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Engineering Properties of Alkali Activated Natural Pozzolan Concrete

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ABSTRACT

The development of alkali activated binders with superior engineering properties and longer durability has emerged as an alternative to OPC. It is possible to use alkali-activated natural pozzolans to prepare environmentally friendly geopolymeric cementitious construction materials. The main benefit of geopolymers cements is their reduction in environmental impact leading to the concept of sustainable development. This paper presents a summary of and experimental study on the engineering properties of geopolymer concrete prepared with Taftan andesite, an activated Iranian natural pozzolan. Experimental work was conducted to determine mechanical strength; modulus of elasticity; ultrasonic pulse velocity of different concrete mixtures. Test data have been used to identify the effects of salient factors such as water to binder ratios and curing conditions that influence the properties of the geopolymer concrete. The results show that mortar and concrete made with the alkali activated natural pozzolan develop moderate to high mechanical strength and modulus of elasticity.

INTRODUCTION

Concrete made with Portland cement is a major construction material used worldwide. Unfortunately, the production of Portland cement releases large amounts of CO_2 into the atmosphere making a major contribution to the greenhouse effect and the global warming of the planet. Portland cement production is estimated to contribute around 7% of global CO_2 emissions. To reduce greenhouse gas emissions, efforts are needed to develop environmentally friendly construction materials. One such alternative is geopolymer cement which can be utilized to manufacture pre-cast concrete, structural and non-structural elements, immobilize toxic waste, and produce concrete products that are resistant to heat and aggressive environments [Hardjito et al., 2004*a*, 2004*b*]. Unlike regular concrete, the chemical reactions that form the geopolymer concrete alternative do not require high temperatures for processing which give off carbon dioxide. The geopolymer concrete manufacture is estimated to reduce CO_2 emission by 22% to 72% (depending on materials used) compared to OPC production [Bondar, 2009].

This paper presents the technology of making geopolymer concrete using a natural pozzolan as its source material and presents the results of laboratory tests conducted on this material. The research data presented in this paper are useful to understand the engineering properties of geopolymer concrete.

PREVIOUS RESEARCH ON GEOPOLYMER BINDERS

The term "geopolymer" describes a family of mineral binders which have a polymeric silicon-oxygen-aluminum framework structure. The mechanism of geopolymerisation consists of dissolution, transportation or orientation, and polycondensation [Van Jaarsveld et al., 1997], in an exothermic process [Davidovits, 1999, Palomo et al., 1999*a*]. The geopolymer paste serves to bind not only the coarse and fine aggregates but any un-reacted material [Hardjito et al., 2004*a*, 2004*b*].

There are many different views as to which are the main parameters that affect the compressive strength and other mechanical properties of geopolymer concrete. Palomo et al. (1999*b*) stated that the significant factors affecting the compressive strength are the type of alkaline activator; the curing temperature and the curing time. However, other researchers have reported that the important parameters for satisfactory polymerization are the relative amounts of Si, Al, K, Na, and molar ratio of Si to Al present in solution, the type of alkaline activator, the water content, and the curing temperature [Xu and Deventer, 2000, Barbosa et al., 2000, Rowles et al., 2003, and Van Jaarsveld et al., 1997]. The presence of silicate ions in the alkaline solution substantially improves the mechanical strength and modulus of elasticity values but it has a slightly adverse effect on the otherwise very strong matrix/aggregate and matrix/steel bond [Fernandez-Jimenez et al, 2006]. Experimental results show that the H_2O/M_2O molar ratio in the mixture composition significantly affects the compressive strength of fly ash based geopolymer concrete, whereas the influence of the Na_2O/SiO_2 molar ratio is less significant [Hardjito et al., 2004*a*, 2004*c*]. An increase of the H_2O/M_2O molar ratio and water to solids ratio decreases the compressive strength of geopolymer [Hardjito et al., 2004*a*, 2004*c*]. In addition, Van Jaarsveld et al. (2002) found that curing at elevated temperatures for long periods of time may weaken the structure of hardened material. Research on fly ash-based geopolymer binder, [Palomo, Grutzeck, and Blanco (1999)] has confirmed that curing temperature and curing time significantly influence the compressive strength but that does not seem to be same for different aluminosilicates. Longer curing time and higher curing temperature increased the compressive strength in fly ash based geopolymer concrete, although the increase in strength may not be as significant for curing at more than 60°C and for periods longer than 48 hours [Hardjito et al., 2004*a*, 2004*b*]. In most cases, 70% of the final compressive strength is developed in the first 4 hours of setting. Because the chemical reaction of the geopolymer paste, made from alkali activated flyash, is a fast polymerization process, the compressive strength does not vary greatly with the age of concrete, after it has been cured for 24h. This observation is in contrast to the well-known behaviour of OPC concrete, where the hydration process extends over a long period and hence strength increases over time [Hardjito et al., 2004*a*, and 2004b]. Another kinetic difference between Portland cement and alkaline activated systems is the existence of a relatively low threshold temperature in the former, above which thermal curing can have an adverse effect on the mechanical development and even on material durability. For an activated ash, on the contrary, a suitable choice of reaction time and curing temperature can yield different reaction products without detracting from material durability, because according to Fernandez, Palomo, and Hombradoz (2006), increases in the curing temperature go hand-in-hand with decreases in the amount of Al incorporated into the final product and a concomitant improvement in mechanical properties. Such improvements parallel the formation of a homogeneous aluminosilicate matrix [Davidovits, 1999].

Puertas et al. (2003) reported that the elastic modulus of OPC mortars was 5.7 GPa, higher than the values for PFA mortars activated with 8M NaOH (4.4 GPa). Fernandez-Jimenez et al. (2006) found that the addition of soluble silicates in the alkaline solution improved the modulus of elasticity in PFA-based geopolymer concrete. However, this improvement was not sufficient and the alkali activated PFA concrete showed a much lower static modulus of elasticity than expected. The values presented for OPC concrete ranged from 30.3 to 32.3GPa while for geopolymeric concrete they ranged from 10.7 (without silicate) to 18.4 GPa (with silicate). Hardjito et al. (2004) observed better elastic modulus results for fly ash based geopolymer concrete samples: 22.95 to 30.84 GPa.

EXPERIMENTAL WORK

Material and Mixing Procedure

In this research, Taftan andesite with CaO/SiO_2 equal to 0.13 was selected as it is the most reactive natural pozzolan in Iran and used to produce Portland pozzolan cement by the Khash Cement Factory. Taftan pozzolan was studied by Iranian Cement Guild [Ezatian, 2002], using optical microscopy and showed it contained feldspar (sodic plagioclase including albite and hornblende), amphibole, quartz, and biotite. The chemical composition was analysed by Kansaran Binaloud X-ray laboratory in Tehran, Iran (2005-2006) using XRF and is presented in Table 1.

Table 1 Physical and chemical composition (oxide percent) of the materials used in this investigation

Material	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	Surface area (cm^2/g)	SG
Taftan andesite	1.85	61.67	15.90	4.32	7.99	2.04	0.438	2.12	3.21	3836	2.22

Potassium hydroxide (KOH) pellets supplied by MERK International Ltd. were dissolved in water to produce the alkaline solutions for geopolymer concrete production. Sodium silicate solution was provided by Iran Silicate Industrial Company in the form of water glass. The chemical composition of the solution provided by the manufacture was: 8.5% of sodium oxide (Na_2O), 26.5% of silicon oxide (SiO_2) and 65% of water; pH=11.4.

The aggregate used in this study was obtained from the Karaj River deposits in the northwest of Iran and comprised 14mm and 4.75mm coarse aggregates and fine sand. The fineness modulus of the combined aggregates was 2.08.

The proportioning of the control concrete mixture was based on the BRE method [Neville, 1995] targeting a 40 MPa (28 days) compressive strength and a slump of 60 mm. The cement was substituted with the same quantity of natural pozzolan plus the solids in water glass and alkaline solution but no additional water was added as the activators were already in solution. The amount of solids in water glass and alkaline solution to total binder ratio by mass was 20 and 25% for ATAF1 and ATAF2 mixes, respectively and the ratio of KOH (ml)/ Na_2SiO_3 (ml) was 7.7 for all mixes. The notation for the mixes is as follows:

CM1: PC control mix with w/c=0.45
CM2: PC control mix with w/c=0.55
ATAF1: Activated Taftan pozzolan with w/b=0.45
ATAF2: Activated Taftan pozzolan with w/b=0.55

Activated Taftan pozzolan mixes with w/b of 0.4 and 0.5 were also tested for the measurement of compressive strength.The concrete samples were cast in different sizes as required by the tests. The mixtures were cast into the pre-oiled moulds in three layers and vibrated by means of a vibrating table to remove any entrapped air. The flow of the mixtures was measured by vebe test and the vebe times were 25 and 12 seconds for ATAF1 and ATAF2 mixes, respectively. It was observed that a geopolymer concrete stick hard to the mould and oiling of the moulds is very important to release the samples. Taftan specimens were de-moulded 24 hours after casting and cured in two curing regimes and at three different temperatures:

1) Sealed curing: Three series of specimens were sealed wrapped in a special plastic covering which was tested to be impermeable and stored in a controlled room kept at 20±2, 40±2 and 60±2°C.
2) Fog curing: Three series of the specimens were cured in the fog chamber set at three different temperatures equal to 20±2, 40±2 and 60±2°C for the measurement of compressive and splitting tensile strength. Fog curing at 40±2°C was used for static modulus of elasticity test.

Testing Procedures

In order to determine the compressive strength of geopolymer concrete each mixture was prepared as 100x100x100 mm cubes and the compressive strength for these samples were tested according to BS EN 12390-3:2009. Details of casting and curing are described in section 3.1. Three samples of each formulation were tested at 1, 7, 14, 28, 90, 180 and 365 days, and the average compressive strength values reported as the results.

The ultrasonic pulse velocity was measured in accordance with BS EN 12504-4-2004. The measurement was conducted on the 100mmx100mm end face of a prism with a length of 500mm. Duplicate sets of samples were tested at 28, 90,180 days.
The splitting tensile strength of all mixes was measured using 100mm Φ x 200mm length cylinders. The samples were prepared and splitting tensile tests performed as described in BS EN 12390-6:2002. The specimens were tested in duplicate sets at 7, 14, 28, 90, 180 days and the average results are reported.

The static modulus of elasticity was determined according to BS1881-121:1983 standard by subjecting a 100mm Φ x 200mm cylinder specimen to uni-axial compression and measuring the deformation by means of dial gauges fixed between certain gauge lengths. Dial gauge reading divided by gauge length gives the strain while load applied divided by area of cross section gives the stress. A series of readings were taken and the stress-strain relationship established. The modulus of elasticity found from actual loading is called static modulus of elasticity.

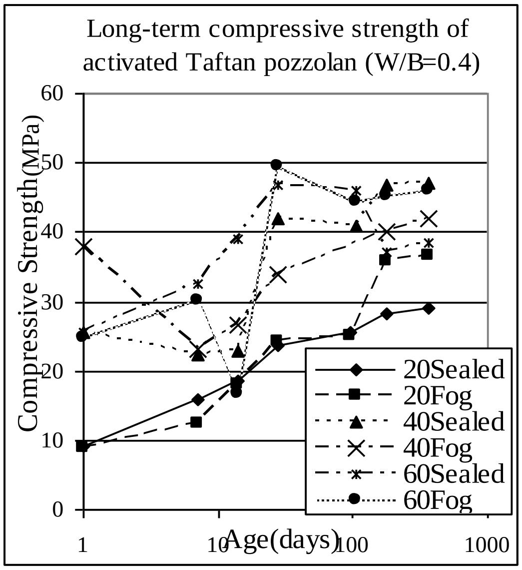
RESULTS AND DISCUSSION

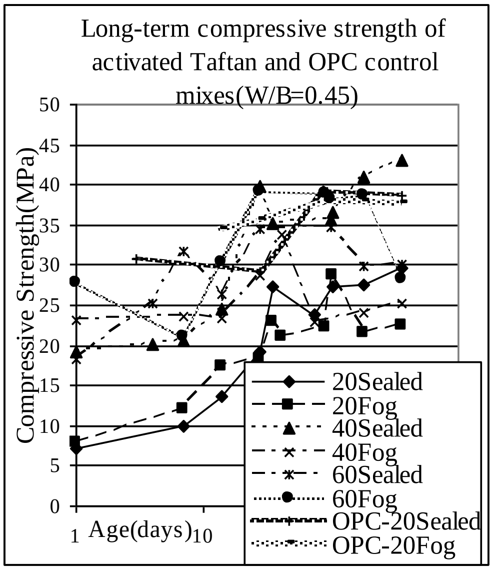
Compressive Strength

The compressive strength results of concrete using activated natural pozzolan and control Portland cement mixes are presented in Figure 1 using logarithmic x-axis.
In all cases, the strengths of the concretes increased with age. The rate of strength gain is high at early ages and gradually decreases at longer ages. Geopolymeric concrete mixes mostly showed lower strengths than OPC control mixes at early ages, but they reached the same and even higher strengths than OPC mixes after long-term aging. Activated Taftan pozzolan with W/B=0.45 (ATAF1) has the highest compressive strength of 43.5 MPa, while activated Taftan pozzolan with W/B=0.55 (ATAF2) reaches 39.1 MPa after 365 days, higher than for the OPC control mix.

It is well known that curing greatly affects the strength development in concrete. Figure 1 clearly shows the effect of different curing temperatures in the two curing conditions: sealed and fog cured. In general, the sealed condition gave the best results in the long term, the same as for OPC control concrete although the difference between the two conditions is not significant. This phenomenon may be related to more water being retained in the pores causing a more open microstructure in fog-cured specimens.

The results suggest that the best temperature for curing alkali-activated Taftan pozzolan is 60°C for achieving high early strength but curing at 40°C under sealed conditions gave the highest strength results in the long-term (Figure 1).





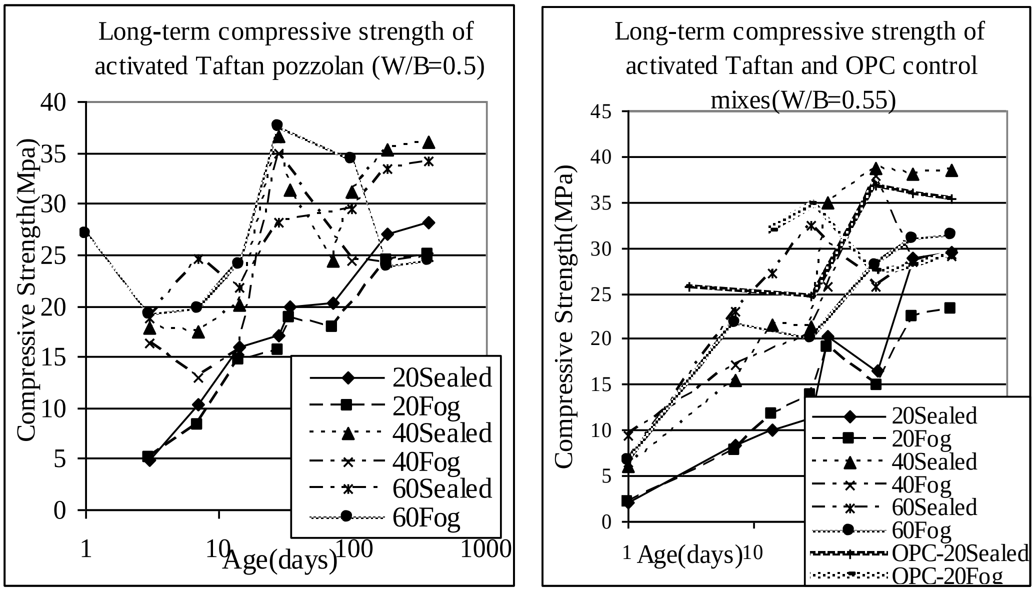


Fig. 1 Effect of different curing condition and curing temperature oncompressive strength development for activated Taftan pozzolan with different water to binder ratios (the fluctuations in strength results are probably due to sample to sample variability)

The effect of water content is illustrated in Figure 2 by plotting the 28 days compressive strength versus water-to-geopolymer solids ratio by mass. The test data shown in Figure 2 demonstrate that the compressive strength of geopolymer concrete decreased as the ratio of water-to geopolymer solids by mass increased giving rise to more free water in the geopolymer concrete leading to a more porous microstructure. The trends of these test results are similar to those observed by Hardjito et al (2004*c*) and Barbosa et al (2000) for their tests on geopolymer concretes. The results shown in Figure 2 also confirm that an increase in the curing temperature increased the concrete compressive strength.

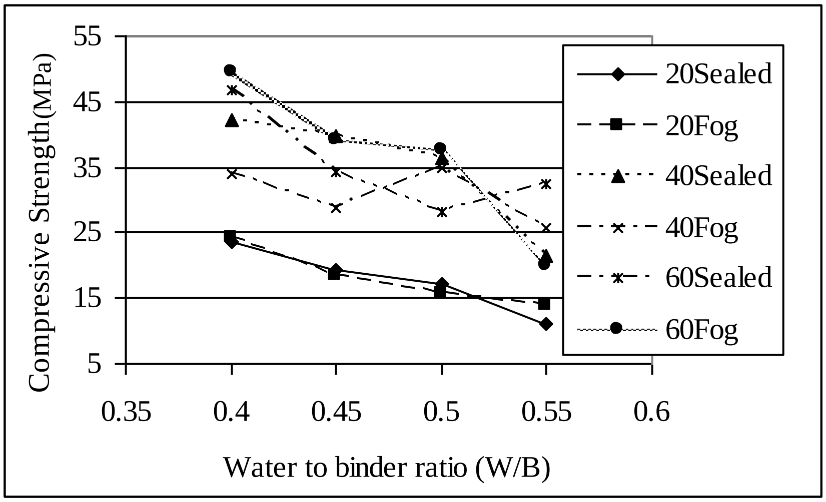


Fig. 2 Compressive strength at 28 days versus water to binder ratio (W/B) for alkali activated Taftan pozzolan at different curing temperature

Ultrasonic Pulse Velocity

Figure 3 shows the results for the ultrasonic pulse velocity test for all mixes. ATAF1 achieved the highest values followed by ATAF2 which has a higher w/b. All of the geopolymer concrete mixes showed lower ultrasonic pulse velocities than the OPC concrete mixes, even with the same or higher compressive strength.

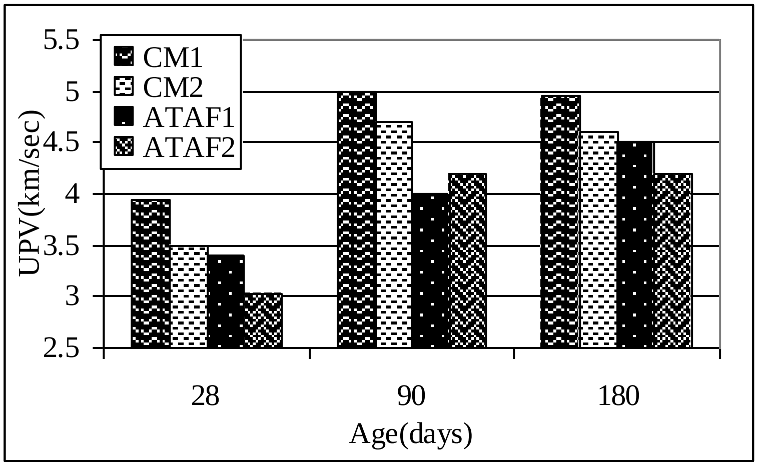


Fig. 3 Ultrasonic Pulse Velocity for different mixes

Indirect Tensile Strength

The results of the indirect tensile strength tests up to 180 days are shown in Figure 4. The trend in tensile strength is similar to that obtained for compressive strength. Figure 4 illustrates there was a difference in the development in tensile strength of different mixes. As far as the geopolymer concrete mixes based on activated natural pozzolan are concerned, higher strengths were observed at longer ages in comparison with control OPC mixes. At early age, ATAF2 showed lower tensile strength results than the OPC control mix, 1.7MPa compared to 2.03MPa while the ATAF1 mix gave 3.57 MPa after 28 days, higher than the corresponding OPC control mix at 2.67Mpa. The results show that the long term tensile strengths of activated Taftan geopolymer concrete mixes are higher than those of OPC control mixes, 3.69 and 3.0 MPa after 365 days compared to CM1 and CM2 at 2.81 and 1.99, respectively.

The tensile strength of activated natural pozzolan geopolymer concrete is more sensitive to improper curing than its compressive strength, the same as in OPC concrete. Figure 4 illustrates the effect of curing conditions and temperatures on tensile strength of concrete made from activated natural pozzlans. The optimum temperature of curing was 40ºC, the same as that found for compressive strength. Figure 4 also shows that a higher water to binder ratio resulted in lower tensile strength, the same trend as for OPC mixes.

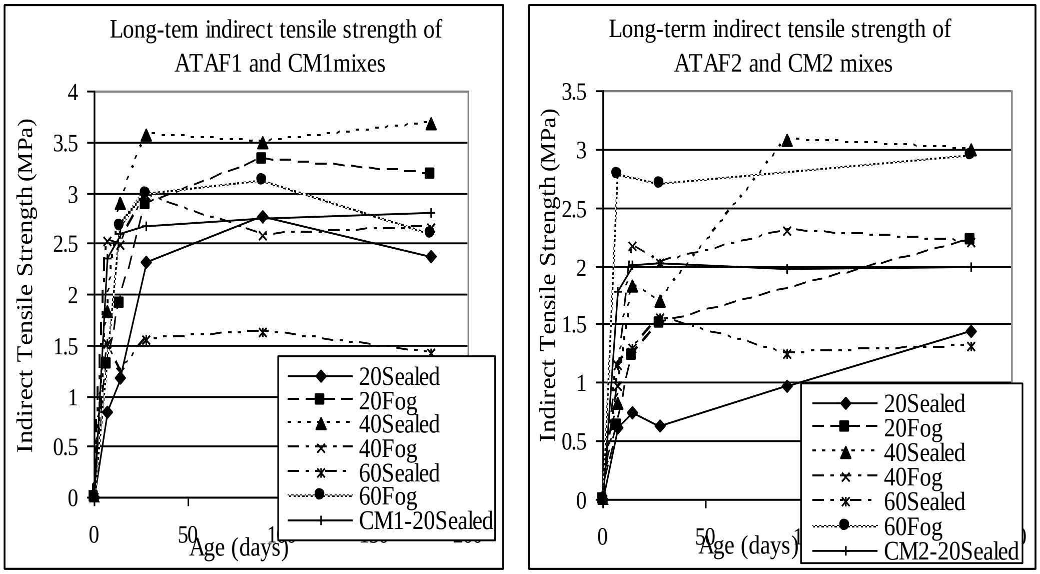


Fig. 4 Effect of different curing conditions and curing temperature on Indirect Tensile strength development for ATAF1 and ATAF2 mixes

Static Modulus of Elasticity

Results of the static modulus of elasticity are shown in Figure 5. In a similar way to the compressive strength results, the static modulus of elasticity increased with age. This improvement was rapid in the first 28 days as most of the modulus value was generally achieved in this period. During the first 14 days the mixes made with activated natural pozzolans have mostly shown lower values of static modulus of elasticity than OPC concrete mixes, except for the ATAF1 mix. The static modulus of elasticity for ATAF1, ATAF2 mixes after 14 days was 33.96, 14.03GPa at 40ºC curing temperature, respectively with that for the CM1 mix was 26.55GPa. Long term results show that the static elastic modulus of some of alkali activated natural pozzolans such as ATAF1 are around 5% to 20% more than OPC mixes. The long term static modulus of elasticity of ATAF1, ATAF2 mixes were 32.7, 26.8GPa compared to OPC concrete mixes which gave 29GPa. The elastic modulus was affected by the curing temperature. At early ages the static modulus of elasticity increased with increasing the curing temperature up to a limit which seems to be related to the water to binder ratio (Figure 5). For ATAF1 with a water to binder ratio of 0.45, the elastic modulus increased with increasing curing temperature up to 40˚C but decreased when the curing temperature rose to 60˚C. For ATAF2 mixes where the water to binder ratio was 0.55, the temperature where the highest static modulus of elasticity was obtained rose to 60˚C. However, over the long term the results drop to the same value as the mix cured at 40˚C.

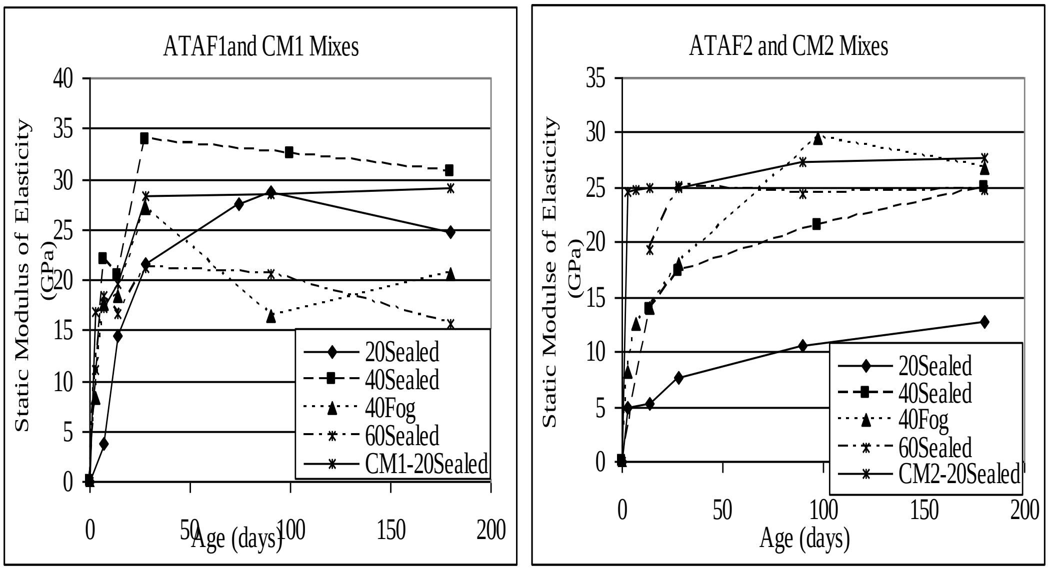


Fig. 5 Effect of different curing condition and curing temperature on Static Modulus of Elasticity development for ATAF1 and ATAF2 mixes

CONCLUSIONS

The main conclusions drawn from this investigation of the engineering properties of geopolymer concrete made from activating natural pozzolans (i.e. alkali activated natural pozzolan or AANP) are summarized as follows:

1) Geopolymer concrete from activated natural pozzolans generally shows lower strengths than OPC mixes at early ages, but they reach the same or even higher strengths than OPC mixes after long-term curing.

2) The strength of geopolymer concrete decreases as the ratio of water to geopolymer solids by mass increases. This allows more entrapment of water within the geopolymer paste and makes a looser microstructure in this type of concrete.

3) It seems that the ultrasonic pulse velocity in the geopolymer concrete is lower than in OPC concrete of the same compressive strength.

4) During the first 14 days, activated natural pozzolan concrete mixes generally have lower values of static modulus of elasticity than OPC concrete mixes. However, the long term results show that the static elastic modulus of alkali activated natural pozzolans concrete is generally around 5 to 20% higher than for OPC mixes.

5) The elastic modulus of AANP concrete is affected by the curing temperatures. At early ages the static modulus of elasticity increased with increasing curing temperature to a limit which seems to be related to the water to binder ratio. If water is lost due to evaporation when curing at higher temperature before the full strength is gained, the static modulus of elasticity decreases.

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