T. R. VAN YUZUNCU YIL UNIVERSITY INSTITUTE OF NATURAL AND APPLIED SCIENCES DEPARTMENT OF CIVIL ENGINEERING

STRENGTH AND DURABILITY CHARACTERISTICS OF PUMICE BASED GEOPOLYMER PASTE

M.Sc. THESIS

PREPARED BY: Zrar Safari Mahmood MAHMOOD SUPERVISOR: Assoc. Prof. Dr. Mucip TAPAN

VAN-2019



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ACCEPTANCE and APPROVAL PAGE

This thesis entitled "Strength and Durability Characteristics of Pumice Based Geopolymer Paste" presented by Zrar Safari Mahmood MAHMOOD under supervision of Mücip TAPAN in the department of civil engineering has been accepted as a M. Sc. thesis according to Legislations of Graduate Higher Education on 10/09/2019 with unanimity of votes members of jury.

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THESIS STATEMENT

All information presented in the thesis obtained in the frame of ethical behavior and academic rules. In addition, all kinds of information that does not belong to me have been cited appropriately in the thesis prepared by the thesis writing rules.

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ABSTRACT

STRENGTH AND DURABILITY CHARACTERISTICS OF PUMICE BASED GEOPOLYMER PASTE

Zrar Safari Mahmood MAHMOOD M. Sc. Thesis Civil Engineering Supervisor: Assoc. Prof. Dr. Mucip TAPAN September 2019, 104 pages

Cement consumption causes several environmental issues due to using a massive amount of energy and releasing gas emissions. Geopolymerization, a new technological process, provides an innovative way to produce concrete without cement usage. In this study, pumice powder, which is rich in silica and aluminum such as fly ash and metakaolin, is utilized as a binder to produce geopolymer paste. The influences of fineness of pumice, different sodium hydroxide concentration, curing temperature and curing period on the strength and freezing and thawing durability characteristics. The mass ratio of sodium silicate solution to sodium hydroxide and alkali binder ratio was fixed to 2.50 and 0.35 respectively. The geopolymer paste specimens were placed at ambient temperature for 24 hours as a rest period with different concentration (8, 10, 12, 14, 16 and 18M) of sodium hydroxide and then cured at room temperature, 60, 80 and 100 °C temperature for 24, 48, 72 and 120 hours. The compressive strengths of geopolymer pastes were tested at the ages of 7 and 28 days. Flexural strength tests were conducted at age of 28 days. The SEM analyses were performed to identify the morphology characteristics and to determine the unreacted particles of the geopolymer pastes. The results showed that optimum flexural and compressive strength can be obtained at 60 °C of oven curing for 120h with 12M. Although, high strengths can be obtained at high curing temperatures with less curing time, but when compared to low temperature and more curing time, flexural and compressive strength gains are less.

Keywords: Alkali activator, Concentration, Curing, Geopolymer, Pumice powder, SEM.



ÖZET

POMZA ILE ÜRETILEN JEOPOLİMER BETONLARIN DAYANIM VE DAYANIKLILIK ÖZELLİKLERİ

Zrar Safari Mahmood MAHMOOD Yüksek Lisans Tezi, inssat Mühendisliği Anabilim Dalı Tez Danışmanı: Doç. Dr. Mucip TAPAN Eylül 2019, 104 sayfa

Cimento tüketimi, büyük miktarda enerji kullanımı ve gaz emisyonlarının serbest bırakılması nedeniyle çeşitli çevresel sorunlara neden olmaktadır. Yeni bir teknolojik süreç olan jeopolimerizasyon, çimento kullanmadan beton üretmek için yenilikçi bir çözümdür. Bu çalışmada, uçucu kül ve metakaolin gibi silika ve alüminyum bakımından zengin olan pomza tozu, jeopolimer betonu üretmek için bağlayıcı olarak kullanılmış ve pomza tozu inceliğinin, farklı sodyum hidroksit konsantrasyonunun, kürlenme sıcaklığının ve kürlenme süresinin, pomza tozu ile üretilen jeopolimer betonların basınç ve eğilme dayanımı ile donma ve çözülmeye karsı dayanıklılık özelliklerine etkisi araştırılmıştır. Tüm örneklerde, sodyum silikat çözeltisinin kütlece sodyum hidroksite oranı ve alkali aktivatör/bağlayıcı oranı sırasıyla 2.50 ve 0.35 alınmıştır. Farklı konsantrasyonda (8, 10, 12, 14, 16 ve 18M) sodyum silikat ve sodyum hidroksit çözeltisi, 24 saat bekletme süresine tabi tutularak jeopolimer beton numunelerinin hazırlanmasında kullanılmıştır. Farklı kürlenme sıcaklıklarına (ortam sıcaklığı, 60 oC, 80 oC ve 100 oC) tabi tutulan beton örnekleri 24, 48, 72 ve 120 saat kürlendikten sonra test edilmistir. Jeopolimer betonların mikroyapısal özelliklerini belirlemek üzere SEM analizleri yapılmıştır. Sonuç olarak, optimum eğilme ve basınç dayanımı, 12 molariteye sahip jeopolimer betonların altmış derecelik fırında 120 saatlik kürlenmesi ile elde edilmiştir. Her ne kadar yüksek kürlenme sıcaklıklarında daha az kürlenme süresi ile daha yüksek dayanımlar elde edilebilmesine rağmen, düşük sıcaklık ve sertleşme süresi ile karşılaştırıldığında eğilme ve basınç dayanımı kazançları daha azdır.

Anahtar Kelimeler: Alkali aktivatörü, Jeopolimer, Konsantrasyon, Kürleme, Ponza tozu, SEM.



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2019

Zrar Safari Mahmood MAHMOOD



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SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used in this study are presented below, along with

descriptions.

Abbreviations and symbols	Description
A/B	Activator to binder
ACI	American Concrete Institute
Al ₂ O ₃	Aluminum oxide
Al	Aluminum
ASTM	American society for testing and materials
C ₃ A	Aluminate
CaO	Calcium oxide
Class C	High calcium fly ash
Class F	Low calcium fly ash
CO ₂	Carbon dioxide
CSH	Calcium silicate hydrate
EDX / EDS	Energy dispersive X-ray spectrometer
Fc	Characteristic compressive strength
EN	European standards
FTIR	Fourier transform infrared spectroscopy
GGBFS	Ground granulated blast furnace slag
kN	Kilo-Newton
КОН	Potassium hydroxide
K ₂ SiO ₃	Potassium silicate
LOI	Loss on ignition
Μ	Molarity
MPa	Mega pascal
mm	Millimeters

Abbreviations and symbols	Description
NaOH	Sodium hydroxide
Na ₂ SO ₄	Sodium silicate
OPC	Ordinary Portland cement
Ph	Potential of hydrogen- scale of acidity
Si	Silicon
SEM	Scanning electron microscope
UPV	Ultrasonic pulse velocity
XRD	X-Ray diffractometer
°C	Degree centigrade
μm	Micrometer
kg/m ³	Kilogram/cubic meter

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1. INTRODUCTION

1.1. General

Concrete is the most commonly used construction material in worldwide. However, the production of Portland cement has some major disadvantages, such as high energy consumption, and emissions of high CO₂ and other greenhouse gases (Bosoaga et al., 2009; Habert et al., 2010; Hasanbeigi et al., 2012). Cement production has dramatically increased due to the massive increase in infrastructure and industrialization (Habert et al., 2010). Several attempts have been made to minimize Portland cement usage in concrete, such as using supplementary cementitious materials as a partial replacement for Portland cement and searching for Portland cement alternatives. In this respect, geopolymer concrete is an innovative way to produce concrete without using Portland cement (Davidovits, 1993; Habert et al., 2011). In 1978, Joseph Davidovits used a geopolymeric reaction of silica and alumina rich sources with an alkali-activated solutions (such as adequate combinations of sodium silicate and sodium hydroxide) to produce geopolymer concrete that was evaluated as a sustainable material (Davidovits, 1991b). Previous studies indicate that several factors play a significant role in the geopolymerization process of geopolymer concrete such as: concentration of alkaline activator (Rattanasak and Chindaprasirt, 2009; Nuruddin et al., 2011; Görhan & Kürklü, 2014; Hanjitsuwan et al., 2014; Singh et al., 2016), type of alkaline activator (Khale and Chaudhary, 2007), source material type and chemical composition (Mehta and Siddique, 2016; Okoye etal., 2015; Reddy et al., 2016), curing temperature and curing period (Kovalchuk et al., 2007; Mustafa Al Bakria et al., 2011; Ghayoula et al., 2014; Mo et al., 2014; Girija, 2015), ratio of alkaline activator solution to source material (Ghafoori et al., 2016; Ibrahim et al., 2017; Phoo-ngernkham et al., 2018), the mass ratio of sodium silicate to sodium hydroxide (Joshi & Kadu, 2012; Morsy et al., 2014; Yi Dong, John S. McCartney, 2016). Although, geopolymers have excellent mechanical properties, including high compressive and flexural strength (Chindaprasirt et al., 2010; Ivan et al., 2011; Bagheri and Nazari, 2014; Atiş et al., 2015; Nath and Sarker, 2017), and durability characterizes such as resistance to chemical

attacks, fire resistance, freezing and thawing (Bakharev (2005a); Bakharev, 2005b; Kong and Sanjayan, 2008; Ariffin et al., 2013; Komljenović et al., 2013; Abdulkareem et al., 2014; Gopalakrishnan and Chinnaraju, 2019) and as well as have low emissions of greenhouse gases, one of the major disadvantages of geopolymer concrete is its high cost, which remains a serious drawback. In order to reduce costs and make geopolymer concrete more environmentally friendly, by product and pozzolanic materials are currently being used. In this respect, many studies have focused on the use of fly ash (Ryu et al., 2013; Hardjito et al., 2004), ground granulated blast-furnace slag (GGBS) (Deb et al., 2014; Gupta & Wei, 2016), metakaolin (Pacheco-Torgal et al., 2011; Duan et al., 2016) and waste glass powder (Vafaei and Allahverdi, 2017) in geopolymer concretes, whereas only a few researchers have conducted studies on the use of pumice powder as a binder to produce geopolymer concrete (Binici, 2013). Pumice is a volcanic material with pozzolanic properties, rich in silica and alumina and makes it possible to use as one of the geopolymer source materials. Moreover, which can be easily obtained in Eastern Turkey in a large volume (Tapan et al., 2013; Kabay et al., 2015). The use of pumice powder could toward sustainable and economical concrete in the development of geopolymer concrete.

On the other hand, recently, several researchers have conducted studies on lightweight geopolymer concretes which is very important for reducing a dead load of element and structures (Posi et al., 2013, 2015; Sukontasukkul et al., 2016). Using lightweight activated binder such as fly ash, metakaolin or GGBS with lightweight aggregates, lightweight geopolymer concretes can be produced. Therefore, the most essential objective of this study is to determine the influences of fineness of pumice powder, different sodium hydroxide concentration, curing temperature and curing period on the strength and freezing and thawing durability characteristics of pumice powder based geopolymer paste.

1.2. Problem Statement

The world faces the challenge of climate change, because of CO_2 gas emissions, a massive amount of CO_2 emissions is produced from the cement industry, which estimated about 5% of total gas emissions. Therefore, the geopolymer technology can be recommended as the suitable alternative of conventional concrete by minimizing uses of Portland cement. In this study the geopolymer paste produced by using pumice powder as source material. The use of pumice as source material is not well known. Pumice is a rich Si and Al natural Pozzolan material, which possible to use as cementitious material either a partial replacement of Portland cement in conventional concrete or could be used as a binder in geopolymer technology. The development of natural Pozzolans based geopolymer concrete toward to reduce the demand on ordinary Portland cement. There are still a few studies about pumice based geopolymer concrete is available. In this study, the several factors investigated to enhance the strength and freezing and thawing characteristics of geopolymer pastes.

1.3. Aim and Objective of the Research

The primary purpose of this thesis is to experimentally study the possibility of using pumice based geopolymer paste. In order to obtain environmentally friendly and local/cost effective products with excellent strength performance and durability properties, the pumice used as source material to produce geopolymer paste. The objectives of this thesis are listed below:

- 1. To study the possibility of using pumice based geopolymer paste. Which is a new green binder to replace ordinary Portland cement, with local/cost effective products, better mechanical strength and improving durability properties.
- 2. Review past literature and make a comparison between them.
- 3. The purpose of the chosen geopolymer paste is to reduce the variables that affect the product by adding aggregates.
- 4. Investigate the influence of different concentration of NaOH on the strength properties of geopolymer paste.
- 5. Study the effect of ambient curing, heat curing temperature, and duration times on compressive and tensile strength of geopolymer paste.
- 6. Study the influence of age on the strength development of geopolymer paste.
- 7. To obtain high compressive strength of geopolymer product.
- 8. Effect of pumice powder fineness on compressive, tensile strength and freezingthawing of geopolymer paste.

- 9. To investigate the freeze and thaw durability properties of pumice based geopolymer paste
- 10. Find the correlation between the ultrasonic pulse velocity values and compressive strength of geopolymer paste.
- 11. Study the SEM micrograph, which shows the porous and unreacted particles of geopolymer pastes. Using the SEM analysis to study the influences of the freezing and thawing on the geopolymer paste specimens.
- 12. The bricks, blocks, and pre-cast elements can be produced by geopolymer paste.

1.4. Research Significance

Geopolymer concrete has significant advantages over conventional concretes and be able to play a significant role in respect to sustainability and environmental concerns. The cement production can be reduced significantly by increasing the usage of geopolymer technology which has potentially reduce the emission of greenhouse gases. In this study the raw pumice used based geopolymer paste. A massive volume of raw pumice available in Turkey, which can be easily accessed and has low-cost production and environmental impacts. The manufacturing of pumice powders no needs further process; therefore, the emission of CO_2 gas will have minimized compared to ordinary Portland cement production. High early strength geopolymer product can be obtained by using pumice as a binder and heating curing. The results of this experimental study will give a good observation influence of alkali activator concentration, heat curing temperature and period on the strength characteristics and freezing-thawing durability properties of geopolymer paste. The end of this thesis provides the foundation into further works to uses this product in some practical applications.

1.5. Thesis Outlines

The thesis is arranged into five sections:

Section 1: This section includes a brief introduction of geopolymers, the main aim, objective, and the significances of this study.

Section 2: This section discusses the geopolymerization mechanism which is a review of the previous studies, the effect of the alkali concentration, fineness, the mass ratio of sodium silicate to sodium hydroxide and curing temperature and period time on the properties of geopolymers and makes comparison between them.

Section 3: Describe the details experimental study involving of mixture proportions and raw materials were used. The test procedures and curing conditions were described in this section.

Section 4: Presents the findings result with descriptions of the effect of concentration heat curing temperature and duration time on the compressive and flexural strength of geopolymer pastes. Also, the effect of pumice powder fineness and freezing and thawing cycles were discussed.

Section 5 and 6: Summarizes the findings in this study and made some recommendations for further studies.



2. LITERATURE REVIEW

2.1. Introduction

Geopolymer technology as a new sustainable building material awarded extensive attention of researchers around the world. Several research works have been published on the various areas of geopolymer alkalis, binders, and techniques. The basic concept of geopolymer is almost the same, but there is different terminology in different studies. The production of one ton of cement needs 3 to 4 Giga-joules of energy and releases about one ton of CO_2 which is one of the greenhouse gases that causes climate change (Khurana et al., 2002; Engin and Ari, 2005; Amiri and Vaseghi, 2015). Cement production is responsible for the release of about 5% of carbon dioxide emissions in the world (Huntzinger and Eatmon, 2009). However, the demand for Portland cement dramatically increases, from 2010 to 2050 increases by almost 200% (Taylor et al., 2006). The emission of CO_2 gas in geopolymer nearly 80% less than Portland cement (Duxson et al., 2007). Over the past decades, substantial study works have concentrated on geopolymer chemistry, and microstructural growth in order to promote the dosage of geopolymer concretes in different applications.

This section studies the fundamental concepts of geopolymer formation and the mechanism of geopolymerization process of different productions of geopolymer concretes. In this research work, the significant parameters which affect the strength and durability characteristics of geopolymer concrete were discussed through the review of previews studies.

2.2. Historical Background of Geopolymer

Geopolymer technology has ancient roots. The history of alkali cement is almost 80 years. The first progress in Alkali- slag combination has been done by Purdon in 1940 (Pacheco-Torgal et al., 2008). Purdon used GGBFS as a binder and NaOH as alkaline solution activator. During the development of geopolymer, several terminologies have been used, such as Alkali – slag, soil cement, alkali-activated, and geopolymer. In 1957, Glukhovsky investigated the alkaline activation of low calcium aluminosilicates, and called "alkaline cement". Victor Glukhovsky reported that rocks and clay minerals reacted to sodium alumino-silicate hydrates (zeolites) during alkali solution and referred to concrete made with this technique as "soil silicate concrete" and called "soil cement" binders (Starchevskaya, 1967). In 1978, Davidovits invented the geopolymer term for the three-dimensional (3D) silico-aluminate materials (mineral polymers resulting from) and due to the resemblances with condensation of organic polymers in regards to their synthesis of hydrothermal (J. Davidovits, 1991a; Joseph Davidovits, 2011). In 1982 Davidovits developed binders by mixing alkalis with kaolinite, limestone, and dolomite.

In 2005, Fernández-Jiménez et al. studied the morphology of alkali activated fly ash cement for monitoring the microstructural development and morphological development of geopolymer depend on several reasons such as the distribution of particle size, fly ash mineral composition and the concentration and types of activator (Fernández-Jiménez et al., 2005).

2.3. The Geopolymerization Process

The binders are rich with Alumino-silicate called inorganic geopolymeric compounds. The geopolymerisation process occurred in the result of an inorganic polycondensation reaction (Palomo, A., M. Grutzeck, 1999). Under the high alkaline condition, the operation of geopolymerization includes an exceedingly rapid chemical reaction of Alumino-silicate minerals (Görhan and Kürklü, 2014). The process of alkaline activation, known as geopolymerization, is produced through the dissolution of silica and aluminum materials with high alkaline activators. This reaction results, three-dimensional tecto-aluminosilicate polymeric chain and ring structure of Si-O-Al-O bonds as can see in Eq 2.1.
$$M_{n}[-(SiO_{2})_{z}-AlO_{2}]_{n}.WH_{2}O$$
(2.1)

Where in M is an alkali element or cation (K, Na, Ca) n is the polycondensation degree and z is 1, 2, 3 or >>3.

Alkali silicon-oxo-aluminate (Si-O-Al) also called the sialate, the sialate consists of SiO₄ and AlO₄ tetrahedras connected to each other by oxygen atoms. The Al The negative charge in 4-fold coordination balanced by the positive ions (Na+, K+, Ca++, Mg^{++} , Ba^{++} , NH_4^+ , $H30^+$). The sialate molecular structure samples are presented in Figure 2.1. The term poly(sialate) comes from poly (Na, K, Li, Ca) and sialate (Si-O-Al), at least one poly-sialate unit containing in all geopolymers (Joseph Davidovits, 1994). They named according to the atomic ratio of Si to Al as can be seen in Figure 2.1.



Figure 2.1. The sialate molecular structure (Joseph-Davidovits, 1994).

According to previous studies, the exact geopolymerization mechanism is not well understood yet However, In the 1950s, Glukhovsky recommended the general mechanism in three stages (Krivenko and V. P 1994):

— destruction-coagulation

- coagulation-condensation
- --- condensation-crystallization

2.3.1. Stage I: Destruction-coagulation

In this stage, the reaction starts immediately after the (fly ash, slag, metakaolin, etc.) comes in contact with the alkali solution activator (Fernández-Jiménez et al., 2006). the Si-O-Si and Al-O-Al bonds from the source material (fly ash, slag, metakaolin, etc.) breaking down by the OH⁻ ions in the very high pH value of alkali activator solution. A schematic of geopolymer formation showed by the reaction Eq 2.2. and 2.3. as following (Joseph Davidovits, 1989; Van Jaarsveld et al., 1997):



As it is presented in Eq 2.2, the OH⁻ ions in alkali activator solution share the electronic concentration nearby the Si atoms by reducing the strength bonds of Si-O-Si and being the bonds closer to breakage. This situation permits the (-Si-OH-) and (-Si-O) molecules formation. While the bond formation of Si-O-Na or Si-O-K disallows the (Si-O-Si) conversion again, the high alkali activator cations neutralize the negative charges. The hydroxide ions affect the bonds of Si-O-Al in the same way. Therefor nano-pores present in the structure of geopolymer (Rill et al., 2010).

2.3.2. Stage II: Coagulation-condensation

In the second stage of the geopolymerization, the precursor ions orientate or condensate into monomers. Continuous reacting of the silica monomers with each other by dimerization reaction that reacts to other monomers to form polymers (Figure 2.2). The alkali solution acts as a structural component during coagulation–condensation stage. A condensation reaction occurs in the solution between the adjacent molecules of silica and alumina.

2.3.3. Stage III: Condensation-crystallization

In the final stage of the geopolymerization mechanism called poly-condensation or polymerization of monomers into polymeric structures. When small heat is applied to the solution, the reaction is activated. The products of this process depend on the chemical composition and mineralogical of the source material utilized, the type of alkali activators, and the curing temperature and periods were used.

Glukhovsky's theories have been extended by Fernandez-Jimenez et al. (2006) and Duxson et al., (2007) for the purpose of clarify the geopolymerization process in general, in 2007, Duxson et al. extremely simplified reaction for the geopolymerisation process, Figure 2.2 presents the conceptual model.



Figure 2.2. A conceptual model for geopolymerization process (Fernandez-Jimenez et al., 2006).

2.4. Geopolymer Binder

Geopolymer concrete consisting of a couple of components: binders and alkaline activators. Figure 2.3. shows the geopolymer system components. Aluminosilicate materials are the binders which are natural or artificial Pozzolans. Natural pozzolans are volcanic glasses in the form of pumice and volcanic ash; siliceous pozzolans in the form of opal and diatomaceous earth; and volcanic tuffs being zeolites. Artificial pozzolans are industrial by-product materials (slag, fly ash, and silica fume) or burnt materials (rice husk ash, metakaolin)(F Pacheco-Torgal et al., 2014). In the past few years, numerous researches have been performed to study the possibility of using industrial waste products as a raw material in geopolymer concrete. The most common supplementary cementitious materials used in concrete and geopolymer binder systems as well are by-product materials. The volcanic pumice is a rich aluminosilicate material, the general chemical compositions of pumice shown in Table 2.1 which available in Turkey. This study investigates the potential uses of pumice as a natural pozzolan in the production of geopolymer concrete.



Figure 2.3. Geopolymer system components.

Table 2.1. General chemical compositions of pumice in Turkey (Bims Sanayicileri Dernegi, 2006)

Chemical Composition	Percentage %
SiO ₂	52.0 - 75.0
Al_2O_3	11.0 - 17.0
Fe ₂ O ₃	0.5 - 5.0
CaO	1.0 - 8.0
MgO	0.5 - 3.0
$Na_2O + K_2O$	3.0 - 9.0
TiO ₂	< 1.0

2.4.1. Fly ash

One of the most commonly used by-product material in the worldwide construction industry is fly ash. Due to the development of thermal energy plants and factories, day by day the massive amount of fly ash is released as waste. Fly ash is a cementitious material which can be incorporated with Portland cement to manufacturing the concrete, and fly ash is commonly used based on geopolymer concrete with the aim of reducing the negative impacts on the environment. The fly ash properties are affected by the raw material used in power plant, the chemical composition, coal feed composition, the burning operating system.

In their study, Palomo et al. (1999) described the activation mechanism of fly ash in highly alkaline environment. The NaOH and KOH solutions were utilized as activator. The influences of curing temperature, period, and mass ratio of alkaline liquid/fly ash on compressive strength were studied. The geopolymer concrete made base on fly ash has been resulted to have about 60 MPa compressive strength after curing at 85 $^{\circ}$ C for 5 hours.

In his doctoral thesis, Hardjito (2005) studied the details of the development process of manufacturing fly ash-based geopolymer concrete. A combination of NaOH and sodium silicate solution was utilized to activate the Si and Al content in fly ash. Also the fresh properties of geopolymer concrete were founded, the concrete remained workable up to 120 minutes with no indication of setting and reduction in the strength. The compressive strength in the range of 40 to 90 MPa obtained for geopolymer concrete made from fly ash, which was almost same to strength of conventional concrete.

Komljenovic et al. (2010), the mechanical and microstructural characteristics of geopolymer concrete made with fly ash were studied. Class-F fly ashes from six different thermal power plants from in Serbia were obtained. The solutions of sodium hydroxide, NaOH+Na₂CO₃, potassium hydroxide, Ca(OH)₂ and Na₂SiO₃, were utilized as alkali activator with various concentrations. The concentration of activator and nature was the most effective factor affected the alkali-activation process. The fineness of fly ash was the critical parameter represented the physical properties of geopolymer concrete. The maximum compressive strength was reported in all cases which the highest content of fine particles of fly ash (< 43mm). By using sodium silicate as

activator the highest compressive strength was obtained. They also indicated that increasing the mass ratio of SiO_2/Na_2O from Na_2SiO_3 solution, the amount of silicon in the reaction process was automatically increased, it resulted increasing the ratio of Si/Al which directly influence the compressive strength values of geopolymer product.

Temuujin et al. (2010) used six different levels of sand aggregate and fly ash was utilized as a binder to produce geopolymer concrete. They investigated the effect of geopolymer binder to sand mass ratio (from 1 to 9) on the physical and compressive strength of geopolymer concrete. Geopolymer binder indicates a powerful bonding to the sand aggregate. The 60 MPa compressive strength of the geopolymer paste was achieved with Young's modulus 2.27 GPa. Decreasing fly ash content and increasing the sand content with constant amount of alkaline activator within the binder system lead to reduce the geopolymerisation level.

An experimental study was performed by Zaetang et al. (2015) to obtained pervious geopolymer concrete. The bottom ash was utilized as coarse aggregate and fly ash was used as geopolymer binder. They studied the influence of sodium hydroxide concentration, curing temperature, and partial incorporating of ordinary Portland cement (OPC) with fly ash on the properties of previous geopolymer concrete. With increasing the replacement level of ordinary Portland cement and the concentration of NaOH, the compressive strength of pervious geopolymer concrete increased. The 90 °C curing temperature was recommended for achieving the optimum of strength. The compressive strength in the range 5.7 to 8.6 MPa, thermal conductivity ranges 0.30 to 0.33 W/m K, and density of 1466–1502 kg/m³ were obtained for the previous geopolymer concrete contained bottom ash as coarse aggregate.

Naghizadeh and Ekolu (2019) Produced geopolymer mortars by a new mix design method. A combined sodium silicate and sodium hydroxide solutions as an activator and fly ash as a binder were used. The mixture design method based on some factors such as the mass ratio of alkali activator to fly ash, NaOH/ Na₂SiO₃ to sodium hydroxide mass ratio and the sodium hydroxide concentration. The proposed method for a known composition and nature of sodium silicate and specific fly ash type. The workability and compressive strengths values of the geopolymer mortars were obtained statistically agreed with preceding design values. They proposed that concept can be used for the mix design of various types of geopolymer binders.

2.4.2. Ground granulated blast furnace slag (GGBFS)

GGBFS or slag is also one of the by-product material produced in the melting process of the iron industry. Slag is produced at a high temperature about 1500 °C in the furnace; therefore, there is a similar chemical composition between slag and ordinary Portland cement. Slag contains a silicon dioxide and metal oxide mixture which can partial incorporated with cement to producing the concrete and utilizing base on alkaliactivated blast furnace slag.

In their study, Shi and Dayt (1999), investigated the influence of fly ash (Class-F and Class-C fly ash) and added lime on the hydration and strength development of activated slag-fly ash concrete, which contained an equal amount of slag and fly ash by mass and compared with 100% alkali-activated slag cements. In case of using NaOH as an alkaline activator solution, when the slag was replaced with Class-F fly ash there was not affected on the hydration or strength development of alkali-activated concrete. However, as a result of the existence of C_3A in fly ash, the replacement of slag with fly ash affected the hydration process but did not affect the strength development. In case of using Na2SiO3 as an activator, both fly ashes (Class-F and Class-C fly ash) had a powerful effect on the strength development and hydration of alkali-activated concrete. They found that the adding of the limited amount of hydrated lime had an influence on the hydration and increase the initial strength and reduced the final strength of activated slag-fly ash concrete. Alonso et al. (2000) investigated the parameters have an effect on the strength characteristics of GGBFS based geopolymer concrete. The influence of NaOH concentration (10 to 14 M), alkaline activator to slag content (in the range 0.40 to 0.50) mass ratio, curing temperature in the range of 30 °C to 90 °C, curing period between 1 to 3 days and mass ratio of NaOH to Na₂SiO₃ (1:1.75, 1:2.50 and 1:3.25) were investigated on the compressive, tensile strength and elastic-modulus of GGBFS based alkali-activated concrete. Through the experimental program, the fractional factorial system was carried out to minimize the number of mixes. Increasing the concentration of NaOH improved the compressive, splitting tensile, elastic modulus, and improved the porosity. Those properties increase with increasing the ratio of Na₂SiO₃/NaOH. Increasing the curing temperature and alkali to slag ratio reduced the compressive, splitting tensile, the modulus of elasticity properties of concrete.

Therefore, heat curing was not proposed for GGBFS based geopolymer concrete, C-S-H needs water for curing when the temperature increases it affected the formation of calcium silicate hydrate and leads to evaporate more water. At the lowest curing temperature (30 °C) all the mechanical properties were improved. While the curing period time was 48 hours, the optimum results of all the tested considerations were obtained.

Aliabdo et al. (2019) investigated the activation of fly ash/slag pastes. The solution of NaOH was utilized as an alkaline activator. The influence of NaOH concentration (2 and 10 M), mass ratios of fly ash / slag (100/0, 70/ 30, 50/ 50, 30/ 70, and 0/ 100) and curing temperature (25 °C and 65 °C) parameters were investigated on the mechanical properties of alkali-activated fly/slag pastes. The equations models were described considering those parameters. The mass ratio of fly ash/slag and the concentration of NaOH were the most significate parameters affect the properties of alkali-activated fly/slag pastes. The XRD, MAS NMR, and FTIR verified that the reaction process of slag completely reacted. The compressive strengths increase, with increasing slag content in the pastes. The NaOH concentration directly related to the development of compressive strength, with 10 M concentration of NaOH the higher compressive strength was obtained. The 50 Mpa compressive strength was obtained at 28 days with the mixture 50% of fly ash and 50% of slag, the NaOH solution concentration was 10 M and the cured at 25 °C.

Hadi and Zhang (2019) conducted a study on the optimum mix design of geopolymer pastes. They studied, the influences of GGBFS content, the alkaline activator solution to the binder ratio, the mass ratio of Na₂SiO₃/NaOH solution, and the water to binder mass ratio on the strength, workability and setting time of geopolymer products. The GGBFS and fly ash were used as source material. The solution of sodium silicate solution and sodium hydroxide were utilized as the alkaline activator. The workability and prolong the setting time were improved by additional water. The optimum compressive strength, workability, and setting time obtained with 40% of GGBFS, 0.5 alkali activator to binder ratio and the sodium silicate/sodium hydroxide ratio was 2.0. The results indicated that the properties of the geopolymer product with 40% of slag has better properties than the ordinary Portland cement pastes.

2.4.3. Metakaolin

Metakaolin is classified as a pozzolanic material which derived from the kaolin clay by the dihydroxylation process at a temperature 500 °C to 800 °C, this energy required to remove the chemical bonds of hydroxyl ions and produce a dehydroxylated form. Metakaolin utilized in concrete as cement replacement. Compare to ordinary Portland cement the metakaolin particle size is much smaller and surface area is more extensive, therefore reacts rapidly and minimizes the diffusion coefficient. The metakaolin is used in the production of geopolymer vary markedly, due to has silicate and aluminate sources and the purity in the crystallinity of the kaolinite.

Granizo et al. (2007) produced the alkali-activated metakaolin. The reaction process of metakaolin activation is directly affected by the initial kaolin composition, type, specific surface and concentration of alkali activator. They studied the influence of those parameters on the flexural strength, porosity, degree of reaction and mineralogical and chemical composition of metakaolin based geopolymer pastes. The metakaolin was activated with two types different specific surfaces, and under heat curing temperature 85 °C, for 2 hours, the NaOH with 6, 8, 10, 12, 15, 18 and 20 molarity were used, two different mass ratio of metakaolin/solution was used. In order to quantify the factors affecting on flexural strength, regression analysis was used. The strength properties of alkaline activated metakaolin products, which activated by NaOH and Na₂SiO₃ solutions were better than the mechanical properties of product which activated by NaOH alone. Increases the Na concentration of activator higher flexural strength values were obtained.

Živica et al. (2012) obtained high strength metakaolin based geopolymer. The very low ratio of water to metakaolin was used, and the fresh mixture was compacted by 300 MPa uniaxial compressive stress. A thermal analysis (DTA, GTA), coupling of scanning microscopy and EDX, mercury intrusion porosimetry and compressive strength were used to investigate the effect of preparation conditions. The geopolymer which pressure compacted was hardened after 24 hours and obtained the compressive strength 146 MPa. However, the reference past was only 0.03 MPa. The pressure compaction increased the compressive strength 2540 times.

Chen et al. (2016) used metakaolin as a precursor in order to produce the alkali active metakaolin and utilized, to protect the concrete surface. The orthogonal experimental design to study the alkali-activated metakaolin-based geopolymers formula. The solution of Na₂SiO₃ was used as alkaline activator, with the SiO₂(3.4): Al₂O₃(1.1): Na₂O (0.5): NaOH (1.0): H₂O (11.8) molar ratio. The effect of curing regimes on the mechanical and microstructure characteristics of the geopolymer products were investigated by XRD and FTIR. The highest compression strength (52 MPa) of metakaolin-based geopolymer was achieved with the best curing condition (60 °C for 168 hours). In order to develop the thermal insulation characteristics of geopolymer concrete made by the metakaolin, metakaolin particles were mixed with hollow micro-sphere glass beads with the most suitable ratio 6:1.

Wianglor et al. (2017) studied the mechanical and microstructure characteristics of metakaolin based geopolymer. Two different curing conditions were used. The metakaolin was replaced with Portland cement by 70, 80, 85, 90, 95 and 100%. The solution of Na₂SiO₃ to NaOH was utilized as the alkali activator. The concentration of NaOH was 10 M, ratio of Na₂SiO₃ to NaOH was 0.67 and the ratio of alkali to binder (0.8) were used. Paste and mortar samples were cured at ambient temperature and 60 °C. However, increasing the replacement level of metakaolin the setting time and drying shrinkage was decreased, but with the increase of amount Portland cement and temperature, the strength of metakaolin based geopolymer concrete increased.

Rocha et al. (2018) studied the influence of Na+ and K+ alkaline activators types on the mechanical, microstructural, and thermal properties of alkali-activated metakaolin mortars. Four different mortar mixtures were prepared with difference alkaline activating solution. More than 80 MPa compressive strength was obtained at age of 28 days. The morphologies of geopolymer products were detected by SEM. A heterogeneous morphology, micro-cracked and porous were produced with alkaline sodium silicate due to fast activation. Therefore, high initial strengths were obtained in the early ages. However, with $K_2 SiO_3$ a homogeneous microstructure displayed with limited pores.

2.4.4. Natural pozzolans

The natural pozzolans such as volcanic ash, volcanic tuff, and pumice were previously used by the Romans to manufacture the concrete. However, they utilize natural pozzolans increases the mechanical and durability properties of concrete products. The use of natural pozzolans in concrete significantly reduce the production cost of concrete and reduction the emission of CO₂ gas. Therefore, the replacement of cement with natural pozzolans partially in concrete production has economic and environmental advantages. The properties of natural pozzolans are different, and changes depend on deposit. And also natural pozzolans are affected by the content of SiO₂ and Al₂O₃, the particle sizes and the structure (degree of amourpheness). High content of silica and alumina in natural pozzolans and especially pumice as shown in Figure 2.4 make it a very markedly raw material in the production of geopolymer concrete.



Figure 2.4. The ternary Al₂O₃ - CaO-SiO₂ of geopolymer source materials.

Allahverdi et al. (2017) used the pumice as a natural pozzolan, which is aluminosilicate materials and activated by the NaOH and Na₂SiO₃solutions. Many geopolymer cement specimens were prepared with different alkali-activators based on combinations of Na₂SiO₃ and NaOH. The influence of water/binder ratio, concentration

of sodium oxide and silica modulus were studied. The workability, setting time, and 28day compressive strengths of the alkali active natural Pozzolan concrete were carried out. They reported that pumice can be activated by using a Na₂SiO₃ and NaOH and achieved appropriate workability and achieved suitable compressive strengths up to 47 MPa with silica modulus, Na₂O concentration, and ratio of water to binder of 0.60, 10 wt.%, and 0.36, respectively.

Najafi and Ali (2009) produced inorganic polymeric binder from natural pozzolan and discussed the effects of curing period and temperature on strength improvement. Three different chemical formulations mixes were made with different stream-curing temperatures and period. The specimens cured at three different temperatures from 45 to 85 °C and for four different curing periods (5, 10, 15, and 20 hours) after 1 and 7 days of pre-curing were applied. The mixture which has the highest compressive strength was selected after cured in the autoclave at 125, 150, 180, and 210 °C temperatures for 20, 30, 40, and 50 hours of curing periods. The highest compressive strength 108.7 MPa was obtained when cured in autoclave at 210 °C curing temperature for 30 hours after 7 days of pre-curing.

In his doctoral thesis, Bonder (2009) used five natural pozzolans as geopolymer precursors to produce geopolymer cement and concrete. The natural pozzolans were activated by Na₂SiO₃ in an extremely alkaline environment. The curing temperatures of 20, 40, 60, and 80 °C were used for geopolymer specimens. Taftan is an Iranian natural pozzolan, can be activated without heat treatments. However, Shahindej natural pozzolans was heated at 700, 800, and 900 °C for further activation to study the influence of the alkaline medium on the strength of geopolymer product. The influence of the concentration (molarity ranges of 2.5 to 10.0 M), form and types of the alkaline hydroxide were studied. The mass ratio of SiO₂ to Na₂O (2.1, 2.4, 3.1) and various curing regimes on both natural pozzolans were used. The workability, air content setting time, compressive, splitting tensile strength, drying shrinkage, ultrasonic pulse velocity, and modulus of elasticity were studied. He also investigated the durability of geopolymer products such as sulphate resistance, permeability, and chloride ion penetration and compared with the conventional concrete. Based on the compressive strength of products the highest reactivity and best behavior was obtained by using of Taftan pozzolan with low L.O.I. and high calcium content. The results reported that a

combination of KOH and sodium silicate solution is the most efficient activator for activating natural pozzolans and higher strengths can be obtained with lower SiO_2 to Na_2O ratios. Natural pozzolans mostly achieved lower strength and modulus of elasticity at early ages compared the conventional concrete, but after long-term curing, higher compressive strength and elasticity modulus can be obtained. The compressive strength does not significantly reduce after exposure to sulphate solution.

Najafi and Allahverdi (2011) focused on the shrinkage behavior of a geopolymer cement paste. Pumice was used as a natural pozzolan in the production of geopolymer paste. The effect of chemical composition, activator SiO₂/Na₂O molar ratio and total molar ratios of Na₂O/Al₂O₃, and water to Al₂O₃ ratio parameters were studied. The hydrothermal curing was used to study the influence of curing conditions on shrinkage. The results demonstrated that the chemical composition and the molar ratio of the alkaline activator mostly affect the shrinkage behavior of natural pozzolan based geopolymer products. The amount of shrinkage was reduced by applying the hydrothermal curing with short procuring in humid atmosphere.

Tchakoute et al. (2013) used two types of volcanic ash for the production of geopolymers. The volcanic ashes were categorized by mineralogical, amorphous phase and chemical compositions, specific surface area, and particle size distribution. The geopolymer samples were cured at room temperature ($24 \pm 3 \text{ °C}$). The setting time, X-ray diffraction, FTIR and compressive strength were performed. They studied the effects of Na₂O / Al₂O₃ and SiO₂ / Na₂O molar ratios of the alkaline activator solutions on the geopolymer products with ambient curing temperature. The more effective geopolymers were obtained with large volume amorphous phase of (Al₂O₃ + SiO₂), synthesized products with molar ratios of Na₂O / Al₂O₃ between 1.04 – 1.31 and great specific surface area (15.7 m² / g). The compressive strength of 50 MPa was achieved after 28 days at ambient curing temperature ($24 \pm 3 \text{ °C}$).

Yadollahi et al. (2015) studied the influences of elevated temperature on pumice-based geopolymer. The pumice utilized in their study was taken from the Hasankale Region near Erzurum, Turkey. The pumice was activated by the combination of Na_2SiO_3 and NaOH solution. Nine mixes have been prepared. The geopolymer specimens were exposed at 100, 200, 300, 400, 500, 600, 700 and 800 °C for 3 hours. Before exposing to high temperature and after that, the ultrasonic pulse velocity and

density of geopolymer pastes were measured, the specimens were cooling at room temperature. The SEM and FTIR analyses were used to investigate the microstructures of these specimens for all temperatures, and the cracks observation increased as temperatures increases from 600 to 800 °C. With increasing exposed temperature level. Compressive strength losses were increased. Compare to the OPC the strength loss of geopolymer concrete is less. According the results were reported pumice based geopolymer has an excellent fire resistance property.

Yankwa Djobo et al. (2016) used volcanic ash to produce the geopolymer mortars and investigated the mechanical properties and durability of geopolymer mortars. The specimens were evaluated at 27 °C and 80 °C. The long-term mechanical properties and durability of geopolymer mortars were worked up to 180 days. The maximum water absorption was reached 7.03% at 27 °C of curing after 28 days and reach 5.91% for specimens cured at 80 oC. The 20 MPa compressive strength was obtained at 27 oC after 28 days. Although, with increases time, the strength not increases significantly. However, the compressive strength of 37.9 MPa was achieved for samples cured at 80 °C after 90 days. The sulfuric acid resistance of geopolymer concrete specimens are improved by 5% when the cured temperature decreased from 80 °C to 27 °C. The gypsum as a secondary phase formation was discovered after acid exposure from the microstructure of geopolymer specimens due to the reaction between calcium from geopolymer gel and sulfuric acid. The compressive strength reduced by 24% and 14% for specimens cured at 27 °C and 80 °C respectively, when the geopolymer mortar specimens tested under wetting and drying cycles after 25 cycles.

Almalkawi et al. (2017) used pumice, volcanic tuff in the manufacture of alkaliactivated cement. The cooling rate and aging procedures of volcanic tuffs demonstration reactivity level. The mechanochemical processing used to heat treatment with different naturally occurring alkali sources or cations of alkaline earth metal into hydraulic cements. They investigated the hydration heat of cement particles, particle size distribution, bond structure, chemical composition, thermal attributes, mineralogy and cement particles morphology and hydrated cement paste.

Ibrahim et al. (2017) developed alkali-activated concrete by the used powder of volcanic rock as a natural Pozzolan as a binder. They examined the influence of curing time, binder content, and alkaline activators type and properties on the characteristics of

natural pozzolan based alkali-activated concrete. The mass ratio of Na₂SiO₃ and NaOH varied from 2.0 to 2.75 and the volume of binder in the range 350 kg/m³ to 450 kg/m³. The workability and setting time of fresh alkali-activated concrete were found. The samples were cured at 60 °C for 0.5, 1, 3, 7, 14 and 28 days. The mineral composition and morphology were determined by the SEM and XRD techniques. The results reported that the alkaline activator composition and binder content substantially affect the properties of geopolymer concrete. The strength improved curing for up to 7 days. However, further increasing in curing temperature up to 28 results to reduce the strength of geopolymers. The optimum strength and microstructural characteristics were obtained when the binder content is 400 kg/m³, the mass ratio of Na₂SiO₃ and NaOH was 2.5, and the mass ratio of alkaline liquid to binder is 0.525.

2.5. Alkali Activators

Sodium (NaOH) or potassium hydroxide (KOH) is the most widely utilized alkaline activators. The properties of geopolymer concrete are essentially affected by the type, proportion, and amount of alkali-activated liquid in concrete mixtures. The utilization of alkaline activators depends on multiple factors such as the solution cost, availability and the reactivity required. Generally, the combination of NaOH with a sodium silicate solution is the most commonly used alkaline activator solution to activation the source materials in geopolymer technology. The ions of Si⁴ + and Al³ + dissolute from source materials by NaOH solution. While Na₂SiO₃ Consists of silicate soluble components in order to progress the condensation process of geopolymer concrete.

Alkali hydroxides such as sodium hydroxide potassium hydroxide or $Ca(OH)_2$ and Na_2SiO_3 were used to activate fly ash by (Leong et al., 2016). The effect of using various alkali activator sodium silicate/sodium hydroxide (sodium silicate/potassium hydroxide or $Na_2SiO_3/Ca(OH)_2$) on workability and compressive strength were performed. The heat curing was used to all samples at 60 °C for 24 hours. Alkali activator/fly ash mass ratio was varied in the range of 0.3 to 0.6. Increasing the mass ratio of alkali activator to fly ash, the workability was increased. However, the workability of fresh concrete was decreased when Na_2SiO_3/KOH and $Na_2SiO_3/NaOH$ ratio were increased. The high compressive strength was not achieved when the high mass ratio of activator to fly ash and Na₂SiO₃/NaOH(KOH) were used. The highest compressive strength was achieved when the mass ratio of alkali activator to fly ash was 0.4, Na₂SiO₃/KOH ratio of 1 and Na₂SiO₃/NaOH ratio of 2. Higher compressive strength of potassium hydroxide based geopolymer was obtained when ratio of Na₂SiO₃/NaOH was 0.5. However, when the Na₂SiO₃/NaOH ratio was more significant than 1.5, higher compressive strength of sodium hydroxide based geopolymers were resulted compare to potassium hydroxide-based geopolymer in the same ratio of Na₂SiO₃/NaOH. They found that high values of oxide molar did not provide high compressive strength and the influence of CaO/Al₂O₃, CaO/SiO₂ and SiO₂/Al₂O₃ oxides on sodium hydroxide- and potassium hydroxide-based geopolymer was almost same. But the effect of Al₂O₃/Na₂O, SiO₂/Na₂O, SiO₂/K₂O, and Al₂O₃/K₂O to sodium hydroxide- and potassium hydroxide-based geopolymer were difference. The lowest compressive strength was obtained when Ca(OH)₂ used as activator based on geopolymer. Using Ca(OH)₂ as activator decreases the dissolubility of Si and Al from in the source material (fly ash). Compare to the NaOH and KOH the uses of Ca(OH)₂ as activator increases the set and gel harden of geopolymer concrete.

2.6. Factor Affecting Mechanical Properties of Geopolymer

2.6.1. Concentration of alkaline activators

The concentration of alkaline activators is the most critical factor affecting the mechanical and durability properties of a geopolymer products. The previous research indicated that an increase in the alkaline activators concentration leads to accelerating chemical dissolution and alumina-silicate solubility improves as the concentration of alkaline activators increases. In the literature, various combinations of activators have been used. The NaOH with Na₂SiO₃, KOH with K₂SiO₃ or sodium hydroxide alone can be used as an aviator solution. But NaOH and Na₂SiO₃ commonly used as an alkaline activator in geopolymer concrete. Numerous studies have been conducted to investigate the effect of alkali activator concentration on the properties of geopolymers (Table 2.2).

Reference	Alkali binders	Alkali / Binder	Na2SiO3/ NaOH	Concentration	Curing conditions	
Mustafa et	low calcium, Class	0.4	2.5	6, 8, 10, 12, 14 and	70°C for 3	
al. (2011)	F fly ash	0.4	2.3	16	days	
Memon et al. (2013)	fly ash	0.5	2.5	8, 10, 12 and 14	70°C for 48	
Hounsi et al. (2014)	kaolin	0.25	КОН	4, 6, 8, 10 and 12	70°C for 24 h	
Patankar et al. (2014)	low calcium fly ash	0.45	1	2.91, 5.61, 8.11, 11.01, 13.11, and 15.06	60°C for 24 h	
Ghafoori et al. (2016)	natural Pozzolan	0.5	Just NaOH	2.5, 5, 7.5 and 10	60°C for 3 h	
Degirmenci (2016)	ground granulated blast furnace slag	0.32	2	8, 10 and 12	80°C for 24 h	
Huseien et al. (2016)	55% GBFS, 15% fly ash, 15% waste ceramic and 15% waste glass bottle.	0.35	3	2, 4, 6, 8, 10, 12, 14 and 16	60°C for 24 h	
Nagaraj and Babu (2018)	fly ash 25% and GGBS 75%	0.5	2.5	2, 4, 6, 8, 10 and 12	Ambient room temperature	

Table 2.2	. Research	activities	investigated	different	alkali	activator	concentrati	on	in 1	the
	producti	on of geop	olymers							

Figures 2.5 illustrations the relationship between the alkali activator concertation and compressive strength values (Mustafa et al.,2011; Memon et al., 2013; Hounsi et al., 2014; Patankar et al., 2014; Ghafoori et al., 2016; Degirmenci, 2016; Huseien et al., 2016 and Nagaraj and Babu, 2018). For instance, Patankar et al. (2014) stated that maximum compressive strength is achieved when the concentration of sodium hydroxide is 11.01 M and curing at 60 $^{\circ}$ C for 24 hours. The compressive strength increased with increasing molarity up to 11.01 M. However, further increasing NaOH decreased the compressive strength (Figure 2.5). Nagaraj and Babu, (2018), Ghafoori et al. (2016), Degirmenci (2016) and Hounsi et al. (2014) reported that the compressive strength of geopolymers increases proportionally with increasing the concentration of alkali activator in range of 2 to 12 molarity (Figure 2.5). However, they used different source materials (fly ash, GGBS, natural Pozzolan, and kaolin), as mentioned in Table 2.2.

Mustafa et al. (2011), Memon et al. (2013) and Huseien et al. (2016) reported that an increase in alkali activator concentration up to 12 M the geopolymerization process developed, which resulting to improve the compressive strength. The optimum alkali activator concertation for geopolymer is changing may be observed due to different chemical composition of the source materials and other parameters such as alkali activator properties, activator to binder ratio and curing condition.



Figure 2.5. The effect of different molarities of alkali activators on the compressive strength through reviewing several studies.

2.6.2. The ratio of M-silicate to M-hydroxide

The mass ratio of M-silicate to M-hydroxide $(Na_2SiO_3 \text{ to } NaOH \text{ or } K_2SiO_3 \text{ to } KOH)$ considered another parameter which has to affect the mechanical durability properties of geopolymer concrete. The compressive strength of geopolymer concretes improved by increases the M-silicate to M-hydroxide mass ratio.

Reference	Alkali binders	Sodium to hydroxide	Alkali / Concentration Binder		Curing conditions
Abdullah et	Class F fly	0.5, 1, 1.5, 2, 2.5 and	0.5 12		70 °C for
al. (2011)	ash	3	0.5	12	24 h
T1	Low				
Joseph and	calcium fly	150050 105	0.55	10	100 °C for
Mathew	ash (Class	1.5, 2, 2.5, 3 and 3.5	0.55	10	24 h
(2012)	F)				
Joshi and	Class C fly	1.75, 2, 2.25, 2.5,	0.05	10	75 °C for24
Kadu (2012)	ash	2.75 and 3	0.35	12	h
Abdullah et	Class F fly	0.5, 1, 1.5, 2, 2.5 and	0.4		70 °C for
al. (2013)	ash	3	0.4	10	24 h
Sukmak et al.	F 11-	07115-102	05	10	65 °C for
(2013)	Fly ash	0.7, 1, 1.5 and 2.3	0.5	10	48 h
Morsy et al.	Class F fly		0.4	10	80 °C for
(2014)	ash	0.5, 1, 1.5, 2 and 2.5	0.4	10	24 h
Pavithra et	Class F fly	1 1 5 0 - 1 2 5	05	10	70 °C for
al. (2016)	ash	1, 1.5, 2 and 2.5	0.5 12		24 h
Nacana: and	Fly ash	2 2 5 2 2 5 4 and			ambient
Nagaraj and	25% and	2, 2.5, 5, 5.5, 4 and	0.5	12	room
Babu (2018)	4.5 GGBS 75%				temperature
Oleiwi et al.	CODES	1 15 2 125	05	10	60 °C for
(2018)	GORL2	1, 1.5, 2 and 2.5	0.5 12		19.9 h

Table 2.3. Previous studies investigated the different mass ratio of Na₂SiO₃/NaOH to prepare the alkali activator

Table 2.3 shows several studies which they investigated the different sodium silicate to NaOH ratio. Figure 2.6 demonstrates the relationship between sodium silicate/sodium hydroxide mass ratio and the compressive strength of geopolymers.

According to Figure 2.6, Abdullah et al., 2011; Joseph and Mathew, 2012; Joseph and Mathew, 2012 and Abdullah et al., 2013, the most recommended sodium silicate to sodium hydroxide is 2.5 to produce geopolymers. However, Nagaraj and Babu, (2018) and Oleiwi et al. (2018) reported that the optimum sodium silicate to sodium hydroxide is 2 and with increasing the sodium silicate to sodium hydroxide ratio the compressive strength decreased.

Figure 2.6, Sukmak et al. (2013) and Pavithra et al. (2016) stated that the maximum compressive strength can be achieved when the mass ratio of sodium silicate to sodium hydroxide is 1.5. Morsy et al. (2014) reported that the strength of geopolymer concrete is improved when the sodium silicate to sodium hydroxide mass ratio increased from 0.5 to 1. However further increasing in the mass ratio result to decrease the compressive strength (Figure 2.6).



Figure 2.6. The effect of different Na₂Si₃/NaOH ratio on the compressive strength through reviewing several studies.

The differences of optimum values of sodium silicate to NaOH mass ratio may be due to different chemical composition of the source materials and other parameters such as alkali activator properties, activator to binder ratio and curing conditions were used. The most important parameter and an indicator which affect the strength and durability properties of geopolymer concrete is the mass ratio of activator to binder (A/B). Table 2.4. shows several research activities, which conducted to study the effect of different alkali activator ratio on geopolymer products.

Reference	Alkali binders	Sodium to hydroxide	Alkali / Binder	Concentration	Curing conditions
Sinsiri et al. (2012)	Fly ash	1.5	0.40, 0.50, 0.60 and 0.70	15	75 °C for 24 hours
Joseph and Mathew (2012)	Low calcium fly ash (Class F)	2.5	0.35, 0.45, 0.55 and 0.65	10	100 °C for 24 h
Sukmak et al. (2013)	Fly ash	2.3	0.4, 0.5, 0.6, and 0.7	10	65 °C for 48 h
(Ghafoori et al. (2016)	Natural Pozzolan	just NaOH	0.5, 0.54 and 0.58	10	60 °C for 3 h
Ibrahim et al.	Natural		0.467, 0.525		
(2017)	pozzolan	2.5	and 0.6	14	$60 ^{\circ}\mathrm{C}$ for 7
Reddy et al. (2018)	Fly Ash and GGBFS	1.5	0.4, 0.5, 0.6, 0.7 and 0.8	14	ambient temperature
Phoo- ngernkham et al. (2018)	Class C fly ash	1	0.45, 0.5, 0.55 and 0.6	10	Ambient temperature

Table 2.4. Research activities studied the different alkali to binder ratio in the production of geopolymer technology

According to some previous studies, a recommended alkali activator can be in range 0.3 to 0.8 (Table 2.4). There is no optimum value or limited range of alkali to binder ratio, due to use many different source materials and curing condition in geopolymer technology.

Reddy et al. (2018) used fly ash, and GGBFS produced geopolymer concrete at ambient temperature with different alkali activator/binder ratio in range 0.4 to 0.8. They reported that increases the alkali activator to binder ratio from 0.4 to 0.8 result to a 50% reduction in compressive strength (Figure 2.7). However, Sinsiri et al. (2012) stated that increasing the alkali activator/binder ratio from 0.4 to 0.5 result to increase the compressive strength, on the other hand increasing the alkali activator/binder ratio from 0.4 to 0.5 result to ratio from 0.5 to 0.8 lead to reduce the compressive strength sharply about 45% (Figure 2.7).



Figure 2.7. The effect of different molarities of alkali activators on the compressive strength through reviewing several studies.

According to Sinsiri et al., 2012; Joseph and Mathew, 2012; Sukmak et al., 2013; Ghafoori et al., 2016; Ibrahim et al., 2017 and Reddy et al., 2018 alkali activator/ ratio range between 0.45 to 0.55 is the most recommended one to produce geopolymer products (Figure 2.7). In general, with increases the ratio of alkali activator to the binder, the compressive strength decreased. This similar to water to cement ratio ordinary Portland cement. When the amount of alkali activator increases in the mixture, the water content already increases due to the water available within the alkali activator which result to make a weaker micro-structure (Bondar et al., 2011).

2.6.4 Fineness of binder

The fineness of binder material is one of the most significant physical properties commanding the activity of alkali binders, a greater surface area is provided by smaller particle sizes of the binder. The particle sizes of binder substantially affect the workability of the fresh concrete, mechanical and durability characteristics of geopolymer concrete as well.

Sathonsaowaphak et al. (2009) used the waste lignite bottom ash as source material to produce geopolymer mortar. The combination of Na₂SiO₃ and sodium hydroxide were utilized as alkali activator. The heat curing was used to accelerate the geopolymerization process. They reported the influence of bottom ash fineness, sodium silicate/sodium hydroxide ratio, alkaline activator/binder ratio, and concentration of sodium hydroxide on workability and compressive strength of the geopolymer product. The influence of extra water and superplasticizer on geopolymer mortars were indicated. The Blaine fineness of 2100, 3400 and 5000 cm²/g which the mean particle sizes of 32.2, 24.5 and 15.7 μ m. The compressive strength was developed with the increase in the fineness of bottom ash. The high compressive strength 24.0–58.0 MPa of geopolymer mortars were found when the mean particle size of bottom ash was 15.7 μ m. Increasing the fineness of bottom ash result in increasing the workability of geopolymer mortar, increasing the fineness of bottom ash result in exercise the size of bottom.

Patankar et al. (2013) studied the influence of different fineness of fly ash on the strength properties of geopolymer concrete. A highly alkaline solution of sodium silicate and sodium hydroxide solution was used to active 5 different fly ashes. The Blaine fineness of fly ash 265, 327, 367, 430 and 542 m²/kg were used, and the sodium hydroxide concentration 13 molar, the ratio of activator to fly ash 0.35 were used. The specimens were cured at 90 oC for 4, 8, 12, 16, 20 and 24 hours. The results indicated that the fineness of fly ash plays an essential role in geopolymer activation. When the fineness of fly ash increased both compressive strength and workability improved. It was also mentioned that the finer particles of fly ash lead to increases the reaction rate and require less curing period to achieve enough strength.

2.6.5. Heat and Curing Time

The high early strength property of geopolymer concrete known as a great advantage, this strength is due to heat curing and time, which require to geopolymerization processes. On the other hand, the most difficult challenge which facing the mix design of geopolymer concrete is founding the appropriate balancing of heat curing temperature and curing time. Geopolymer concrete can be produced at the ambient temperature without external heating sources but the gain strength much slower rate as time compare heat curing. The increase in the heat curing led to increasing the and strength of geopolymer concrete. In addition, long curing period develops the properties geopolymer concrete. The previous indicated that a more extended curing period enhanced the polymerization process and led to higher strength. Both oven dry and steam curing can be used to cure the geopolymer concrete and can affect the mechanical and durability properties of geopolymer concrete differently. Many researchers investigated the geopolymer specimens under different curing temperature and duration times to know the most economical and suitable curing conditions (Table 2.5).

Figures 2.8 and 2.9 show the effect of different curing temperatures and period on the compressive strengths of geopolymers respectively, the data from (Hardjito et al., 2004; Mishra et al., 2008; Rovnaník P., 2010; Memon et al., 2011; Bakri et al., 2011; Patankar et al. 2014; Joseph B., 2015 and Ilkentapar et al.,2017) studies were obtained to draw those graphs. For example, Rovnaník P. (2010) investigated the effects of 4 different curing temperatures (20, 40, 60, and 80 °C) for 4 hours to activate the metakaolin. As can be seen from Figure 2.8, Rovnaník P. (2010) the high compressive strength was obtained in their study when the curing temperature of specimens was 20 °C for 4 hours. The results of the study indicated that increasing the curing temperature from 20 to 80 °C had not much effect on geopolymerization process, and the compressive strength increased just 10%. Almost the similar results reported by Memon et al. (2011). However, they used fly ash as source material. Bakri et al. (2011) reported that the optimum compressive strength can be obtained (Figure 2.8) by increasing the curing temperatures form room temperature and 60 °C for the same curing period when fly ash used as a geopolymer binder. However, further increasing in curing temperature result to decrease the compressive strength significantly.

Reference	Alkali binders	Sodium to hydroxide	Alkali / Binder	Concentration	Curing conditions
Hardjito et	Fly ash	2.5	0.35	8-16.	60 °C for 4,8,12,16,
al. (2004)	2				24, 48, 72 and 96 h
Mishra et	Fly ash	0.6	0.5	12	60 °C for 24, 48 and
al. (2008)					72 h
Rovnaník	Metakaolin		0.82		20, 40, 60 and 80 °C
(2010)					for 4 h.
					(70 °C for 24, 48, 72
Memon et	Class F Fly	2.5	0.5	12	and 96 h)and (60, 70,
al., (2011)	ash				80 and 90 °C for
					of 48 h)
Mustafa					23, 50, 60, 70, and 80
Al Bakria	flv ash	2.5	0.5	12	°C
et al.	J				for 24 h.
(2011)					
Patankar et	Low				40, 60, 90, 120 °C for
al. (2014)	calcium fly	1	0.5	11.01	24 h
	ash				22 (0 7 0 00 00
Joseph	T-1 1	2.5	0.55	10	23, 60, 70, 80, 90,
(2015)	Fly ash	2.5	0.55	10	100, 110 and 120 °C
İllırantanar					for 24n
at al					at 75 0 C for 4 24 49
(2017)	Elvesh	Inot NoOU	0.46		at 73 C 10F 4, 24, 48,
(2017)	Fly ash	JUST NAOH	0.46		12 and 168 h

 Table 2.5. Previous studies investigated the specimens curing under different curing temperature and duration times to produce geopolymer concretes.

Furthermore, as it appears from the Figure 2.8, Joseph B. (2015) in their study, they used 8 different curing temperatures (room temperature, 60, 70, 80, 90, 100, 110

and 120 oC) for 24 hours, the compressive strength significantly improves with increasing the curing temperature, the optimum compressive strength was obtained when the specimens cured at 100 oC for 24 hours. In another study Patankar et al. (2014) investigated the geopolymer concrete under four different curing temperatures (40, 60, 90, 120 °C) for 24 hours, they stated that the increases in curing temperature up to 120 oC, directly increase the compressive strength of geopolymer products.



Figure 2.8. The effect of different molarities of alkali activators on the compressive strength through reviewing several studies.

Figure 2.9 illustrations the influence of curing period on the compressive strength of geopolymers. As can be observed from Figure 2.9, Hardjito et al., 2004; Mishra et al., 2008; Memon et al., 2011, and Ilkentapar et al. (2017), base all mentioned studies the compressive strength was proportionally increased with increasing curing period from 4 to 168 hours.



Figure 2.9. The effect of different molarities of alkali activators on the compressive strength through reviewing several studies.

2.7. Durability Properties of Geopolymer Concrete

The durability properties of geopolymer technology are considered as a significant factor in the success and development of this technology.

Bakharev (2005a) investigated the durability property of geopolymer concrete. After the geopolymer specimens exposed to sulfate environment for a period of 5 months, the durability of geopolymer specimens varied differently depend on the activator type used in the production of geopolymer specimens and concentration and cation type in the sulfate. The geopolymer specimen immersion into 5% solutions of magnesium and sodium sulfate, and a 5% sodium sulfate +5% magnesium sulfate solution. When the specimen immersion into 5% sodium sulfate +5% magnesium sulfate, the smallest changes were found. However, the specimen immersion into 5% solution of strength and microstructural changes. In the sulfate solution of magnesium, the compressive strength of geopolymer specimens increased. However, the significant deterioration was detected in ordinary Portland cement in the same conditions. Using

the sodium hydroxide as an activator in the production of geopolymer concrete was more resistible in sulfate solutions compare to the uses of sodium silicate or the solution of sodium and potassium hydroxide.

Fu et al. (2011) prepared alkali-activated slag concrete. The slag was used as a binder, and Na₂SiO₃ and NaOH were used as activator. The investigated the freeze-thaw resistance by freeze-thaw cycle and microstructure and inner freeze-thawing damage distribution by SEM and EDS tests. The results indicated that slag based geopolymer concrete has excellent freeze-thaw resistance. The damage degree of geopolymer concrete after freeze-thaw cycles essentially related to the dynamic elasticity modulus. When relative dynamic elasticity modulus of geopolymer concrete reduced after freeze-thaw cycles, the damage degree increases.

Degirmenci (2017) investigated the resistance of pozzolan based geopolymer mortars for freeze-thaw cycles high temperatures. The effect of high temperatures (300, 600, and 900 °C) on the properties of the geopolymer product was investigated. At 900 °C the lowest strength was achieved for all mixes. The body disruption or deformation was not detected in geopolymer specimens after 25 cycles. The compressive strength loss of natural Pozzolan based geopolymers were found was higher than the compressive strength loss of fly ash and GGBS based geopolymer after the same cycles of freeze-thaw condition.

2.9. Environmental advantages and economic analysis

The natural pozzolans and by-product materials can access easily with no extra manufacturing costs. The usage of geopolymer concrete products in the construction industry reduce environmental impacts. The geopolymer technology is environment friendly, can be used as a green construction material. The use of by-product wastes in geopolymer technology help reduces solid wastes. Unlike cement, the natural pozzolans and by-product materials can be used as a binder in geopolymer concrete mixture with no further processing. However, the use of some aspects such as alkaline activator and other hazardous activities impact the greenness of geopolymer productions. The price of one-ton natural pozzolans is almost equal to the fraction price of the one-ton cement. The cost of geopolymer concrete has been estimated up to 30% economy than that of

the conventional concrete (B V Rangan, Hardjito, & Wallah, 2014). The cost of geopolymer production in term of commercial context dependent on several factors such as the source location, optimal activator composition, energy source, dosage, and transportation cost.

Mclellan et al. (2011) studied the comparison of the lifecycle cost and carbon emission between geopolymer paste and ordinary Portland cement-based on the typical Australian context. The production of geopolym0er concrete reduced the greenhouse gas emissions by 44-64 % and compared to ordinary Portland cement, and the commercial costs are 7% lower to 39% higher.





3. MATERIALS AND METHODS

This chapter presents details of the experimental methods performed in the development and testing of geopolymer paste specimens and the specification of the materials used to produce the geopolymer specimens were described. The material and geopolymer paste specimen test program and parameters were also explained.

3.1. Materials

3.1.1 Pumice powder

The raw pumice used in this investigation was collected from a quarry in Ercis, Van, located in Eastern Turkey. The chemical composition of raw pumice used in this study is summarized in Table 3.1. The XRD and FTIR analysis of the pumice powder is shown in Figure 3.1 and Figure 3.1 respectively. In order to reduce the pumice size, the pumice aggregate was crushed in the laboratory by using a dodge jaw crusher. The pumice powder was prepared by grinding the crushed pumice for 4, 6 and 8 hours in a ball mill to study the effect of fineness on the strength and freezing and thawing durability properties of geopolymer paste.

Chemical Composition	Percentage %
SiO ₂	75.23
Al_2O_3	14.04
Fe_2O_3	1.95
MgO	0.22
CaO	0.52
Na ₂ O	2.09
K_2O	5.05
TiO ₂	0.11
P_2O_5	0.03
MnO	0.22
SO3	0.29
Cl	0.04
LOI	4.40

Table 3.1. Chemical composition of pumice powder (%)



Figure 3.1. XRD patterns of pumice powder.



Figure 3.2. FTIR analysis of pumice power used in this study.

The particle size distribution of the pumice powder which grinding for 4 and 8 hours is shown in (Figure 3.3).



Figure 3.3. The fineness of pumice powders used in this study.

3.1.2. Alkaline liquids

The alkaline liquid used in this investigation was a combination of sodium silicate (Na₂SiO₃) and sodium hydroxide (NaOH) solution. The sodium hydroxide solution was chosen because it has lower cost compare the potassium hydroxide. The sodium silicate solution used in this study was obtained from Koray Chemistry, Istanbul, Turkey and has a chemical composition of $SiO_2 = 27.1\%$, $Na_2O = 9\%$, and $H_2O = 63.9\%$ (by mass) with modulus ratio (SiO₂/Na₂O) of 3.01 and a specific gravity of 1.367 g/cm³ as shown in Table 3.2. The sodium hydroxide flakes with 98% purity dissolving in water were used to produce sodium hydroxide solution. Distilled water, available in the laboratory, was used to prepare NaOH solutions. During the dissolution of NaOH pellets in water a substantial heat released. The mass of NaOH flakes in a solution varied based on the desired concentration of the solution in terms of molarity (8, 10, 12, 14, 16 and 18 M) with the molecular weight of NaOH (40 g). For instance, NaOH solution with a concentration of 12M (Molar), which was commonly used in this study, consisted $12 \times 40 = 480$ grams of NaOH solids per liter of the solution. The mass of NaOH solids was measured as 361 grams per kg for 8M concentration of NaOH solution. The sodium silicate to sodium hydroxide mass ratio was fixed at 2.5 for all mixtures. After the sodium silicate and sodium hydroxide solution mixed using the laboratory type stirring and mixing equipment, the alkaline liquid mixture was subjected to a 24 hours waiting period and then used for preparing geopolymer paste specimens.

Analysis	Result	Specifications range
Appearance	No-color Clear	No-color
Density (20 °C)	1.367 g/cm^3	$1.3580 - 1.3950 \text{ g/cm}^3$
Bome (20 °C)	38.68 °B	38 - 40
Sodium Oxide (Na ₂ O)	9.03 %	8.10 - 10.1 %
Silica (SiO ₂)	27.08 %	24.60 - 28.60 %
Module	2.93	2.8 - 3.4

Table 3.2. Analysis results of sodium silicate

3.2. Specimen Preparation

Six mixes with different sodium hydroxide concentrations (8, 10, 12, 14, 16 and 18 molarity) were prepared. Several trial mixes were made for the various alkali activator to binder ratios. One day prior to geopolymer paste preparation, the sodium hydroxide and sodium silicate solution were mixed to complete the geopolymerisation process of the alkali activator solution. Before the pumice powder was mixed with the alkali activator, high range water reducing admixture (Master-Glenium ACE 450) with 2% by mass of pumice powder was mixed with the alkali activator in order to increase the workability of the fresh geopolymer paste. A constant alkali to binder (A/B) ratio of 0.35 was used for all mixtures in order to obtain cost effective and workable geopolymer concrete. The through mixing of the geopolymer paste was carried out in a 60-liter capacity pan mixer for 12 minutes. Figure 3.4 shows the geopolymer ingredients were used in this study. All the materials were mixed at ambient temperature in the laboratory. A jolting table with 60 drops was used to compact specimens according to EN 196-1 (CEN, 2005). The concrete specimens were kept at ambient temperature after casting, for a rest period of 24 hours. The mixture proportions of the specimens are given in Table 3.3. A constant 1300 kg and 325 kg of pumice powder and sodium silicate were used respectively. The specimen notation of different geopolymer pastes shown in Figure 3.5.



Figure 3.4. Geopolymer paste ingredients.



Figure 3.5. Specimen notation for different geopolymer paste.

3.3. Curing of Specimens

After casting, the test specimens were covered with vacuum bagging film in order to minimize evaporation of liquid solutions during curing temperature of geopolymer paste specimens. After a 24 hour resting period at ambient temperature, all specimens were cured in a dry oven at different curing temperatures (ambient temperature, 60 °C, 80 °C, and 100 °C) as shown in Figure 3.6. The paste specimens were subjected to different curing times of 24, 48, 72, and 120 hours, as shown in Table 3.3. After the curing process was finished, all specimens were kept at ambient room temperature until the testing time which was the 7th and 28th days (Figure 3.7).


Figure 3.6. Curing the specimen in oven dry for different curing temperature and duration time.



Figure 3.7. The specimens placed in room temperature until the testing time.

Sample code	Molarit y	powder Pumice	A/B ratio	Admixt bre	ε O!S ^{zg} N	Na H2O	OH Flake	HO ^g N/ E O!S ^{zb} N	Curing Temperature (°C)	Period
M8-Room M8-24h- (60, 80 &100) M8-48h- (60, 80 &100) M8-72h- (60, 80 &100) M8-120h- (60, 80 &100)	×	1300 kg	0.35	%2	325 kg	87.4 kg	41.6 kg	2.5	23 °C 60, 80 and 100 °C 60, 80 and 100 °C 60, 80 and 100 °C 60, 80 and 100 °C	24 h 48 h 72 h 120 h
M10-Room M10-24h- (60, 80 &100) M10-48h- (60, 80 &100) M10-72h- (60, 80 &100) M10-120h- (60, 80 &100)	10	1300 kg	0.35	%2	325 kg	77 kg	52 kg	2.5	23 °C 60, 80 and 100 °C 60, 80 and 100 °C 60, 80 and 100 °C 60, 80 and 100 °C	24 h 48 h 72 h 120 h
M12-Room M12-24h- (60, 80 &100) M12-48h- (60, 80 &100) M12-72h- (60, 80 &100) M12-120h- (60, 80 &100)	12	1300 kg	0.35	%2	325 kg	67 kg	62 kg	2.5	23 °C 60, 80 and 100 °C 60, 80 and 100 °C 60, 80 and 100 °C 60, 80 and 100 °C	24 h 48 h 72 h 120 h

Table 3.3. Mixture Proportion

	jî	к Ģ		12	С	Na	HO	H C	Curing	
Sample code	y Molar	oimu¶ obwoq	A/B ratio	timbA oru	ε ν ^ε δίς ε	H2O	Flake	N ² S ² BN	Temperature (°C)	Period
M14-Room									23 °C	
M14-24h- (60, 80 &100)	7	1300	0.25	C 70	375	695	0 C	v c	60, 80 and 100 $^{\circ}$ C	24 h
M14-48h- (60, 80 &100)	- 1	kg	<i>cc.</i> 0	70/	رعر لام	70.2 kg	/ 2.0 Kg	C.7	60, 80 and 100 °C	$48 \mathrm{h}$
M14-72h- (60, 80 &100)		C)	2	0		60, 80 and 100 $^{\circ}\text{C}$	72 h
M14-120h- (60, 80 &100)									60, 80 and 100 $^{\circ}$ C	120 h
M16-Room									23 °C	
M16-24h- (60, 80 &100)	7	1200	0.25	c 2	300	15 0	c co	u C	60, 80 and 100 °C	24 h
M16-48h- (60, 80 &100)	10	kg kg	CC.0	70%	ر ع لا م	4.).0 kg	2.co кg	C.7	60, 80 and 100 $^{\circ}\mathrm{C}$	48 h
M16-72h- (60, 80 &100)))))		60, 80 and 100 $^{\circ}$ C	72 h
M16-120h-(60, 80 &100)									60, 80 and 100 $^\circ\mathrm{C}$	120 h
M18-Room									23 °C	
M18-24h- (60, 80 &100)	10	1300	035		375	25 1	03 6	v c	60, 80 and 100 $^{\circ}$ C	24 h
M18-48h- (60, 80 &100)	01	kg kg	<i>cc</i> .0	70	kg kg	kg 4	kg kg	C.4	60, 80 and 100 °C	48 h
M18-72h- (60, 80 &100)))))		60, 80 and 100 $^{\circ}$ C	72 h
M18-120h- (60, 80 &100)									60, 80 and 100 $^{\circ}\mathrm{C}$	120 h

Table 3.3. Mixture Proportion (Continuous

3.4. Details of Tests

3.4.1. Compressive strength

The compressive strength test was performed on the prism specimens ($40 \times 40 \times 16 \text{ mm}^3$). The pressure test was done on the examples by a 2000 kN limit testing machine with a loading rate of 0.5 kN/sec. After the bending tests, the compressive tests were performed on the half beams using 40 mm x 40 mm cross-section according to ASTM C-349-08 (ASTM Standard, 2018) except that the broken portions of prisms selected for the compression test shall have a length of not less than 65 mm and shall be free of cracks, chipped surfaces, or other obvious defects. ASTM standards were also followed while calculating the compressive strength results, Record the total maximum load indicated by the testing machine and calculate the compressive strength in megapascals to the nearest 0.1 MPa, as follows (Eq. 3.1):

Sc = 0.00062 P

(3.1)

where:

Sc = compressive strength, MPa, and

P = total maximum load, N.

This method provides a means of obtaining compressive strength values from the same specimens previously used for flexural strength determinations by Test Method C348. The compressive strength test was performed at the age of 7th and 28th days. The test was also conducted after five cycles of freezing and thawing.

3.4.2. Flexural strength

The flexural strength tests were conducted on 40 x 40 x160 mm³ prisms conforming to ASTM C348 at the age of 28 days. The flexural strength of the specimens was determined by using standard three-point-bending test according to ASTM specifications (ASTM C348, 2002). Three prisms for each parameter were tested in order to determine the effect of molarity, curing temperature, and curing time on flexural strength of pumice powder based geopolymer pastes. According to ASTM specifications, flexural strength was determined based on the record the total maximum load indicated by the testing machine (Figure 3.8) and calculate the flexural strength (for the particular size of specimen and conditions of test herein described) in MPa as follows equation (Eq. 3.2):

Flexural strength =
$$0.0028 P$$
 (3.2)

Where flexural strength is measured in MPa and P is the maximum load of the tested specimen in KN.



Figure 3.8. The flexural strength test.

3.4.3. Ultrasonic Pulse Velocity (UPV)

In this investigation, the UPV test as a non-destructive testing (NDT) method was conducted to inspect the homogeneity and strength of the matrix of the specimens (Figure 3.9). The S-wave digital indicating tester with a 54 kHz transducer were used to measure transit time of wave passed through the specimens. The UPV test was also performed in order to evaluate the correlation between UPV value and compressive

strength of pumice powder-based geopolymer concretes. In this study, ultrasonic pulse velocity test was undertaken after before and after five cycles of freezing and thawing.



Figure 3.9. The ultrasonic pulse velocity test.

3.4.3. Freezing-Thawing test

The freeze-thaw cycles test was performed for geopolymer paste specimens. The total of five freeze-thaw cycles was subjected due to time constraints. The test was conducted on $40x40x160 \text{ mm}^3$ prisms at age of 28 days. One day before the testing time all samples placed into the water to absorb the water. The geopolymer specimens put in freezer cabinet at temperature of - 40 °C for period of 24 hours, while the thawing period of 24 hours was used at room temperature. Five freeze and thaw cycles were repeated, after five cycles the ultrasonic pulse velocity and compressive strength were performed to investigate the effect of the freeze-thaw cycles on deterioration resistant of geopolymer paste specimens. Figures 3.10 illustrates the specimens in thawing period after taken off from the freezer cabinet.



Figure 3.10. The geopolymer specimens in the thawing period after freezing cycle.

3.4.4. Scanning electron microscopy (SEM).

The SEM test was performed on the geopolymer paste specimens in order to determine their surface morphologies, as well as the effect of curing temperature and curing time on the strength characteristics of pumice powder based geopolymer pastes (Figure 3.11).



Figure 3.11. The scanning electron microscopy test.

4. RESULTS AND DISCUSSION

4.1. Compressive Strength

4.1.1. Effect of sodium hydroxide concentration on compressive strength

The concentration of NaOH significantly influences the compressive strength of geopolymers (Rattanasak and Chindaprasirt, 2009; Nuruddin et al., 2011; Hanjitsuwan et al., 2014; Görhan and Kürklü, 2014; Singh et al., 2016). The use of high NaOH concentration in geopolymer concrete leads to the higher dissolution of the pumice particles and tends to increase the geopolymerisation reaction, which results in higher compressive strengths. This is also true for fly ash based geopolymer concretes (ASTM C348, 2002; Álvarez-Ayuso et al., 2008; Görhan and Kürklü, 2014). Figure 4.1 to 4.6 demonstrate the influence of NaOH concentration on the compressive strengths of pumice powder based geopolymer pastes at the age of 7 and 28 days respectively. The test results show that the compressive strength of geopolymer paste increases by increasing the concentration of NaOH up to certain molarity. In the present study, the compressive strength of geopolymer paste increases by increasing the NaOH concentration from 8M to 12M; however, it decreases with the further increase in NaOH concentration from 12M to 18M. This may be due to the fact that large quantities of hydroxide ions led to aluminosilicate gel precipitation in the very early stages and subsequent geopolymerization was hindered, leading to reduced strength (Lee and Van Deventer, 2002; Yip et al., 2008; Chithambaram et al., 2019). The lowest strength was obtained with an NaOH concentration of 18 M. Although, several studies confirm that the maximum strength was obtained at the NaOH concentration of 12M (Prinya Chindaprasirt et al, 2009; Al Bakri et al., 2011; Somna et al., 2011; Memon et al., 2013), other studies have concluded that a higher sodium hydroxide solution concentration proportionally led to higher compressive strengths (Kupaei et al., 2014). Additionally, by increasing the concentration of NaOH, the dissolution of alumina and silicate from the source of aluminosilicate leads to more reaction finalization, which results in strength increases. Therefore, the authors believe that the molarity (NaOH

concentration) of the mixture can be arranged according to the Al and Si contents of sourced material in order to maximize the compressive strengths of pumice powder based geopolymer pastes. The unit weight of geopolymer paste is about 1500 kg/m³, due to its excellent compressive strength and reduced unit weight the geopolymer paste in this study could be used in varying geopolymeric production such as mortar for repairing concrete structures, bricks, concrete insulations, sandwich composites, and pre-cast products.

4.1.2 Effect of curing period on compressive strength

Figure 4.1 to 4.6 illustrate the effect of curing period on the compressive strength of geopolymer pastes at different curing temperatures (room temperature, 60 °C, 80 °C and 100 °C). As can be seen from Figure 4.1 to 4.6, the strength gain of geopolymer at 60 °C is proportionally increased with increased curing time. Optimum strength was obtained from the 12 molarity specimens which were subjected to 120 hours of oven curing at 60 °C. Figure 4.2 demonstrates that up to 72 hours of curing time, the strength gain of geopolymer is proportionally increased with the increase of curing time but after that, the strength decreased slowly as the curing time increased. This may be attributed to the fact that most of the polymerizations were completed after 72 hours of curing at 60 °C. Figure 4.3 shows that high strengths can be achieved with high curing temperatures and shorter curing periods. This high early strength gain can be related to the accelerated reaction of geopolymerisation. But when compared to low curing temperature and longer curing times, the compressive strength gains are less. The results in this investigation demonstrate that the optimum period of curing time for pumice powder based geopolymer concretes is 120 hours at 60 °C. Several other researchers also concluded that, although more extended curing period improves the polymerization process, optimum compressive strength was obtained at a 96 h period of curing at 60 °C (Joseph and Mathew, 2012; Brown et al., 2015). On the other hand, the increase in strength after 48 hours of curing is not significant. This finding is not in parallel with Atis et al.'s finding which states that curing at a lower temperature for a shorter period of time is sufficient to achieve satisfactory results for geopolymer concretes prepared using natural material as the source material (Atis et al., 2015).



Figure 4.1. Effect of curing period on the compressive strength at 60 °C at 7 days.



Figure 4.2. Effect of curing period on the compressive strength at 80 $^{\circ}$ C and at 7 days.



Figure 4.3. Effect of curing period on the compressive strength at 100 °C at 7 days.



Figure 4.4. Effect of curing period on the compressive strength at 60 °C at 28 days.



Figure 4.5. Effect of curing period on the compressive strength at 80 °C at 28 days.



Figure 4.6. Effect of curing period on the compressive strength at 100 °C at 28 days.

4.1.3. Effect of curing temperature on compressive strength

Figure 4.7 to 4.14 illustrate the effects of curing temperature on the compressive strength of pumice powder based geopolymer paste for the various curing periods from 24 to 120 hours. As can be seen from the figures, the compressive strength of geopolymer paste is significantly affected by curing temperature. The compressive strength of pumice powder based geopolymer pastes gradually increased when increasing curing temperatures up to NaOH concentrations of 12 molarity. Increasing the concentration of NaOH by more than 12 molarity resulted in a gradual decrease in compressive strength. The reactivity between aluminosilicate materials and hence the number of molecular bonds and amorphous phases were increased by increasing the temperature, which led to more significant strengths. Geopolymer paste gain strength at room temperature was found to be very slow. The results of this study indicate that early high strength development can be achieved by using high curing temperature (59 MPa was obtained after 24 hours of curing at 100 °C). Increasing the curing time at higher temperatures resulted in lower strengths. This loss of strength could be due to the evaporation of solution from specimen. They may dry out at temperatures above 60 °C; thereby, reducing strength. This finding is in line with the results of previous research (Hardjito et al., 2004; Joseph & Mathew, 2012; Mo et al., 2014; Mustafa Al Bakria et al., 2011).

Moreover, the results indicate that the compressive strength of the specimens cured at ambient temperatures continued to improve strength beyond the age of 7 days (at which point 15% of strength is attained for 12M). Thus, the specimens cured at ambient temperature continued to improve strength beyond the 7 days. The 7-day compressive strength of geopolymer concretes was increased by increasing the curing temperature. When the curing temperature increases from ambient temperature to 60 °C, 80°C and 100 °C, the percentage of strength gain increases to 97%, 96% and 97% respectively for the same curing period and molarity (120 h and 12M). The maximum strength of 76.73 MPa was obtained for 12M geopolymer pastes under 120 hours of 60 °C curing. For the same specimens, an increase in temperature of curing from 60 °C to 80 °C led to a decrease in compressive strength from 76.73 to 64.28 MPa. On increasing



the curing temperature to 100 $^{\circ}$ C the compressive strength of the same specimens decreased to 59.89 MPa.

Figure 4.7. Effect of curing temperature on the compressive strength for 24 hours at 7 days.



Figure 4.8. Effect of curing temperature on the compressive strength for 48 hours at 7 days.



Figure 4.9. Effect of curing temperature on the compressive strength 72 hours at 7 days.



Figure 4.10. Effect of curing temperature on the compressive strength for 120 hours at 7 days.



Figure 4.11. Effect of curing temperature on the compressive strength for 24 hours at 28 days.



Figure 4.12. Effect of curing temperature on the compressive strength for 48 hours at 28 days.



Figure 4.13. Effect of curing temperature on the compressive strength for (a) 24 hours, (b) 48 hours, (c) 72 hours and (d) 120 hours at 28 days.



Figure 4.14. Effect of curing temperature on the compressive strength for (a) 24 hours, (b) 48 hours, (c) 72 hours and (d) 120 hours at 28 days.

4.2 Flexural Strength

Figure 4.15 to 4.18 shows the results of the flexural strength tests performed at the age of 28 days. Figure 4.15 to 4.18 shows the influence of NaOH concentration on the flexural strength of geopolymer paste under different curing temperatures and curing times. The results illustrate that the flexural strength of geopolymer paste increases with an increase in the concentration of NaOH from 8M to 12M. However, a significant decrease in flexural strength was observed when the NaOH concentration increased beyond 14M. This finding is in line with the previously published research (Atiş et al., 2015). As with compressive strength, the optimum flexural strength was obtained with 120 h of curing at 60 °C when the concentration was 12M. Overall the flexural strength was increased by increasing the curing period and it was decreased by increasing the curing temperature.



Figure 4.15. Flexural strength of geopolymer paste at 28 days with room temperature.



Figure 4.16. Flexural strength of geopolymer paste at 28 days with temperature of 60 $^{\circ}\mathrm{C}.$



Figure 4.17. Flexural strength of geopolymer paste at 28 days with temperature of 80 $^{\rm o}{\rm C}.$



Figure 4.18. Flexural strength of geopolymer paste at 28 days with temperature of 100 °C.

4.3. Fineness of Pumice Powder

The raw pumice was crushed and grinded to a fine powder in ball mill for 4, 6, and 8 hours. Three different fineness of pumice powder were investigated in this study (Figure 4.19). Increasing the time period of grinding in ball mill resulted in increasing the fineness of pumice powder. In order to know the effect of fineness of pumice powder on compressive and flexural strength the optimum molarity (12M) cured at 60 °C temperature and ambient temperature was chosen for four different heat curing periods (24, 48, 72 and 120 hours). Figure 4.6 illustrates that increasing the fineness of pumice powder result to decreasing the compressive strength of geopolymer paste specimens cured at 60 °C. However, Sathonsaowaphak et al. (2009) and Jamkar et al. (2015) reported that increasing the fineness result to increase the compressive strength due to reducing the pores within the source material particles. Increasing the fineness pumice powder lead to increase the surface area, therefore, the author observed that may more alkaline activator and increasing the fineness of pumice powder change the nature and the reaction behavior of source material.



Figure 4.19. The effect of grinding time on the compressive strength of geopolymer pastes at age of 7 days.

According to the results obtained in this study, when the specimens cured at ambient temperature, increasing the grinding time (fineness) of pumice powder from 4 to 8 hours result to increases the compressive strength of geopolymer paste from 4 to 7 MPa respectively at the age of 7 days. The curing period substantially affects the compressive strength of geopolymer paste specimens, and the optimum compressive strengths were obtained when the maximum curing period were used at 60 °C, with increasing curing period the compressive strength increase as well. Therefore, the curing period significantly affects the strength development of geopolymer paste made with pumice powder. The 28-day compressive strength of geopolymer specimens presented in Figure 4.20, the results indicate that with increasing the specimen age from 7 to 28 days the compressive strength proportionally developed. The compressive strength of geopolymer pastes cured at 60 °C for 120 hours of 4, 6 and 8-hours of grinding time, developed by 3%, 21%, and 62% respectively, when the age of specimens increases from 7 to 28 days.



Figure 4.20. The effect of grinding time on compressive strength of geopolymer pastes at age of 28 days.

Figure 4.21 illustrates the influence of grinding time on flexural strength of geopolymer pastes at age of 28 days. The flexural strength of geopolymer specimens decreases with increasing the fineness of pumice powder. When the grinding time of pumice increased from 4 to 8 hours, the flexural strength reduced by 51%. Increasing the curing period result to increase the flexural strength of geopolymer pastes.



Figure 4.21. The effect of grinding time on flexural strength of geopolymer pastes at age of 28 days.

4.4. Freezing-thawing Resistance

This study investigated, the influence of 5 cycles freezing-thawing on the strength of geopolymer paste specimens. The durability properties of geopolymers are affected by many factors. In this study, the influence of alkaline activator, curing temperature and duration time on the freezing and thawing resistant of pumice powder based geopolymer pastes were investigated.

4.4.1. Effect of NaOH concentration on freezing and thawing resistance

The concentration of NaOH significantly influences the freezing and thawing properties of geopolymers pastes. The use of high NaOH concentration in geopolymer concrete leads to the higher dissolution of the pumice particles and tends to increase the geopolymerisation reaction, which results in higher compressive strengths. Figure 4.9 demonstrates the influence of NaOH concentration on the compressive strength of pumice powder based geopolymer pastes after five cycles of freezing and thawing at the age of 28 days. The test results indicate that the compressive strength of geopolymer

paste increases by increasing the concentration of NaOH up to certain molarity. The compressive strength of geopolymer paste after freezing and thawing test increases by increasing the NaOH concentration from 8M to 16M; however, it decreases with the further increase in NaOH concentration from 16M to 18M. This may be due to the fact that large quantities of hydroxide ions led to aluminosilicate gel precipitation in the very early stages and subsequent geopolymerization was hindered. However, it leading to reduced strength before freezing and thawing test but as well as leading to decrease the strength loss after five cycles of freezing and thawing. The lowest strength was obtained with an NaOH concentration of 8 M. Additionally, by increasing the concentration of NaOH, the dissolution of alumina and silicate from the source of aluminosilicate leads to more reaction finalization, which results increasing the freezing and thawing durability properties of pumice based geopolymer paste. Therefore, the authors recommended that higher molarity (NaOH concentration) of the alkaline activator solution can be used in order to improve the durability properties of pumice powder based geopolymer paste. Concerning the strength reductions, significant changes were observed before and after freezing and thawing cycles. The strength reduction after five cycles of freezing and thawing of specimens cured at 60 °C for 120 hours was 60% when the concentration was 12 M. However, the strength reduction was 39% when the concentration was 16M with the same curing condition and ages.

4.4.2. Effect of curing period on freezing and thawing resistance

Figure 4.22 to 4.24 illustrates the effect of curing period on the freezing and thawing resistance of geopolymer pastes at different curing temperatures (room temperature, 60 °C, 80 °C and 100 °C). As can be seen from Figure 4.22 to 4.24, the strength of geopolymer paste at 60 °C is proportionally increased with increased curing time. the maximum compressive strength after five cycles of freezing and thawing was obtained from the 16 molarity which were subjected at 60 °C for 120 hours. However, before conducting freezing and thawing the optimum compressive strength at 80 °C was obtained when cured for 72 rather than cured for 120 hours. But after five cycles of freezing and thawing the maximum compressive strength was obtained when the specimens cured for a maximum curing period (120 hours) as can be seen clearly in Figure 4.22 to 4.24. This may be attributed to the fact that most of the polymerizations

were completed after long periods of curing. Figure 4.24 shows that high strengths can be achieved with 72 hours of curing period at 100 $^{\circ}$ C. the strength of geopolymer paste decreases when cured at 100 $^{\circ}$ C for a longer curing period due to evaporate the solution before the geopolymerization was finished.



Figure 4.22. Effect of curing period on compressive strength after 5 cycles of freezing and thawing for 60 $^{\circ}$ C.





Figure 4.23. Effect of curing period on compressive strength after 5 cycles of freezing and thawing for 80 $^{\circ}$ C.

Figure 4.24. Effect of curing period on compressive strength after 5 cycles of freezing and thawing for 100 °C.

4.4.3. Effect of curing temperature on freezing and thawing resistance

Figure 4.25 to 4.28 illustrates the effects of curing temperature on the freezing and thawing resistance of pumice powder based geopolymer paste for the various curing periods from 24 to 120 hours. As can be seen from the figures, the strength reduction of geopolymer paste is significantly affected by curing temperature after performed the freezing and thawing test. The compressive strength of pumice powder based geopolymer pastes gradually increased when increasing curing temperatures. Increasing the temperature result to improve the reactivity between aluminosilicate materials and hence the number of molecular bonds and amorphous phases. Which led to more significant improvement in freezing and thawing durability property of geopolymer paste. The strength properties of geopolymer paste increases by 13%, after five cycles of freezing and thawing when with 16M concentration of NaOH cured at 100 °C for 24 hours. The strength results of some mixes exhibited an increase instead of decreasing. This is mainly related to the fact that the geopolymeric matrix is compact possesses a

good adherence degree which makes it resistant to the effect of freezing and thawing, in addition to that, it is expected that freeze-thaw cycles are responsible for a promotion process which happens to the matrix during these cycles. The matrix then yields better results in terms of strength properties.



Figure 4.25. Effect of curing temperature on compressive strength after 5 cycles of freezing and thawing for 24 hours.





Figure 4.26. Effect of curing temperature on compressive strength after 5 cycles of freezing and thawing for 48 hours.

Figure 4.27. Effect of curing temperature on compressive strength after 5 cycles of freezing and thawing for 72 hours.



Figure 4.28. Effect of curing temperature on compressive strength after 5 cycles of freezing and thawing for 120 hours.

4.4.5. Effect of fineness on freeze-thaw property

Figure 4.29 shows the effect of grinding time on compressive strength of geopolymer pastes after five cycles of freeze-thaw at the age of 7 days. The result indicates that increase the fineness of pumice powder has a significant affect the freezing and thawing resistance of geopolymer paste. When the grinding time increased from 4 to 8 hours, the compressive strength of geopolymer specimens at 60 °C for 120 hours (after five cycles of freezing and thawing) decreased by 18%. Although the strength reduction of specimens was 51% before freezing and thawing for the same curing conditions. When the geopolymer pastes cured at 30 °C for 120 hours was, the strength loss of 8-hours grinding time was 41% after five cycles. However, the strength loss was 61% for 4-hours grinding time in the same curing condition and freezing and thawing cycles as can be seen in Figure 4.29.



Figure 4.29. The effect of grinding time on compressive strength of geopolymer pastes after five cycles of freeze-thaw at age of 7 days.

4.5. Ultrasonic Pulse Velocity

Figure. 4.30 shows the correlation between compressive strength and ultrasonic pulse velocity (UPV). The relationship between the compressive strength and UPV values of all geopolymer specimens can be shown by an empirical exponential equation of $f_c = 1.0394e^{0.001(UPV)}$ The corresponding coefficients of determination (R²=0.73) indicates decent relevance between the data points of compressive strength and UPV.



Figure 4.30. The correlation between compressive strength and UPV values.

The correlation between the compressive strength after five cycles of freezethaw and ultrasonic pulse velocity shown in Figure 4.31. The relationship the between the compressive strength and UPV values of all geopolymer specimens can be shown by a power equation of $f_c = 7E-06UPV^2 - 0.015UPV + 4.8379$. The corresponding coefficients of determination ($R^2 = 0.86$) indicate decent relevance between data points of compressive strength and UPV.



Figure 4.31. The correlation between compressive strength and UPV values after 5 cycles of freezing and thawing.

4.6. Scanning Electron Microscopy (SEM).

The M12-120h-60C sample in Table 3.2, obtained the maximum compressive strength of 76.73 MPa when it was cured at 60 °C for 120 hours. Figure 32(a) to 32(c) compare the fracture behavior of the same geopolymer specimen concentration with different curing temperatures and curing times. Figure 32(a) illustrates a specimen which has been cured at ambient temperature and has a compressive strength of 27.31 MPa while Figure 32(b) shows a specimen with 120 h of curing at 60 °C with a compressive strength of 76.73 MPa. Figure 32(a) shows numerous pumice particles that have not yet reacted compared to the specimen shown in Figure 32(b) and (c). Figure 32(b) shows that the pumice particle paste is completely dissolved and has reacted with the activating solution, and it seems free of voids and is extremely dense. However, in Figure 32(c) the pumice particle paste is completely dissolved and has reacted with the activating solution due to a high curing temperature, there are several small cracks that could be related to shrinkage, which were created by the long curing time at a high temperature. Figure 32(c) shows that the pumice particles are close to each other which makes voids and several weak interfaces in the geopolymer paste that lead to easier fracture and lower strength.





Figure 4.32. The SEM micrograph of geopolymer specimens a). M12-Room temperature, (b). M12-120h-60°C, (c). M12-24h-80°C.



Figure 4.33. The SEM micrograph of geopolymer pastes (a). M12-Room temperature, (b). M12-120h-60°C, (c). M12-72h-80°C, (d). M12-24h-100°C

Figure 4.33 presents the SEM micrograph (500x) at various stages of curing temperature and durations. The glassy phase formation seemed to increase with increased curing temperatures. The geopolymer specimen at room temperature curing, which shows in Figure 4.33(a), appears more porous rather than be denser matrixes, because of unreacted particles and voids. On the other hand, for the geopolymer pastes shown in Figure 4.33(b), curing at 60 °C for a long duration gave the desired strength, due to a well-connected structure. Increasing the cured temperature from 80 °C to 100 °C localized several voids which decreased the geopolymer strength as present in Figure 4.33(c) and (d).

Figure 4.34(a) to (f) presents the SEM micrograph (10 k x) of the geopolymer paste specimens after five cycles of freezing and thawing in different curing temperature and durations. The glassy phase formation seemed to increase with increased curing temperatures. The geopolymer specimen at room temperature curing, which shows in Figure 4.34(a), appears more porous rather than be denser matrixes, because of unreacted particles and voids. When the samples cured at ambient temperature the water within the solution remains, in the freezing period the volume of water increase, increase the volume of water result in increasing the pore sizes. On the other hand, for the geopolymer pastes shown in Figure 4.34(b), curing at 60 °C for a long duration gave the desired strength, due to a well-connected structure and less pores. Increasing the cured temperature from 80 °C to 100 °C improve the freezing and thawing resistance. Also as increasing the curing period the strength loss was decreased the geopolymer strength as present in Figure 4.34(c), (d) and 17 (e) and (f).



Figure 4.34 The SEM micrograph of geopolymer specimens a). M12-Room temperature, (b). M12-120h-60 °C, (c). M12-24h-80 °C, (d). M12-72h-80 °C, (e). M12-24h-100 °C, (f). M12-48h-100 °C.

4.7. Application and Limitation of Geopolymer

Geopolymer technology can be potentially used for precast applications due to controlling the environment required for this production. Also geopolymer concrete can use in other applications such as bricks, precast pipes, and pavers. Although last 20 years, the geopolymer technology has been extremely investigated and tried to use in practical applications, there are still some limitations:

- There is not a standard specification and mix design process for geopolymer concerts. Because there are many parameters that affect the mix design such as source material type, concentrations of activator, activator types, alkali to binder ratio and curing conditions.
- 2. Many base materials can be used as the binder, which has a different combination of chemical compositions such as natural Pozzolans, by-products, and waste powders.
- 3. The cost of the alkaline solution is high.
- 4. During the dissolution of NaOH in water a major heat releases, in a large-scale application will be difficult to control.
- 5. The use of high alkalinity as activator solution is hazardous, and there are many safety risks of people handling mixtures.
- The control of fresh mixture is still lack. There are no substantial admixtures to progress the properties of geopolymer concrete such as superplasticizer and shrinkage reducer etc.
- 7. The quality of geopolymer concretes, which produced in the low ambient condition is poor.
- 8. There are many practical difficulties challenges in applying high temperature curing procedures to obtain appropriate mechanical and durability properties in the real applications, mainly in cast-in-situ constructions.
- 9. The demand for uses this product in place of cement is still limited.


5. CONCLUSION AND RECOMMENDATIONS

The test results indicated that compressive strength is extremely closely related to sodium hydroxide (NaOH) concentration. The compressive strength of geopolymer paste increased as the NaOH concentration was increased from 8M to 12M. A further increase in NaOH concentration from 12M to 18M result in decline of the compressive strength of the geopolymer paste. Moreover, the results demonstrated that curing temperature was one of the most practical factors in the compressive strength during heat of low temperature and long duration of heat curing. The compressive and flexural strength during temperature and long duration of heat curing the curing temperature up to 60 °C, and it decreased when the temperature increased to 80 °C and 100 °C. An increase in curing temperature from 60 °C to 80 °C led to a decrease in compressive strength from 76.73 to 64.28 MPa with the same concentration and curing time. The results in this investigation confirm that to achieve high compressive and flexural strength an optimum curing period is 120 h at 60 °C.

The result indicates that increase in the fineness of pumice powder has a significant affect the freezing and thawing resistance of geopolymer paste. When the grinding time increased from 4 to 8 hours, the compressive strength of geopolymer specimens decreased by 18% when cured at 60 °C for 120 hours (after five cycles of freezing and thawing).

The test results reported that the compressive strength of geopolymer paste increases by increasing the concentration of NaOH up to certain molarity. The compressive strength of geopolymer paste after freezing and thawing test increases by increasing the NaOH concentration from 8M to 16M; however, it decreases with the further increase in NaOH concentration from 16M to 18M. The strength reduction after five cycles of freezing and thawing of specimens cured at 60 oC for 120 hours was 60% when the concentration was 12 M. However, the strength reduction was 39% when the concentration was 16M with the same curing condition and ages.

After five cycles of freezing and thawing the maximum compressive strength was obtained when the specimens cured for a maximum curing period (120 hours).

However, the highest strength can be achieved with 72 hours of curing period when the specimens cured at 100 $^{\circ}$ C. The strength of geopolymer paste decreases when cured at 100 $^{\circ}$ C for a longer curing period due to evaporate the solution before the geopolymerization was finished.

The strength properties of geopolymer paste increases by 13%, after five cycles of freezing and thawing when with 16M concentration of NaOH cured at 100 oC for 24 hours. The strength results of some mixes exhibited an increase instead of decreasing.

The result indicates that increase the fineness of pumice powder has a significant affect the freezing and thawing resistance of geopolymer paste. When the grinding time increased from 4 to 8 hours, the compressive strength of geopolymer specimens at 60 oC for 120 hours (after five cycles of freezing and thawing) decreased by 18%. Although the strength reduction of specimens was 51% before freezing and thawing for the same curing conditions.

The SEM results revealed that some pumice particles did not reacted at room temperature which led to easier fractures and lower strength. The glassy phase formation seemed to increase with increased curing temperatures. The geopolymer specimen cured at room temperature, appears more porous rather than be denser matrixes, because of unreacted particles and voids. On the other hand, for the geopolymer pastes cured at 60 °C for a long duration gave the desired strength, due to a well-connected structure.

The present study was focused on the influences of pumice powder, alkaline activator concentration, curing temperature and duration time on strength and freezing-thawing properties of geopolymer pastes. The results were found in this study, clearly show the achievements of the study, but several test and parameters are recommended by another for the future investigations, the recommendations for the further researches are summarized as follows:

- 1. Study the effect of those parameters on mortar and concrete pumice based geopolymers.
- 2. Study the effect of activator concentration on fresh properties such as workability, setting, and consistency of geopolymers.

- 3. The shrinkage, water permeability, exposure to seawater, sulphates acids, chloride penetration and must be studied.
- 4. Future studies should focus on most suitable mix design for pumice based geopolymer concretes, rather than focusing on the possibility of using pumice as source material and study the different parameters affecting on the strength and durability characteristics to be achieved standard mix design all over the world.
- 5. Study the effect of additional water and the different type and percentage of admixture or superplasticizers to improve the fresh properties of geopolymer products.
- 6. Add lime, nano-silica or some other sources into pumice powder in order to improve the durability and as well as the strength of geopolymer products which is expected to create.
- 7. Study the economic and environmental analysis of pumice based geopolymer paste, mortar and concretes and made a comparison with ordinary Portland cement concrete.
- 8. Prepare the pumice based geopolymer concrete on a big scale beam and columns rather than in the laboratory scale due to low and more extensive accessibility of this source material in Turkey. Which result to increase the application of pumice based geopolymer concretes.



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APPENDIX 1. EXTRA FIGURES OF FREEZING AND THAWING



The relationship between curing period and compressive strength at different curing temperature after 5 cycles of freezing and thawing for 8M on the age of 28 days.



The relationship between curing period and compressive strength at different curing temperature after 5 cycles of freezing and thawing for 10M on the age of 28 days.



The relationship between curing period and compressive strength at different curing temperature after 5 cycles of freezing and thawing for 12M on the age of 28 days.



The relationship between curing period and compressive strength at different curing temperature after 5 cycles of freezing and thawing for 14M on the age of 28 days.



The relationship between curing period and compressive strength at different curing temperature after 5 cycles of freezing and thawing for 16M on the age of 28 days.



(a) 18 M

The relationship between curing period and compressive strength at different curing temperature after 5 cycles of freezing and thawing for 18M on the age of 28 days.

APPENDIX 2. PREPARATION OF SOLUTION AND MIXTURES



Preparing solution



Preparing mixes

APPENDIX 3. EXTENDED TURKISH SUMMARY (GENİŞLETİLMİŞ TÜRKÇE ÖZET)

1. GİRİŞ

Beton dünya çapında en yaygın kullanılan yapı malzemesidir. Bununla birlikte, Portland çimentosu üretimi, yüksek enerji tüketimi ve yüksek CO₂ ve diğer sera gazı emisyonları gibi bazı büyük dezavantajlara sahiptir (Bosoaga ve diğerleri, 2009; Habert ve diğerleri, 2010; Hasanbeigi ve diğerleri, 2012). Altyapı ve sanayileşmedeki büyük artış nedeniyle çimento üretimi önemli ölçüde artmıştır (Habert ve ark. 2010). Portland çimentosu kullanımını kısaltmak için ilave çimento esaslı malzemelerin kullanılması ve Portland cimentosu alternatiflerinin aranması gibi betonda Portland cimentosu kullanımını en aza indirmek için birkaç girişimde bulunulmuştur. Bu bakımdan jeopolimer beton, Portland cimentosu kullanmadan beton üretmenin yenilikçi bir yoludur (Davidovits, 1993; Habert ve diğerleri, 2011). 1978'de Joseph Davidovits, sürdürülebilir bir malzeme olarak değerlendirilen jeopolimer betonu üretmek için silika ve alumina bakımından zengin kaynakların alkali ile aktive edilmiş bir çözelti (örneğin, sodyum silikat ve sodyum hidroksitin yeterli kombinasyonları gibi) ile bir geopolimerik reaksiyonunu kullandı. Pomzanın, silis ve alumina bakımından zengin, puzolanik özelliklere sahip volkanik bir malzeme olması, jeopolimer beton üretmek için kaynak malzeme olarak kullanılmasını mümkün kılar. Üstelik Doğu Anadolu'da büyük hacimlerde kolaylıkla elde edilebiliyor olması, pomza tozu kullanımı ile sürdürülebilir ve ekonomik jeopolimer betonun geliştirilmesini mümkün kılabilir (Tapan ve ark., 2013; Kabay ve ark., 2015). Geopolimer beton üretiminde pomza tozu bir bağlayıcı olarak kullanıldığında, ısı kürü ile yüksek erken mukavemetli jeopolimer ürünler elde edilebilir. Dolayısıyla, tez kapsamında yapılan bu çalışma ile pomza tozu kullanılarak üretilen geopolimer betonların alkali aktivatör konsantrasyonunun, ısıl kür sıcaklığının ve kürlenme sürelerinin bu betonların mekanik ve fiziksel dayanımları üzerindeki etkileri araştırılmış; pomza tozu inceliği, farklı sodyum hidroksit konsantrasyonu, kürlenme sıcaklığı ve kürlenme süresinin, pomza tozu ile üretilen jeopolimer betonların dayanım ve donma ve çözülme dayanıklılık özelliklerine etkileri belirlenmiştir.

2. KAYNAK BİLDİRİŞİ

Bir ton çimento üretimi için 3 ila 4 Giga-joule enerji gerekir ve iklim değişikliğine neden olan sera gazlarından biri olan yaklaşık bir ton CO₂ salınır (Khurana ve diğerleri, 2002; Engin ve Ari, 2005; Amiri ve Vaseghi, 2015). Çimento üretimi, dünyadaki yaklaşık %5 karbon dioksit emisyonunun serbest bırakılmasından sorumludur (Huntzinger ve Eatmon, 2009). Bununla birlikte, Portland çimentosu talebi, 2010'dan 2050'ye kadar neredeyse %200 oranında artmıştır (Taylor ve ark. 2006). Jeopolimerde CO₂ gazı emisyonu Portland çimentosundan yaklaşık% 80 daha azdır (Duxson ve ark. 2007). Geçtiğimiz yıllarda, farklı uygulamalarda jeopolimer betonlarının dozajını arttırmak için jeopolimer kimyasına ve mikroyapısal büyümeye odaklanan önemli çalışmalar yapılmıştır.

Jeopolimer beton üretimi ile ilgili çok çeşitli araştırma çalışmaları yayınlanmıştır. Alkali cüruf kombinasyonundaki ilk gelişme 1940 yılında Purdon tarafından yapılmıştır (Pacheco-Torgal ve ark., 2008). Purdon bir bağlayıcı olarak Granüle Yüksek Fırın Cürufu (GYFC)'yi ve alkalin çözelti aktivatörü olarak da NaOH'i kullanmıştır. Jeopolimerin gelişimi sırasında, Alkali-cüruf, toprak çimentosu, alkali aktif ve jeopolimer gibi birkaç terminoloji kullanılmıştır. 1957'de Glukhovsky, düşük kalsiyum alüminosilikatların alkalin aktivasyonunu araştırarak elde ettiği bağlayıcıyı "alkali çimento" olarak adlandırmıştır. Victor Glukhovsky, kayalar ve kil minerallerinin alkali çözelti sırasında sodyum alümino-silikat hidratlara (zeolitler) tepki gösterdiğini ve bu teknikle yapılan ve "toprak silikat betonu" olarak adlandırılan ve "toprak çimentosu" bağlayıcıları olarak adlandırılan betona atıfta bulunduğunu bildirmiştir (Starchevskaya, 1967). 1978'de Davidovits, üç boyutlu (3D) siliko-alüminat materyaller (bundan kaynaklanan mineral polimerler) için ve bunların hidrotermal sentezleri bakımından organik polimerlerin yoğunlaşması ile benzerliklerinden dolayı jeopolimer terimini icat etti (J. Davidovits, 1991a; Joseph Davidovits, 2011). 1982'de Davidovits, alkalileri kaolinit, kalker ve dolomit ile karıştırarak bağlayıcılar geliştirdi.

2005 yılında Fernández-Jiménez ve ark. (2005), jeopolimer betonlarının mikroyapı ve morfolojik gelişimlerini izlemek için alkali aktif uçucu kül çimentosunun morfolojisi üzerinde çalıştı. Parçacık büyüklüğü dağılımının, uçucu kül mineral

bileşiminin ve aktivatör konsantrasyonunun ve türlerinin jeopolimer betonlarının mikroyapısal özellikleri üzerindeki etkilerini araştırdılar (Fernández-Jiménez ve diğerleri, 2005).

3. MATERYAL VE YÖNTEM

3.1. Materyal

3.1.1 Pomza Tozu

Bu araştırmada kullanılan ham pomza, Van, Erciş'te bulunan bir maden ocağından alınmıştır. Pomza tozu inceliğinin geopolimer betonun dayanım ve dayanıklılık üzerindeki etkilerinin belirlenebilmesi için, pomza agregasının boyutu laboratuarda bulunan çeneli kırıcıda kırılarak küçültülmüş, sonrasında bilyalı değirmende öğütülerek (4 saat, 6 saat ve 8 saat) farklı inceliklerde pomza tozu elde edilmiştir.

3.1.2. Alkali Aktivatör

Bu araştırmada sodyum silikat (Na₂SiO₃) ve sodyum hidroksit (NaOH) çözeltisinin bir kombinasyonu alkali aktivatör olarak kullanılmıştır. Sodyum hidroksit çözeltisi, potasyum hidroksite göre daha düşük maliyetli olduğu için seçildi. Bir çözeltideki NaOH parçalarının kütlesi, molarite (8, 10, 12, 14, 16 ve 18 M) cinsinden çözeltinin arzu edilen konsantrasyonuna bağlı olarak değişmiştir. Sodyum silikatın sodyum hidroksite kütlece oranı tüm karışımlar için 2.5 olarak alınmıştır. Sodyum silikat ve sodyum hidroksit çözeltisi, laboratuar tipi karıştırma ekipmanı kullanılarak karıştırıldıktan sonra, alkalin sıvı karışımı 24 saat bekletme süresine tabi tutuldu ve daha sonra jeopolimer beton numunelerinin hazırlanmasında kullanıldı.

3.2. Yöntem

3.2.1. Numune Hazırlama ve Numunelerin Kürlenmesi

Farklı sodyum hidroksit konsantrasyonlarına sahip altı karışım (8, 10, 12, 14, 16 ve 18 molarite) hazırlandı. Uygun maliyetli ve uygulanabilir bir jeopolimer beton elde etmek için tüm karışımlar için 0.35'lik sabit bir alkali-bağlayıcı (A / B) oranı kullanılmıştır. Beton numuneleri, dökümden sonra, 24 saatlik bir dinlenme süresi boyunca ortam sıcaklığında tutulduktan sonra kür sıcaklığının ve kür süresinin geopolimer betonların dayanım ve dayanıklılık üzerindeki etkilerini belirleyebilmek için ısıl kür işlemine tabi tutulmuştur. Ortam sıcaklığında 24 saatlik bir dinlenme süresinden sonra, tüm numuneler farklı sertleşme sıcaklıklarında (ortam sıcaklığı, 60 oC, 80 oC ve 100 oC) kuru bir firinda bekletilmiştir. Beton örnekleri 24, 48, 72 ve 120 saatlik farklı kürlenme sürelerine maruz bırakılarak tüm numuneler test süreleri doluncaya kadar oda sıcaklığında tutulmuştur.

4. BULGULAR VE TARTIŞMA

4.1. Basınç Dayanımı

Jeopolimer betonda yüksek NaOH konsantrasyonunun kullanılması, pomza taneciklerinin daha yüksek çözünmesine yol açarak daha yüksek basınç dayanımlarına neden olan jeopolimerizasyon reaksiyonunu arttırma eğilimindedir. Test sonuçları incelendiğinde, NaOH konsantrasyonunun belirli molariteye kadar yükseltilmesinin, jeopolimer betonunun basınç dayanımını arttırdığını göstermektedir. Jeopolimer betonunun basınç dayanımı, NaOH konsantrasyonunun 8M'den 12M'ye yükseltilmesiyle artmış, 12M'den 18M'ye arttırılması ile azalmıştır. Bunun nedeni, çok miktarda hidroksit iyonunun çok erken aşamalarda alüminosilikat jel çökelmesine neden olması ile jeopolimerizasyonun engellenmesinin basınç dayanımlarının azalmasına sebep olması ile açıklanabilir (Lee ve Van Deventer, 2002; Yip ve diğerleri, 2008; Chithambaram et et al., 2019). En ivi basınç dayanımı 60 °C'de 120 saat firinda kürlenmeye maruz kalan 12 molarite numunede elde edilmiştir. Bu araştırmadan elde edilen bulgular değerlendirildiğinde, pomza tozu bazlı jeopolimer betonlar için optimum kürlenme süresinin 60 °C'de 120 saat olduğu anlaşılmaktadır. Oda sıcaklığında kürlenen jeopolimer betonların basınç dayanımlarının çok düşük olduğu ve kürlenme süresi

arttıkça basınç dayanım artışının çok az olduğu tespit edilmiştir. Bu çalışmanın sonuçları, yüksek kürlenme sıcaklığının kullanılmasıyla erken yüksek dayanım gelişiminin sağlanabileceğini göstermektedir (100 oC'de 24 saat kürlenme sonrasında 59 MPa elde edilmiştir).

4.2. Eğilme Dayanımı

Sonuçlar, NaOH konsantrasyonunun 8M'den 12M'ye arttırılması ile pomza tozu ile üretilmiş jeopolimer betonun eğilme mukavemetinin arttığını göstermektedir. Bununla birlikte, NaOH konsantrasyonu 14M'nin üstüne çıkarıldığında, eğilme mukavemetinde önemli bir azalma gözlenmiştir. Bu bulgu daha önce yayınlanmış araştırmalarla uyumludur (Atiş ve ark., 2015). Basınç mukavemetinde olduğu gibi, konsantrasyon 12M olduğunda, 60 °C'de 120 saat kürlenme ile en iyi eğilme mukavemeti elde edilmiştir.

4.2. Pomza Tozu İnceliğinin Dayanım Üzerindeki Etkileri

Bu çalışmada üç farklı incelikte pomza tozu kullanılmıştır. Ponza tozu inceliğinin arttırılması, 60° C'de kürlenmiş jeopolimer beton örneklerinin basınç dayanımının azalmasına neden olmuştur. Sathonsaowaphak ve ark. (2009) ve Jamkar ve ark. (2015), incelik seviyesinin arttırılmasının, kaynak malzeme parçacıkları içindeki gözenekleri azalttığı için basınç dayanımını arttırdığı sonucunu bildirmesine ragmen; ponza tozunun inceliğinin arttırılmasının, yüzey alanını arttırdığı ve daha fazla alkalin aktivatörünü gerektirdiği ve sonuç olarak ponza tozunun inceliğinin arttırılmasının kaynak malzemenin doğasını ve reaksiyon davranışını değiştirdiği gözlemlenmiştir.

4.4. Donma-Çözünme Dayanımı

Donma-çözülmenin jeopolimer beton örneklerinin dayanımları üzerindeki etkilerini belirlemek amacıyla üretilen numuneler 5 defa donma-çözünme çevrimine tabi tutulmuştur. Jeopolimerlerin dayanıklılık özellikleri birçok faktörden etkilenir. Donma ve çözülme testinden sonra jeopolimer betonların basınç dayanımı, NaOH

8M'den konsantrasyonunu 16M'ye yükseldiğinde artmis: ancak. NaOH konsantrasyonunda 16M'den 18M'ye yükselme ile azalmıştır. Bunun nedeni, çok miktarda hidroksit iyonunun cok erken asamalarda alüminosilikat jel cökmesine neden olması ve ardından jeopolimerizasyonun engellenmesinin olabileceği düsünülmektedir. Bes donma ve çözünme döngüsünden sonraki en düşük basınç dayanım kaybı 120 saat kürlenmeye tabi tutulan numunelerde görülmüstür. Bazı karısımların basınc dayanımları donma-çözünme döngüsünden sonra azalmak yerine artmıştır. Pomza tozu inceliğinin arttırılmasının jeopolimer betonunun donma ve çözülme direncini önemli ölçüde etkilediği görülmüştür. Öğütme süresi 8 saate arttırıldığında, 120 °C'de 120 saat kürlenen jeopolimer betonların basınç dayanımları (beş donma ve çözülme döngüsünden sonra) % 18 oranında azalmıştır.

5. SONUÇLAR

Test sonuçları, basınç dayanımının sodyum hidroksit (NaOH) konsantrasyonuyla son derece yakından ilişkili olduğunu göstermiştir. Jeopolimer betonunun basınç dayanımı, NaOH konsantrasyonu 8M'den 12M'ye çıkarıldıkça artmıştır. NaOH konsantrasyonunda 12M'den 18M'ye arttırılması, jeopolimer betonların basınç dayanımının düşmesine neden olmuştur. Kürlenme sıcaklığının, jeopolimerin basınç dayanımında en önemli faktörlerden biri olduğu tespit edilmiştir. Jeopolimer betonu, düşük sıcaklıktaki ısınma ve uzun süreli ısı kürlemesi sırasında yüksek basınç ve eğilme dayanımı kazanmış, jeopolimer betonunun basınç ve eğilme mukavemeti, kürleme sıcaklığının 60 °C'ye yükseltilmesiyle arttırılmış ve sıcaklık 80 °C ve 100 °C'ye yükseltildiğinde ise azalmıştır. Sertleşme sıcaklığındaki 60 °C'den 80 °C'ye arttırılması, aynı konsantrasyon ve kürlenme süresinde basınç dayanımının 76.73'ten 64.28 MPa'ya düşmesine neden olmuştur. Bu araştırmadaki sonuçlar, yüksek basınç ve eğilme mukavemeti elde etmek için optimum kürlenme sıcaklığının ve süresinin 60 °C'de 120 saat olduğunu doğrulamaktadır.

CURRICULUM VITAE

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