aluminosilicate source materials presents a sustainable alternative for replacing Portland cement and they have been considered the cements for the future. The development of the geopolymers arose in the late of the 1970's and being fostered by work of Davidovits (Swanepoel and Strydom, 2002). Geopolymers can be produced from natural raw materials and industrial by-products that are rich in silica and alumina composition. Aluminosilicate compounds are abundant in the earth's crust and exist a large number of raw material sources rich in alumina and silicon with the ability for producing geopolymers. Among the materials which have been used for manufacturing geopolymer binder materials are fly ash (FA) (Bakharev, 2005; Xie and Xi, 2001), calcined clays (Zhang et al., 2004), blast furnace slag (Martinez et al., 2006), metakaolin (Duxson et a.l, 2007) and pozzolans (Martinez et al., 2006; Alcantara et

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al., 2000). Generally, alkali metals (sodium or potassium) silicate or alkali hydroxide are often used as an alkali activator for production of the geopolymer binder materials. Some of the studies estimated that producing cementitious binding materials by means of geopolymerization could result in an 86% reduction of carbon dioxide gas emissions for each ton of Portland cement (Davitovits, 2000).

The natural zeolites could be possible used as a precursors in a geopolymer synthesis (Nikolov and Rostovsky, 2017). The natural zeolite shows good pozzolanic activity when used in cement pastes (Lilkov et al., 2011) and also could add specific properties to the resulted product. Natural zeolites are hydrated aluminosilicates of alkaline and alkaline earth metals forming a group of minerals which have microporous structure based on SiO_4 and AlO_4 tetrahedrons. This property of zeolite structure is a basis for useful properties like ion exchange, selective sorption and catalytic activity (Lithareva et al., 2010).

Natural zeolite like clinoptilolite is an aluminosilicate mineral and it has been utilized as the solid source binder material when producing geopolymers. When manufacturing geopolymer pastes sand is not been used in the mix design, Villa et al. (2010) obtained compressive strength of around 30 MPa in geopolymer paste specimens when used natural zeolite (clinoptilolite) activated with sodium silicate and sodium hydroxide solutions in different proportions and cured at different temperatures. The optimum temperature range found was between 40°C and 80°C. On the other hand, Baykara et al. (2017) studied the effect of sodium hydroxide concentration, calcium hydroxide content and sodium silicate to sodium hydroxide ratios on geopolymer paste specimens when utilized natural zeolite (mordenite) and cured at various temperatures. Geopolymers of compressive strength 10 MPa after curing for 24 hours at 60°C was found. In case of manufacturing geopolymer mortars, sand is used in the mixture, Nikolov et al. (2010) produced geopolymer based on natural zeolite (clinoptilolite) and quartz sand for the synthesis of mortar using sodium hydroxide, sodium silicate and sodium carbonate as an alkali activators. The resulting geopolymer mortars showed a maximum compressive strength of 3.7 MPa after 28 days. Nikolov et al. (2017) prepared geopolymer based on natural zeolite and river sand for production of mortar using sodium hydroxide and sodium silicate as an alkali activators. Geopolymer mortars yield a compressive strength of 17 MPa after curing 28 days. Sudagar et al. (2018) studied geopolymers that contained 0%, 25%, 50% 75% replacement of metakaolin by zeolite to evaluate the compressive strength after 1, 14 and 28 days. They found the addition of zeolite in minor amounts concurrently aided in increasing the compressive strength of geopolymers.

Since zeolite is a natural pozzolan and occurs abundantly on the earth, it could provide an important opportunity to be used as geopopymer binding material and when used as partial replacement to well-known geopolymer precursors like fly ash it could provide an opportunity to decrease the amount of usage for these materials. The aim of this study was to evaluate the conditions of manufacturing of geopolymer binder materials based on natural zeolite (clinoptilolite) and C-type fly ash in order to obtain geopolymer cementitious materials that have attractive mechanical properties similar to ordinary Portland cement. In this study, 50% of natural zeolite and 50% of C-type fly ash were used to produce zeolite-fly ash based geopolymer mortars. The compressive and flexural strengths of zeolite-fly ash based geopolymer mortars were investigated considering four different sodium silicate (NS) to sodium hydroxide (NH) ratios (1, 1.5, 2 and 2.5) and two different sodium hydroxide molarities (10M and 12M). The results obtained from this study will be very useful for the application of zeolite-fly ash based geopolymers for structural purposes.

2. Experimental Stage

2.1. Materials

Natural zeolite (clinoptilolite) and C-type fly ash were used as a solid precursor to produce zeolite-fly ash based geopolymer mortars. The natural zeolite used in this study was obtained from Gordes Zeolit, Manisa, Turkey. The C-type fly ash used was obtained from Sivas Kangal Thermal Sivas, Turkey. In order to activate zeolite and fly ash, a combination of sodium silicate (NS) and sodium hydroxide (NH) solutions was used in a different silicate to hydroxide ratios. The sodium silicate solution with alkaline modulus of 1.9-2.2 and sodium hydroxide pellets were taken from a local market. The commercially available sodium hydroxide pellets with 98% purity was used and dissolved in water to produce sodium hydroxide solution with different concentrations. In this work, two sodium hydroxide concentrations (10M and 12M) and four different sodium silicate to sodium hydroxide ratios (1, 1.5, 2 and 2.5) were used. The effects of these parameters on the mechanical strengths of zeolite-fly ash based geopolymer mortars were investigated. Table 1 demonstrates the chemical composition and specific gravities of natural zeolite (NZ) and C-type fly ash (CFA) materials.

Table 1. Chemical composition and physical properties of NZ (Sevgi and Burhan, 2018) and CFA (Tahir et al., 2010).

Chemical Composition	CFA	NZ
CaO (%)	27.62	4.43
Al_2O_3 (%)	16.69	13.2
SiO_2 (%)	38.34	65.6
Fe_2O_3 (%)	5.11	1.78
MgO (%)	1.60	1.27
SO_3 (%)	4.44	0.07
Na_2O (%)	-	0.21
K_2O (%)	-	2.8
MnO (%)		0.05
Loss on ignition (%)	0.79	10.32
Specific gravity (g/cm^3)	2.3	2.41

Clean and dry river sand passing through ASTM 2 mm sieve was used as fine aggregates for this experimental study. The general gradation of the natural river sand used was provided in Table 2 and Fig. 1.

Table 2. Grading for aggregate used in this work.

Sieve Size (mm)	31.5	20	16	11.2	8	4.75	2	1	0.5	0.3	0.15	0.063
Passing Sand (%)	100	100	100	100	99.7	96.14	61.03	38.78	24.13	12.13	2	0.27

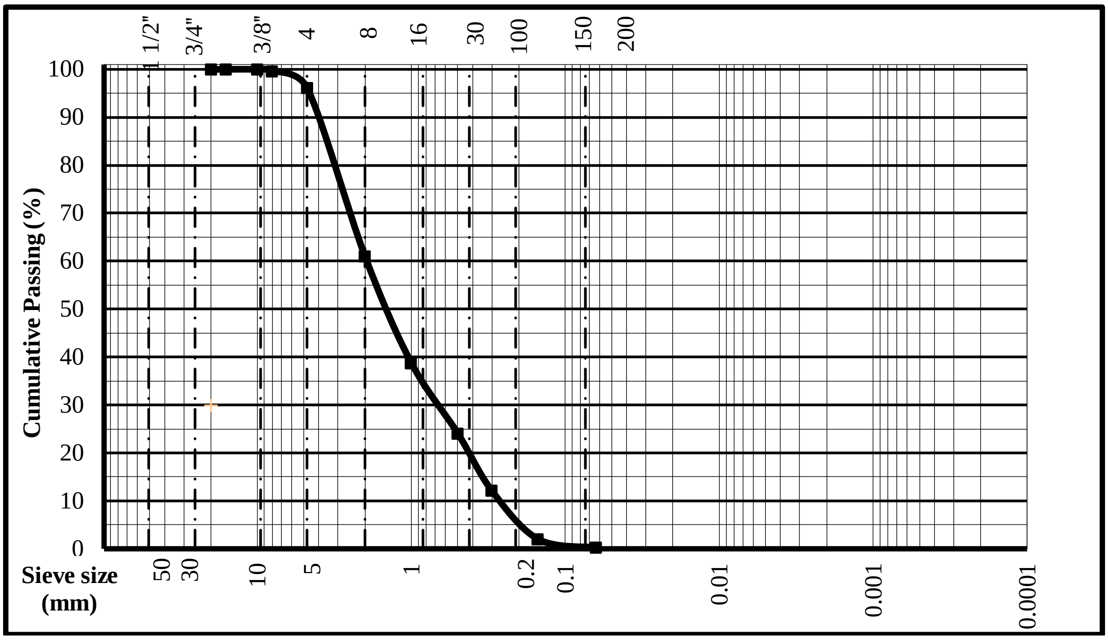

Fig. 1. Aggregate sieve analysis.

2.2. Mix Design

Table 3 shows the mix proportions of the zeolite-fly ash based geopolymer mortars with different sodium hydroxide concentrations and sodium silicate to sodium hydroxide ratios. To synthesize geopolymer mortars, water/binder was kept constant at 0.45 while activator/binder was made variable. Sand/bınder was taken 2.5 to all geopolymer mortars produced in this study. The amount extra water added to the mixture was changed according to the mixture flowability.

During mixing process, sand, zeolite and fly ash were first added in the pan mixer as a dry condition and mixed for almost 2 minutes until the mixture becomes homogeneous. Then sodium silicate and sodium hydroxide were added separately at the same time and the mixture was mixed for another 2 minutes. Finally, extra water was added into mixture and mixed for another 1 minute. The total time for mixing the raw materials was 5 minutes. For alkali activation to occur further and to enhance workability, addition of water to the geopolymer materials were reported in the past researches (Soutsos, et al., 2016).

Table 3. Mix design of zeolite-fly ash based geopolymer mortars with different molarities and sodium silicate to sodium hydroxide ratios (g).

Material	12M	12M	12M	12M	10M	10M	10M	10M
NS/NH	1	1.5	2	2.5	1	1.5	2	2.5
Natural zeolite	225	225	225	225	225	225	225	225
C type Fly ash	225	225	225	225	225	225	225	225
Sand	1125	1125	1125	1125	1125	1125	1125	1125
Sodium silicate (NS) solution	120	180	240	300	100	150	200	250
Sodium hydroxide (NH) solution	120	120	120	120	100	100	100	100
Water	202.5	202.5	202.5	202.5	202.5	202.5	202.5	202.5

*NS: Sodium silicate; NH: Sodium hydroxide

2.3. Curing conditions and testing

After the mixing process of the geopolymer mortars were finished, they were cast into the molds of size 40x40x160 mm^3 and then applied compaction using vibrating table for 72 seconds to remove entrapped airs. The geopolymer mortar samples were placed in the oven for 90 minutes, then they were removed from the oven and demolded. In this study, the samples were put into fireproof oven bags and placed in the oven at 80°C for 24 hours and then after the oven, they were left in the laboratory environment (25°C and 45% relative humidity) in a closed container until the testing day. The past studies reported that high temperature around 60 to 80°C is required to have a good compressive strength for zeolite based geopolymers (Davitovits, 2000 and Villa et al., 2010). The compressive and flexural strengths tests were prepared by using 40x40x160 mm^3 prismatic specimens according to the TS EN 196-1 standard where the geopolymer samples were test at the ages of 7, 14 and 28 days. At first stage the sample was tested for flexural strength which makes the sample into two halves. The resulting two halves were used to measure the compressive strength of the geopolymer mortar specimen.

3. Results and Discussion

3.1. Effect of 12M NH concentration on strength

Compressive and flexural strengths test results of zeolite-fly ash based geopolymer mortars with different sodium hydroxide molarities and sodium silicate to sodium hydroxide ratios (NS/NH) were given in Figs. 2-5. Figs. 2 and 3 indicate the compressive strength and flexural strength test results of zeolite-fly ash based geopolymer specimens with 12M NH concentration and different NS/NH ratios respectively. The compressive strength values of the specimens with 12M NH after 7-day curing were found to be 17.2, 17.2, 17.4 and 19.1 MPa for NS/NH ratios of 1, 1.5, 2 and 2.5 respectively. After 14 days of curing, the compressive strength values increased slight and become 18.3, 17.6, 17.9 and 19.5 MPa for the different NS/NH ratios. Finally, the compressive strength values after 28 days of curing for geopolymer mortars with 12M NH and NS/NH ratios of 1, 1.5, 2 and 2.5 are found to be 19, 18.2, 18.2 and 20.1 respectively.

Flexural strength values of the specimens with 12M NH also show a linear increase after curing 7 days. As shown from Fig. 3, flexural strength values for geopolymer mortars with 12M NH and NS/NH ratios of 1, 1.5, 2 and 2.5 at 7 and 14 days were 4.5, 4.6, 4.6, 5.2 MPa and 4.3, 4.2, 4.9, 5.2 MPa respectively. Finally, flexural strength values after 28 days of curing for geopolymer mortars with 12M NH and NS/NH ratios of 1, 1.5, 2 and 2.5 were found to be 5.2, 4.8, 5.1 and 5.3 respectively.

3.2. Effect of 10M NH concentration on strength

Figs. 4 and 5 show the compressive strength and flexural strength test results for geopolymer mortar specimens with 10M NH concentration and NS/NH ratios of 1, 1.5, 2 and 2,5 respectively. The compressive strength values passed 17 MPa for geopolymer mortars with NS/NH ratios of 1.5, 2 and 2.5 while the compressive strength values of the geopolymers with low NS/NH ratio of 1 reached around 12 MPa. The results pointed out that the compressive strength values for the geopolymer mortar specimens with 10M NH concentration were found to be increased when the alkaline activator ratio was increased. The compressive strengths of the geopolymer mortars slightly increased with increasing curing period. For NS/NH ratio of 2.5, the compressive strength values increased 16.4 MPa for 7 days to 17.9 MPa for 28 days of curing period. The highest flexural strength values for geopolymer mortar specimens with 10M NH concentration reached 5.2 MPa when the NS/NH ratio was 2.5. Fig. 5 shows that some of the flexural strength values slightly decreased with curing period. For NS/NH ratio of 2.5, the flexural strength reached maximum of 5.2 MPa for 7 days of curing and decreased to 5.1 MPa for 28 days of curing.

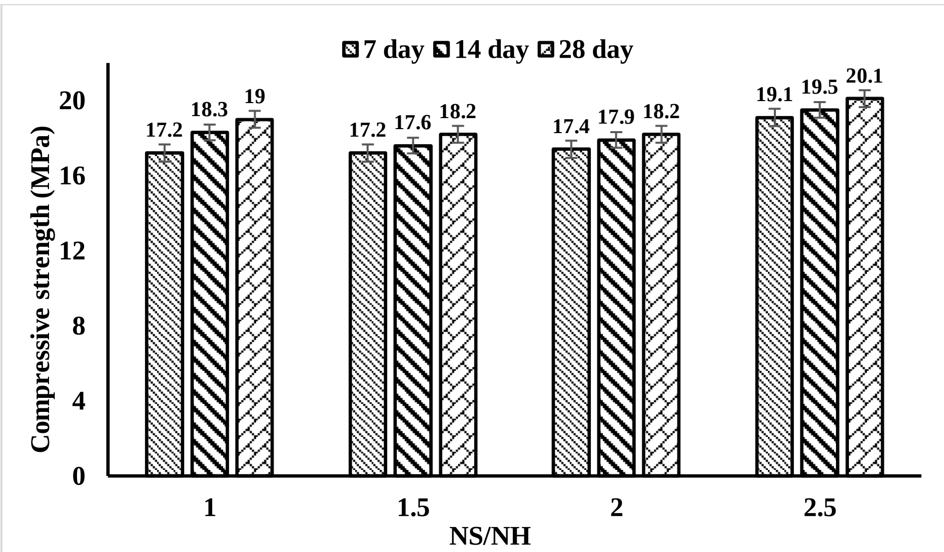

Fig. 2. Compressive strength values with 12M NH after 7, 14 and 28 days.

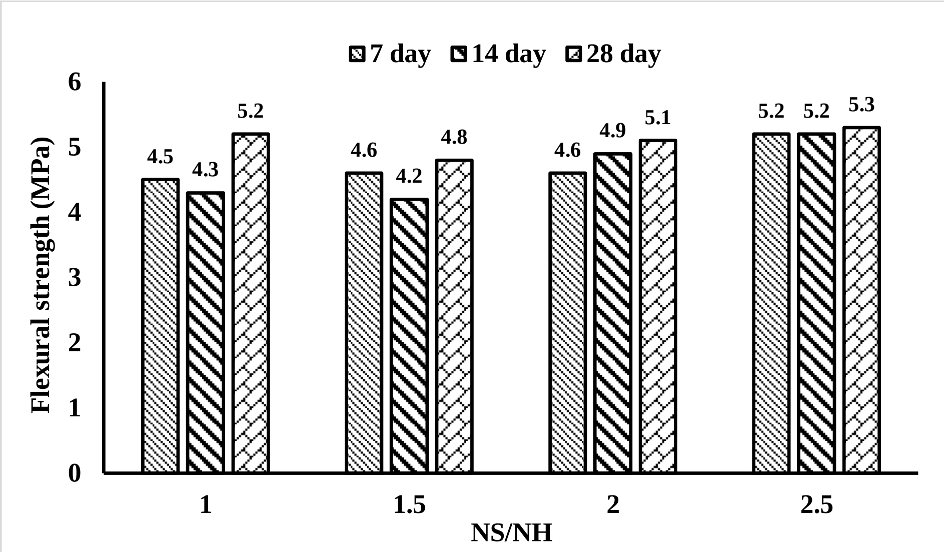

Fig. 3. Flexural strength values with 12M NH after 7, 14 and 28 days.

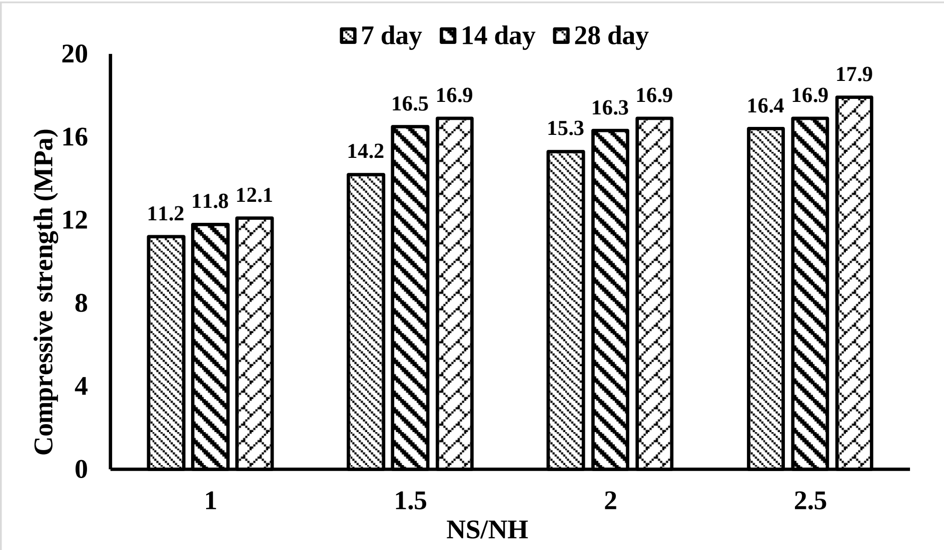

Fig. 4. Compressive strength values with 10M NH after 7, 14 and 28 days.

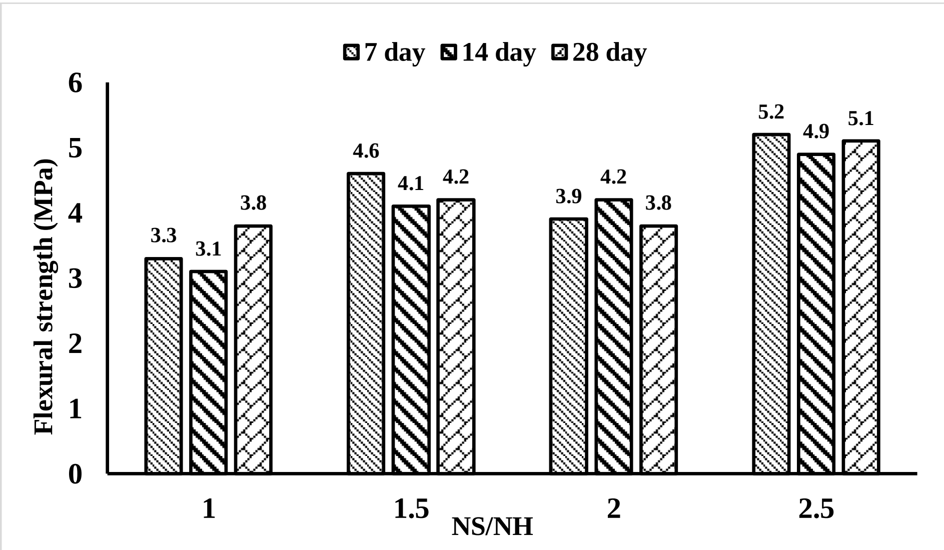

Fig. 5. Flexural strength values with 10M NH after 7, 14 and 28 days.

3.3. Effect of alkaline activator ratios on strength

Figs. 6 and 7 show the influence of alkaline activator (NS/NH) ratios on the compressive and flexural strengths of the zeolite-fly ash geopolymer mortars with different NH concentration molarities. The compressive strength values of the geopolymer mortars with 10M NH molarity increased from 12.1 MPa to 17.9 MPa for 28 days of curing period when NS/NH ratios increased from 1 to 2.5. However, the compressive strength values of the geopolymer mortars with 12M NH first reached 19 MPa when NS/NH ratio was 1 and finally reached maximum value of 20.1 MPa when NS/NH ratio 2.5.

As Fig. 7 indicates, the flexural strength values of the geopolymer mortars with 10M NH molarity for 7 days of curing increased from 3.3 MPa to 5.2 MPa when NS/NH ratios increased from 1 to 2.5. The flexural strengths increased from 3.8 MPa to 5.1 MPa when NS/NH ratios increased from 1 to 2.5 for 28 days of curing. For geopolymer mortars with 12M NH molarity, the flexural strengths increased from 4.5 MPa to 5.2 MPa when NS/NH ratios increased from 1 to 2.5 for 7 days of curing. Finally, the flexural strengths of geopolymer mortars with 12M NH molarity increased slightly from 4.3 MPa to 5.3 MPa for 28 days of curing when NS/NH increased from 1 to 2.5.

For the comparison of the utilized alkaline activator ratios, the compressive strength values of the specimens with different NH concentrations for different curing periods are given in Table 4.

The results pointed out that the maximum compressive strength was obtained in the specimens with a NS/NH ratio 2.5 and NH concentration of 12M, while the minimum compressive strength was achieved on the specimens with a NS/NH ratio of 1 and 10M NH concentration. A maximum compressive strength of 17 MPa for only zeolite geopolymer mortar specimens with a NS/NH ratio of 2.5 was also obtained in the study of Ulloa et al. (2018). In addition, the compressive strength values of the zeolite-fly ash geopolymer mortar specimens with 12M NH concentrations increased with the curing period.

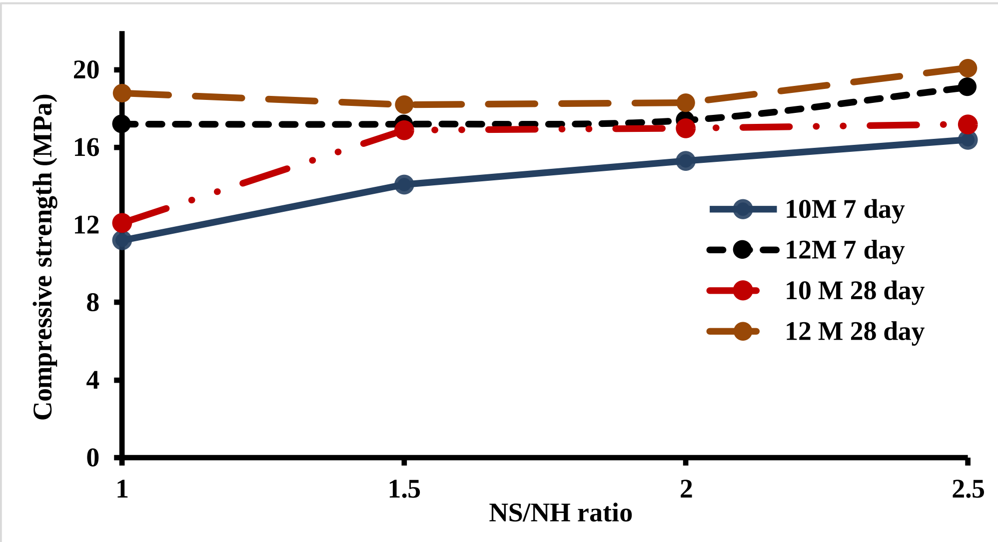

Fig. 6. Compressive strength values of geopolymers with various alkaline activator ratios.

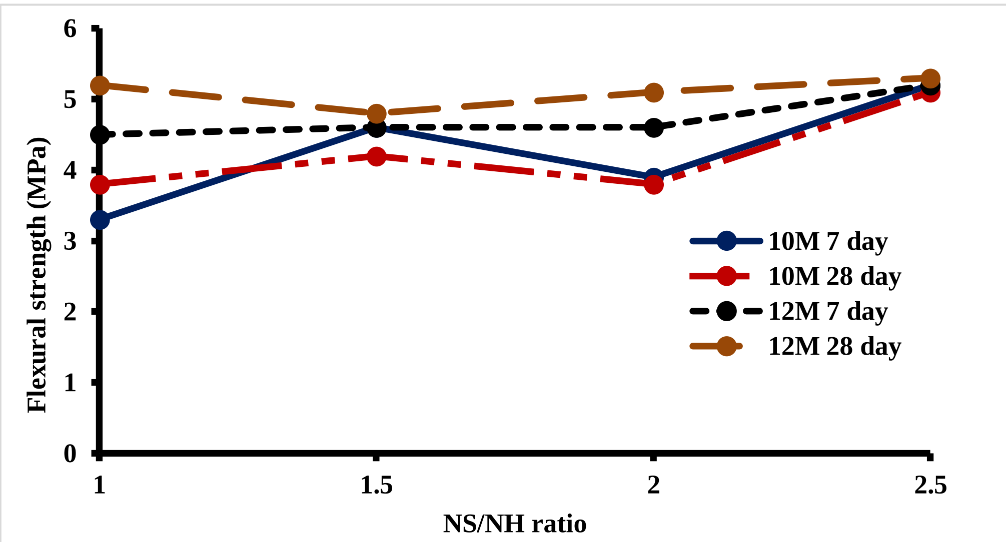

Fig. 7. Flexural strength values of geopolymers with various alkaline activator ratios.

Table 4. Compressive strength values for geopolymers produced in this study.

NS/NH ratio	10M 7 day	10M 14 day	10M 28 day	12M 7 day	12M 14 day	12M 28 day
1	11.2	11.8	12.1	17.2	18.3	19
1.5	14.2	16.5	16.9	17.2	17.6	18.2
2	15.3	16.3	16.9	17.4	17.9	18.2
2.5	16.4	16.9	17.9	19.1	19.5	20.1

4. Conclusions

In this study, effect of two different sodium hydroxide concentrations (10M and 12M) and four various alkaline activator (sodium silicate/sodium hydroxide) ratios (1, 1.5, 2 and 2.5) on the mechanical strengths (compressive and flexural strengths) of zeolite-fly ash based geopolymer mortar cured under ambient temperature for 7, 14 and 28 days were investigated. The results of the experimental study are summarized as follows:

- The compressive strength values of the geopolymer mortar specimens were mostly influenced by the alkaline activator (NS/NH) ratio and sodium hydroxide (NH) concentrations while curing periods applied to the geopolymer mortars slightly influenced the compressive strength values. For the specimens with 12M NH concentrations, the compressive strength values increased from 17.2 to 19.1 MPa for 7 days, from 18.3 to 19.5 MPa for 14 days and from 19 to 20.1 MPa for 28 days of curing for different NS/NH ratios.
- The compressive strength values of the geopolymer mortars produced by using 10M NH were smaller than that of 12M NH. The compressive strength values of the geopolymer specimens with 10M NH concentrations increased from 11.2 to 16.4 for 7 days, 11.8 to 16.9 MPa for 14 days and 12.1 to 17.9 MPa for 28 days of curing period for different NS/NH ratios. From this observation, it can be concluded that as the amount of NH in the mixture increase, the compressive strength of the geopolymer mortars showed an increase.
- The compressive strength values for the geopolymer mortar specimens with different sodium hydroxide concentrations were found to be increased when the alkaline activator ratio was increased. The maximum compressive strength of 20.1 MPa was obtained when used an activator ratio of 2.5 while the minimum compressive strength of 11.2 MPa was obtained when used an activator ratio of 1.
- For the specimens with 12M NH concentrations, the flexural strength values increased from 4.5 to 5.2 MPa for 7 days, from 4.3 to 5.2 MPa for 14 days and from 5.2 to 5.3 MPa for 28 days of curing for different NS/NH ratios. While the flexural strength values of the geopolymer specimens with 10M NH concentrations increased from 3.3 to 5.2 for 7 days, 3.1 to 4.9 MPa for 14 days and 3.8 to 5.1 MPa for 28 days of curing period for different NS/NH ratios.
- The flexural strength values of the geopolymer mortar specimens with 12M NH concentration were found to be higher than that of 10M NH concentration.
- The flexural strength of 12 M NH geopolymer mortars showed a linear increase when the alkaline activator ratios was increased. While flexural strength of 10M NH geopolymer mortars behaved differently from 12M NH geopolymer mortars. The flexural strength of 10M NH geopolymer mortars first show an increase from activator ratio of 1 to 1.5 and then the flexural strength showed a decrease when activator ratio increases from 1.5 to 2 and finally the flexural strength showed an increase again when activator ratio increased from 2 to 2.5.

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