T.C.

ERCIYES UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCE

DEPARTMENT OF CIVIL ENGINEERING

INVESTIGATION OF DURABILITY PROPERTIES OF
GEOPOLYMER CONTAINING METAKAOLIN

Ph.D. Thesis

By

Zainab Hataf Naji AL-AZZAWI

Supervisor

Professor Dr. Okan KARAHAN

Assistant Professor Dr. İsmail İsa ATABEY

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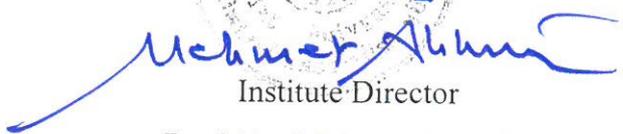
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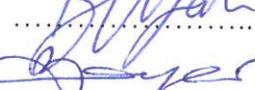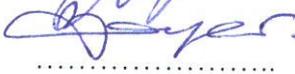
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ABSTRACT

A laboratory study was carried out to prepare and evaluate the properties of Portland cement equivalent geopolymer mixture made with fly ash and metakaolin cured in air conditions at ambient temperature. Fly ash was used as main binding material for geopolymer mortar mixture, and metakaolin was used as a replacement material at different ratios. Properties of mortars, including unit weight and density, flow workability, flexural strength, compressive strength, ultrasonic pulse velocity, water absorption and porosity, sorptivity, wetting-drying, freezing-thawing, rapid choloride ion penetration, drying shrinkage, abrasion resistance, high temperature resistance and accelerated corrosion tests were conducted. Metakaolin was replaced with fly ash in mass basis, replacement dosages of 0%, 10%, 20%, 30%, 40%, and 50%. Geopolymer mortars were produced with river sand, class F fly ash, metakaolin, metasilicate, and water. Metasilicate was used at 10% Na^+ concentration as an alkali activator. Also, standard Portland cement mortar was produced for comparison. Water-binder and sand-binder ratios were 0.50 and 3.0, respectively. Prismatic, cubic and cylinders samples were prepared in dimension of 40×40×160 mm^3, 71×71×71 mm^3, Ø100× 200mm respectively. Geopolymer samples were cast and cured at 20±1°C with 50±10% relative humidity in air curing until testing. Compressive and flexural strengths were measured at 3, 7, 28, 90, and 180 days, other tests were examined at 28 days of age. Drying shrinkage was measured until 360 days. The results showed that the compressive and flexural strengths of geopolymer mortar were improved with metakaolin replacement. Only fly ash geopolymer mixture developed 15.1 MPa compressive strength, while a mixture containing highest (50% replacement ratio) amount of metakaolin gave highest (60.2 MPa) compressive strength at 28 days under air curing. Similarly, metakaolin

replacement with fly ash improved other properties of geopolymer like: ultrasonic pulse velocity, abrasion and high temperature resistance, and drying shrinkage and other properties. Based on laboratory results, utilization of metakaolin in fly ash based geopolymer eliminated the necessity of heat curing for geopolymer synthesis.

Key words; Fly ash, metakaolin, air curing, geopolymer, strength

METAKAOLIN İÇEREN GEOPOLIMERIN DURABILITE ÖZELLIKLERININ ARAŞTIRILMASI

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ÖZET

Uçucu kül ve metakaolin ile hazırlanan Portland çimentosuna eşdeğer dayanıma sahip geopolimer karışımların oda sıcaklığı kür koşullarındaki özelliklerinin belirlenmesi için laboratuvar çalışması gerçekleştirilmiştir. Geopolimer harç karışımında uçucu kül bağlayıcı olarak seçilmiş ve farklı oranlarda metakaolin ile yer değişimi yaparak kullanılmıştır. Harçların özelliklerini belirlemek için birim ağırlık ve yoğunluk, işlenebilirlik, eğilme dayanımı, basınç dayanımı, ultrasonik ses hızı, su emme ve boşluk oranı, kılcal su emme, ıslanma-kuruma, donma-çözülme, hızlı klor geçirimliliği, kuruma büzülmesi, aşınma direnci, yüksek sıcaklığa dayanıklılık ve hızlandırılmış korozyon deneyleri gerçekleştirilmiştir. Metakaolin uçucu kül ile ağırlıkça 0%, 10%, 20%, 30%, 40%, ve 50% oranlarında yer değiştirerek kullanılmıştır. Geopolimer harçlar kum, F sınıfı uçucu kül, metakaolin, sodyum metasilikat ve su ile üretilmiştir. Metasilikat alkali aktivatör olarak %10 Na oranında kullanılmıştır. Aynı zamanda Portland çimentolu harçlar kontrol numunesi olarak üretilmiştir. Su-bağlayıcı oranı 0.50 ve kum-bağlayıcı oranı 3.0 seçilmiştir. Numuneler $40 \times 40 \times 160$ mm^3 prizmatik, $71 \times 71 \times 71$ mm^3 küp ve $\emptyset 100 \times 200$ mm silindir kalıplarda hazırlanmıştır. Geopolimer numuneler 20 ± 1°C ortam sıcaklığında ve $50 \pm 10\%$ bağıl nemde hazırlanıp test zamanına kadar havada kür edilmiştir. Basınç ve eğilme dayanımı deneyleri 3, 7, 28, 90 ve 180 günlük, durabilite deneyleri ise 28 günlük numunelere uygulanmıştır. Kuruma büzülmesi numunlerine 360 günlük okuma yapıldı. Elde edilen sonuçlara göre, metakaolinin uçucu kül ile yer değişimi yapması basınç ve eğilme dayanımı özelliklerini iyileştirmiştir. 28 gün havada kür sonucu, uçucu küllü geopolimer harçları

15.1 MPa basınç dayanıma ulaşırken en fazla ağırlıkça metakaolin değişiminde (%50 oranında) en yüksek basınç dayanıma (60.2 MPa) ulaşılmıştır. Benzer şekilde uçucu külün metakaolin ile yer değişimi ultrases hızı, aşınma direnci, yüksek sıcaklığa dayanıklılık ve kuruma büzülmesi gibi diğer özellikleri de iyileştirmiştir. Laboratuvarda elde edilen sonuçlara göre uçucu külün metakaolin ile yer değiştirmesi sonucu uçucu küllü geopolimer sentezi için ısıl kül ihtiyacını ortadan kaldırmıştır.

Anahtar kelimeler: Uçucu kül, metakaolin, hava kürü, geopolimer, dayanım.

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INTRODUCTION

The vital and significant element for the production of concrete is the Portland cement. Due to its different advantageous characteristics such as high temperature resistance, molding, and flexibility in shipping, it becomes one of the most popular construction materials around the globe. However, the major problems in the cement industry are the requirement of vast energy [1, 2] and emission of CO_2 [3, 4]. Several studies have been conducted to develop an alternative method and materials to generate new types of cementitious materials in order to overcome these problems. Geopolymer which is an environmentally friendly new type of inorganic binder that can be obtained from alkali-activated aluminosilicate materials was first developed by Davidovits [5].

Although the production of a geopolymer requires less energy and exhibits lower CO_2 during the production stages, it showed comparable durability and mechanical properties characteristics as that of Portland cement [6]. It is important to note that researchers are also attracted by the nature that is helpful for re-using quantities of waste materials [7].

Geopolymer has similar or even better characteristics, including excellent high temperature resistance, good resistance to chemical attack low permeability, and high early compressive strength compared to ordinary Portland cement, [8-11]. This is based on polycondensation reaction of three-dimensional networks of a geopolymer [12]. It has been found that aluminosilicate and other industrial by-products are suitable materials for the production of a geopolymer.

The last decades, fly ash-based geopolymer has been extensively studied to identify their nature and characteristics [13-16]. The results obtained from these studies showed that Fly ash geopolymer exhibited higher durability and mechanical properties and was suitable for making geopolymer.

In addition, other material called metakaolin has also been investigated extensively to identify their suitability in producing geopolymer and was also proven that it is highly

suitable for producing geopolymer materials with acceptable durability and mechanical properties [17-20].

Turkey is an important part of energy policy in the form of solid fuel for energy production based on thermal power plants operated by the coal fire. As a result of coal burning, a waste material called fly ash is produced. This fly ash can be used as a pozzolanic material is exposed by the combustion of pulverized coal in thermal plants. The waste product from the chimney is obtained by various methods. It is uncomfortable to leave it to the environment because it creates environmental problems. Energy Market Regulatory Authority (EMRA) according to the 2015 electricity market development report, the rate of total coal utilization in Turkey is 28%. [21].

Using fly ash for synthesizing geopolymers crucial to lower costs and protect the environment [22]. Kaolin is a non-renewable resource and the natural reaction product of clay. On the other hand, coal-based thermal power plants, fly ash are produced as a by-product [23]. That said, the fly ash had recently come into fashion as a widely used original material to produce geopolymer materials. Several important factors could alter the properties of geopolymers based on fly ash. These factors are the solution used as the alkali activator, curing time, its curing temperature, and ash's particle [24].

It is important to note that approximately 600 million tons of fly ash is produced in the coal-based thermal power plants as waste materials globally each year. Even though between 75 and 80 percent of the waste is fly ash (500 million tons), only around 20 to 30 percent is used as a fill material when making concrete [25].

Modern developments have greatly improved the use of fly ash in geopolymers because it is easy to use and handle in production and it can greatly improve the final product's durability [26]. Still, because not all fly ash contains high reactivity, it with a low reactivity can be used with other geopolymer precursors in securing desired strength [22].

Metakaolin (calcined kaolin) has high purity and reactivity and typically for the other materials. On the other hand, it was also revealed that metakaolin leads to synthesize geopolymers containing low permeability [27] and high resistance [28]. Yet, according to Provis et al. [29], emphasized that considerable water demand caused problems in metakaolin-based geopolymer mixtures.

Fly ash is widely utilized and regarded as the most convenient resource which is compatible with the concrete application as it supplies a large amount of raw material

across the world, obtained through coal-fired electricity production as a result of its largest proportion of commercial use and the potency to diminish the CO_2 footprint [30]. About metakaolin, it expedites the primary configuration and enhances the transport and mechanical features; particularly it can render high compressive resistance of cementitious substances early as it provides the finer particles' filling effect and high pozzolanic reactivity [31, 32].

The microstructure, properties of fly ash geopolymers have been investigated by several studies researchers under different synthesizing conditions [33-36]. However, the option for the substitution of metakaolin by fly ash in the metakaolin-based geopolymer has not been investigated properly [22].

In this thesis, we were studying the effect of metakaolin on the mechanical properties and durability properties of fly ash-metakaolin based geopolymers. In the current study, we used fly ash, which is categorized as F and supplied by Çatalagzi thermal power plants in Turkey. Metakaolin was obtained by OTS İnşaat Ltd. Şti Turkey. We took 6 types of metakaolin dosages (0%, 10%, 20%, 30%, 40%, and 50%) besides we cast Portland cement mortar. According to the compressive strength, which is normally tested in 3, 7, 28, 90, and 180 days, the optimum improvement in strength had been obtained at 28 days. Therefore, durability properties were tested in our sample at 28 days.

The aim of the current study was to;

a. Production of a geopolymer without any need to heat curing.

b. Find out a geopolymer can applied in the site without the need to heat or any type of curing.

c. Investigate the effect of replacement of fly ash by metakaolin on the mechanical properties and durability of geopolymers.

d. Attempt to the cement consumption that will lead to reducing emissions CO_2 to the environment by producing geopolymers with using waste materials.

CHAPTER ONE

GENERAL INFORMATION AND LITERATURE STUDY

The cement sector has an important share in the economic indicators of the countries. However, cement production has negative effects such as environmental impact and production cost. These and other reasons make the need for a new binder other than cement interesting. For this reason, it is possible to produce a non-cement binder using alkali activators from amorphous materials containing Al_2O_3, SiO_2 and CaO in its structure such as fly ash, floor ash, and blast furnace slag. The reaction of aluminosilicate fly ash with activators produces amorphous inorganic polymers called geopolymers, while the reaction of blast furnace slag produces hydrated calcium silicate similar to calcium silicate hydrate (C-S-H) gel [37].

Two major disadvantages of cement production are CO_2 emissions and high energy costs. The highest cement production in the world compared to the population of the countries is made in China [38] as we show in Figure 1.1. In the coming years, a significant increase will be seen in the CO_2 emission into the atmosphere (Figure 1.2). Besides, fuel use in the high cost item in the cement sector (Figure 1.2) is another important problem of production [39].
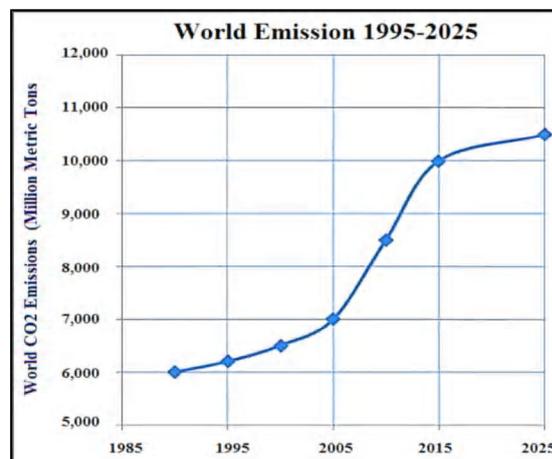
Figure1.1 World CO_2 emission [40]
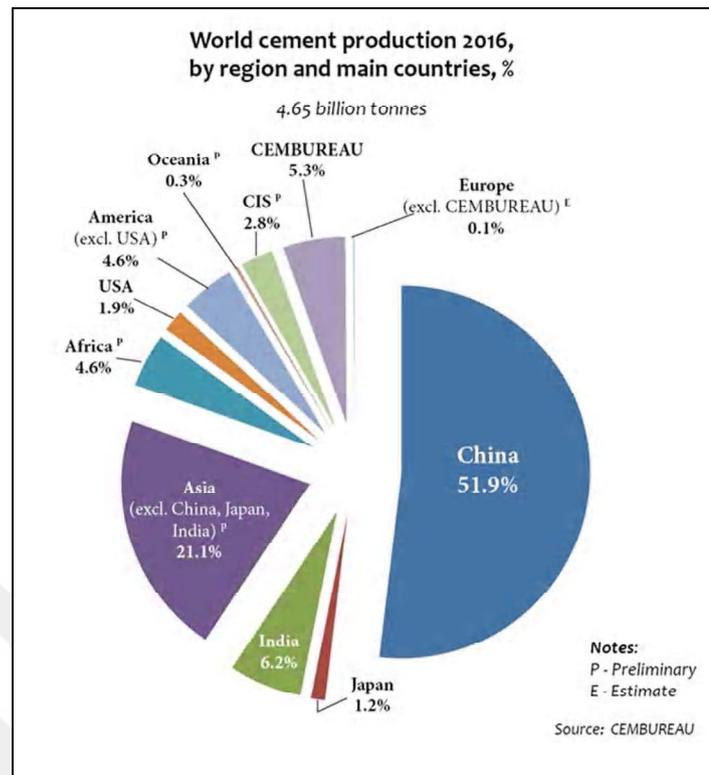
Figure1.2 The production cement in the world in 2016 [41]

Geopolymers, are a family of alkali activated aluminosilicate materials, has obtained worldwide interests in the last two decades, due to the major driver of promising a sustainable alternative to cement [8, 42, 43]. Precursors used in geopolymers production include calcined clay and different Si- and Al-containing industrial byproducts [44-47], among which metakaolin has higher reactivity and chemical consistency than the others, and has possibility to synthesis good thermal resistance [48] and low permeability geopolymers [49,50]. Whilst, well drawbacks in the MK-based geopolymers. Metakaolin particles have a high specific surface area that is leading to excessive mixing water demand [29]. Furthermore, the high water/binder ratio will lead to apparent deleterious effects on the micro-structure, durability and efflorescence of the mixture geopolymer products [49, 29].

Fly ash is a waste material and has become one of the main materials in the production of geopolymers [25]. Its spherical particles could work like ''ball bearing'' to decrease the viscosity of the paste, and work like ''micro-aggregate'' to progress particle packing to refine the internal structure of the binder [29, 51]. Many research works have been focused on the reaction kinetics, binder chemistry and internal structures of both

metakaolin and fly ash geopolymer systems [52-56, 30]. The replacement of fly ash by metakaolin in mix design of geopolymer mixtures generally provides economic potential and perfect engineering properties [52, 57-59].

1.1. Fly Ash

Fly ash (FA) is a by-product produced in the coal-fired Thermal Power Plants (TPP) during the combustion of pulverized coal to generate electric power. It is important to mention that there are two major parts of coal: one part is inorganic mineral matters and another part is the combustible organic matter. The organic constituents of the coal (mainly carbon, in addition to other combustible materials) are burned out when pulverized coal is combusted. However, the inorganic mineral constituents of the coal such as feldspar, quartz, shale, and clay remain suspended in the flue gases. At this time point, coarser particles are formed due to the agglomeration of some of the noncombustible mineral matters. It is important to note that these coarser particles are heavy and accumulated at the bottom of the burner and collected as bottom ash. The remaining parts are mostly melted in the flue gases and primarily composed of the mineral materials. When these melted particles are carried to a comparatively lower temperature area by the flue gases, these particles then constitute glassy amorphous ash particles after the cooling and solidification of the melted particles. The ash particles are separated from the flue gases and collected in a silo as FA using different methods, including bag houses or mechanical separators and electrostatic precipitators [60-62]. A schematic diagram of the production and collection of FA in a coal-based thermal electricity plant is presented in Figure 1.3.
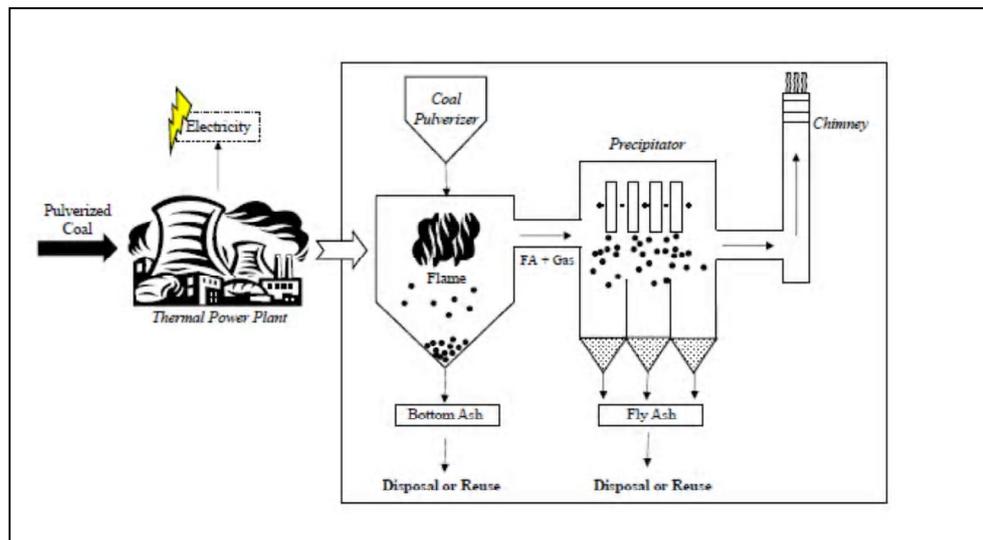
Figure 1.3 Fly ash production process in coal-fired thermal power plants [63]

The requirement of energy is increasing day by day throughout the world and this situation increased in the consumption of coal leading to the production of a higher amount of fly ash. It is important to note that there is an annual production of more than 750 million tons of fly ash. Among them, only 25% is used in the areas including structural fills, mining applications, soil stabilization, ceramics and glass, agriculture, and cement and concrete sector. Almost 75% of the produced FA is not utilized, although it could be evaulated in different sectors. There are serious environmental concerns because of the different heavy metal content of the fly ash. These heavy metals include nickel, zinc, lead, arsenic, chromium, vanadium, and cadmium. It is important to mention that a huge amount of unutilized FA is generally dumped in the ocean or in the landfill area which causes serious damage in the ocean ecosystem as well as in the agricultural ecosystem. Dumping of unused FA is not only an environmental concern but also an economic concern because it also requires a cost for transportation and storage area. The impacts that we may face due to the dumping of FA in the sea and landfills are allergies in the human body, air pollution, oceans, water reservoirs, and soils [64, 65].

There are mainly three sources of energy production in Turkey: coal-fired thermal power plants(TPP), natural gas power plants, and hydroelectric power plants. The list of these TPPs is presented in Table 1.1.

Table 1.1 List of primary thermal power plants fueled by coal in Turkey (Global energy observatory website, 2015).

Coal-Fired Power Plants	Unit	Installed Power (MW)	Coal Type	Sox control device	First Unit	Last Unit
Zetes	3	1390	Imported Coal	-	2010	2010
Yeniköy	2	420	Lignite	FGD	1986	1987
Yatağan	3	630	Lignite	FGD	1983	1985
Tunçbilek	3	365	Lignite	-	1956	1979
Sugözü	2	1320	Imported Bituminous Coal	FGD	2003	2003
Soma A/B	2+6	44+990	Lignite	-	1957	1991
Seyitömer-Çelikler	4	600	Lignite	-	1973	1989
Kemerköy	3	630	Lignite	FGD	1995	1995
Orhaneli	1	210	Lignite	FGD	1992	1992
Kangal	3	457	Lignite	FGD	1987	2000
İçdaş Biga	3	405	Imported Coal	FGD	2005	2009
Çayırhan-Park Termik	4	620	Lignite	FGD	1987	2000
Çatalağzı	2	300	Anthracite	-	1948	1991
Afşin Elbistan-B	4	1440	Lignite	FGD	2006	2006
Afşin Elbistan-A	4	1355	Lignite	-	1984	1987
18 Mart Çan	2	320	Lignite	-	2004	2004

*FGD: flue gas desulfurization

The major fuel input in the lignite coal in the thermal power plants in Turkey which can be seen from Table 1.1. It is important to note that depending on the thermal power plant technology and the type of coal, the weight of producing ash varied from 17-46% when the lignite coal is combusted [66]. The amount of total mineral waste (such as gypsum, slag, fly ash, and bottom ash) in the thermal power plants was approximately 25.5 million tons according to a statistical report carried out in 2008. Unfortunately, only 3% of the produced waste materials were recycled, 16% was used in the mines, and more than 80% of these wastes were disposed [67]. If we assume that 80% of the waste is fly ash, the total annual production of the FA is approximately 20 million tones [68]. Important environmental and economic problems are leaded due to the disposal of the very high amount of fly ash. To solve environmental concerns, many units adopted

different technologies. For instance, to solve the sulfur dioxide (SO_2) emission some facilities adopted flue gas desulfurization (FGD) technology.

1.1.1. Fly Ash Classification

The classification of FA, depending on the percentage of chemical components taken into consideration ASTM C 618 and TS EN 197-1 standards [69-71]. FA has four main components. These are; silica (SiO_2), alumina (Al_2O_3), iron (Fe_2O_3) and calcium (CaO). The proportions of these components are very variable and depend on the coal source used. According to ASTM C 618 standard, the FA is classified into F and C classes:

a) F class of FA, obtained from bituminous coal and total SiO_2 + Al_2O_3 + Fe_2O_3 percentage FA with more than 70%. The same time as CaO percentage in these ashes is less than 10%, it is also called. The F class of FA has pozzolanic properties.

b) If the FA are Class C, the total amount of SiO_2 + Al_2O_3 + Fe_2O_3 is more than 50%. At the same time, CaO is more than 10% in Class C, in this case, FA is also called high-calcined FA.

Generally, C class of FA, semi-bituminous and lignite coal sources, the F class of FA are produced from bituminous and anthracite coal sources. Low combustion of coal carbon may also be present in FA [72].

Most of the C-FA, more than 15% by weight CaO although some may contain less than 10% by weight CaO. With water when mixed, these ashes are hydrated almost in the same way as Portland cement. The degree of self-hardening usually depends on the calcium oxide content of the fly ash. The Typical crystal phase of ashes is anhydrite ($CaSO_4$), tricalcium aluminate ($Ca_3Al_2O_6$), lime (CaO), quartz (SiO_2), periclas (MgO), mullite ($Al_6Si_2O_{13}$), merwinite (Ca_3 Mg (SiO_4) $_2$) and ferrite ((Mg, Fe) (Fe_3Al)$_2$ O_4).

In the F class of FA, the calcium oxide content is less than 6% by weight and therefore FA class, designated as low calcium ashes, does not self-harden, but usually shows pozzolanic properties. In the presence of water, bituminous fly ash particles produced from coal react with lime or calcium hydroxide create binding compounds similar to those produced by class C of FA [73-76].

The major difference is that Class C of FA exhibits both cementitious and pozzolanic properties, whereas Class F of FA only exhibits pozzolanic properties. In addition, there is a lower total content of calcium oxide in Class F of FA compared to Class C of FA. It is important to note that in Turkey, we used the standard TS EN 197-1: Cement - Part 1: conformity, specifications, and composition criteria for common cement. Based on these criteria the FA can be divided into two categories:

a) Class V of FA, spherical, mostly pozzolanic is a fine powder composed of particles. The vast majority of these ashes reactive silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) while the remainder contains iron oxide and other components. In these ashes, reactive lime (CaO) content is less than 10%, reactive silica content is more than 25% It should be.

b) Class W of FA is a fine powder with hydraulic and/or pozzolanic properties. It consists essentially of reactive lime (CaO), reactive SiO_2 and Al_2O_3, iron oxide (Fe_2O_3) and other components. In these ashes, reactive lime (CaO) ratio is more than 10% and the amount of reactive silica is more than 25% is required [70].

Based on the SO_3 and CaO content, FA may be divided into different subgroups [77]

a) Silicocalcic FA: This kind of FA is commonly produced from lignite coal-like sulfocalcic fly ashes. It is important to note that the CaO and SiO_2 contents are comparatively higher in this type of fly ashes.

b) Sulfocalcic FA: Combustion of lignite coal generally produced this type of fly ash. This type of fly ashes has more SO_3 and CaO compared to other fly ashes.

c) Silicoaluminous FA: Those that are produced from anthracite coal and some bituminous coals. The main structure commonly consists of SiO_2 and Al_2O_3.

1.1.2. Characteristics of Fly Ash

Physical, chemical and mineralogical properties of fly ash adequate knowledge are required. Coal particles, volatile matter it is burned at high temperatures (1400°C to 1800°C) in the furnace where it evaporates and carbon is burned. However, the inorganic material in the coal is impure and converted to ash. It can reach 95% of this mineral substance. Clay, pyrite, quartz, and calcite are formed the majority [61].

During combustion, these mineral particles in the presence of excess air at high temperatures, they undergo physical and chemical changes. As a result, many crystalline and glassy phases occurs [78].

1.1.2.1. Mineralogical and Chemical Composition

The chemical composition of the FA is highly influenced by the type of coal was combusted. Several factors may influence the composition of the fly ash. These include coal type (e.g. lignite, sub-bituminous, bituminous, and anthracite), handling of coal, and techniques in storing coal and system of burning coal which potentially determine the chemical characteristics of fly ashes. The variety of the chemical composition of the fly based on the burned coal type is presented in Table 1.2 [25].

The chemical composition of the FA mainly consists of four main components which are iron oxide (Fe_2O_3), calcium oxide (CaO), alumina (Al_2O_3), and silica (SiO_2). In addition, there are some other minerals such as potassium oxide (K_2O), sodium oxide (Na_2O), magnesium oxide (MgO), and sulfur oxide (SO_3) can be found in fly ash. Besides, organic composites, chromium (Cr_2O_3), phosphorus (P_2O_5), and oxides of titanium (TiO_2) could also be found in FA as minor constituents [79].

The minerals that present in the coal determine the mineral and chemical compositions of FA [80]. The main sources of silica content in the FA are the quartz and other minerals (smectite, illite, and kaolinite) found in the coal. In the fly ash, the alumina contents generally come from the organic constituents and sometimes from the clay minerals. The iron oxide in the FA derived from the minerals containing iron in the coal. It is important to mention that the calcium oxide in FA derived from the $CaSO_4$ and $CaCO_3$ in the coal. The magnesium oxide in the fly as arose from the dolomite, ferromagnesian minerals, smectite, and other organic constituents. In the fly ash, the SO_3 content generally comes from gypsum ($CaSO_4.H_2O$) and pyrite (FeS_2) present in the coal. The alkali contents ($Na_2O + K_2O$) in FA generally derived from the minerals containing sodium and potassium in the coal. Due to the incomplete combustion in combination with carbon dioxide and water are the main causes of the carbon content in FA [79].

Both crystalline phases and glassy phases are the primary components of fly ashes. According to the types of fly ashes, the most common crystalline phases that are available in the FA are listed in Table 1.3. It is important to note that the crystalline phases which are maghemite (Fe_2O_3), tetracalcium aluminoferrite ($Ca_4 (Al,Fe)_4O_{10}$), dicalcium silicate (Ca_2SiO_4), portlandite $Ca(OH)_2$, calcite ($CaCO_3$), and cristobalite (SiO_2) may be rarely existed in FA [80].

Table 1.2 The Fly Ash chemical compositions based on the coal type [78].

Oxide (Wt%)	Bituminous	Subbituminous	Lignite
L.O.I	0–15	0–3	0–5
K_2O	0–3	0–4	0–4
Na_2O	0–4	0–2	0–6
SO_3	0–4	0–2	0–10
MgO	0–5	1–6	3–10
CaO	1–12	5–30	15–40
Fe_2O_3	10–40	4–10	4–15
Al_2O_3	5–35	20–30	10–25
SiO_2	20–60	40–60	15–45

Table 1.3 Mineral phases that are commonly found in Fly Ash [78]

Name of the mineral	Chemical formula
Class F and C fly ash: common phases	
Quartz	SiO_2
Mullite	$Al_6Si_2O_{13}$
Magnetite	Fe_3O_4
Hematite	Fe_2O_3
Class C fly ash: Additional phases	
Anhydrite	$CaSO_4$
Ferrite spinel (instead of magnetite)	$(Fe, Mg)(Fe,Al)_2O_4$
Merwinite	$Ca_3Mg (SiO4)_2$
Melilite (akermanite-gehlenite)	$Ca_2Mg_{0.5} Al Si_{1.5}O_7$
Tricalcium aluminate	$Ca3Al2O6$
Periclase	MgO
Lime	CaO

1.1.2.2. Morphological Properties of Fly Ash

FA morphology (shape) and particle size may vary depending on the source of coal, how and in which system it is burned, how dust particles are collected [81].

The FA contains glassy spherical and irregular shaped particles ranging in size from 0.5μm to 150μm. Whether FA is high or low calcified determines the shape and size of

the particles. Glassy spherical shaped particles, hollow or non-hollow spherical structures, structures containing a cluster of small spheres in a large sphere, structures with irregularly distributed and amorphous spaces on the surface, structures with liquid droplets on the surface, deformed structures on the surface they may take various forms with amorphous remains [82].

Non-spherical particles consist of minerals like quartz, feldspar, do not undergo combustion reactions in coal, therefore irregularly shaped and porous structures are generated [83].

Low calcined ashes generally have a homogeneous microstructure in shape distribution. These ashes are full spherical particles without hollow spaces. High calcareous ashes are spherical and angular, irregularly shaped; the combination of particles has an inhomogeneous microstructure [84].

The particle size of ash is less than 40 μm (10-20μm) and its shape is spherically increased the pozzolanic activity of it. Fine spherical particles with a smooth surface as they have a large surface area, they increase the speed of gaining strength by entering lime-silicate reactions more quickly. For this reason, crystalline active phases (anhydrite, lime) and less glassy phase are important in ash with high lime content, while the shape, size distribution and glassy phase of particles are important in low lime ashes. An example of the morphological structure of fly ash in Figure 1.4 SEM images is presented [85].
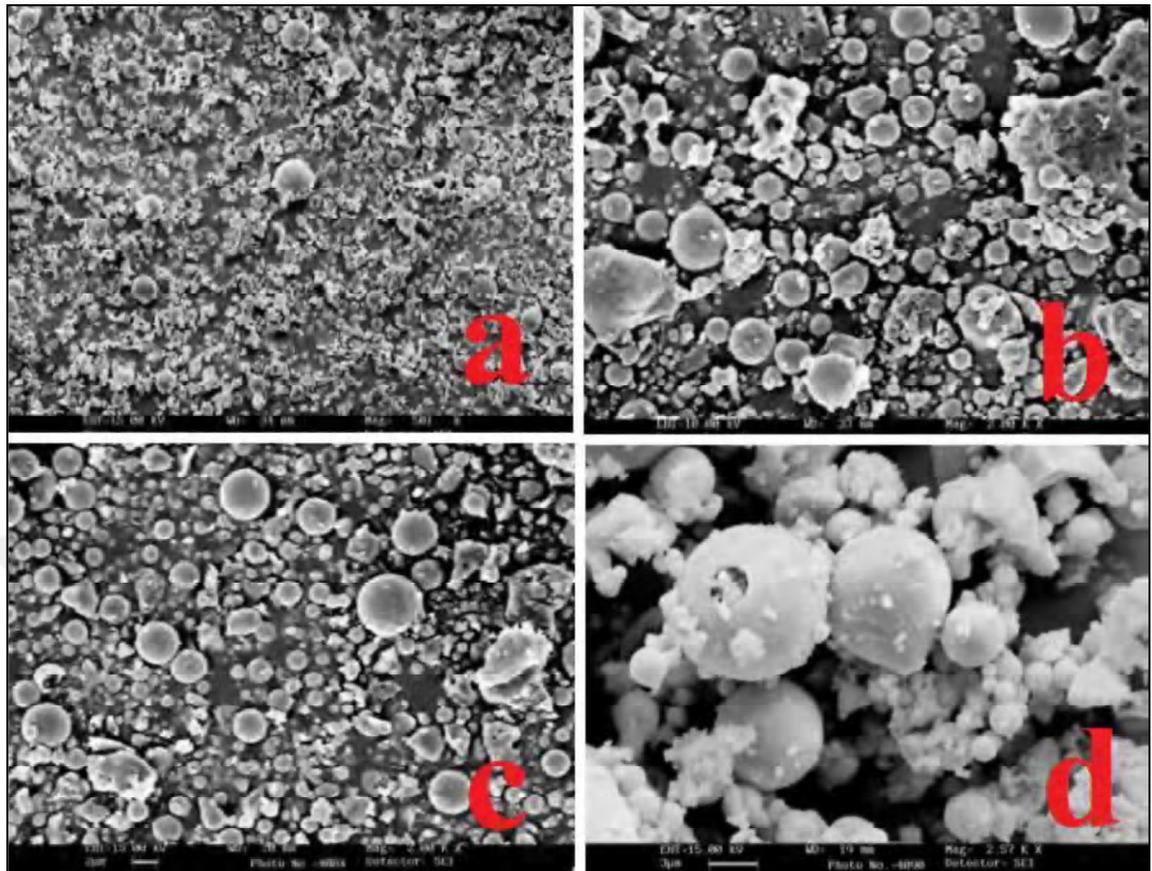
Figure 1.4 (a) Overview of the particle distribution (x500), (b) Angular particles (x2000), (c) Density spherical particles (x2000), (d) Solid glassy beads (x2500) [16]

1.1.3. Physical Properties

The type of dust collection method used (electrostatic precipitators, mechanical separators or bag houses), the temperature and uniformity of coal combustion, the degree of coal pulverization, coal uniformity, and coal source can influence the character of particle size and shape of FA [79].

Among the researchers throughout the world, there are several arguments regarding the determination of the fineness of the fly ash. Although some researchers believed that specific surface (Blaine method) is a comparatively reliable method for the determination of the fineness of fly ashes, while other scientists believe that this method is particularly helpful and reliable only for the Portland cement. Researches have shown that in fly ashes, the surface area differs between 1800-5000 cm^2/g. However, it is important to note that the determination of the retained material on the 45 μm sieve is the most practical method for the measurement of the fineness of FA [86]. Also, x-rays

sedimentation, nitrogen adsorption, hydrometer analysis, and laser diffraction particle size analysis can also be used to determine the fineness of the FA [76].

The examination of micro particles revealed that fly ashes are generally composed of very small particles which angular or irregular and glassy particles within the size of 0.2μm-200μm range. The hollow spherical particles are commonly known as cenosphere. Many small spheres in a large sphere can also be found in fly ashes which are generally known as pherospheres [82, 87-88]. The gravity range of fly ashes is 1.9 to 2.8. The color of fly ashes is generally tan or gray, although there are some differences exist in the color of FA [89].

1.1.6. Application of Fly Ash

Around 600 million tons of FA emerges every year in the world [85]. In Turkey today, there are more than 15 million tons of FA is produced as waste [90]. Resulting FA is an economic and environmental problem, therefore, the use of FA by researchers is interestingly noticeable recently. FA in the construction industry in general;

- In cement systems as additives, raw materials or substitutes,
- Thin, coarse and lightweight aggregate
- As mineral admixture in concrete,
- As an additive in brick production,
- The FA had been used in block, panel, wall, concrete pipe, aerated concrete, glass, paint, plastic
- In the construction of dams, highways, and nuclear power plants and geotechnical applications
- Soil strengthening works
- Geopolymer can be used in mortar and concrete production [91]

In general, FA is used in concrete production with cement as we noticed in the sectors listed above. FA using with cement in two cases, either as through the grinding process firstly, as a raw material together with clinker and gypsum or as an additive to the milled cement. According to TS EN 197-1 Portland-FA, cements had been classified into four groups (CEM II / A-V, CEM II / B-V, CEM II / A-W and CEM II / B-W) [92].

When used FA as an additive with cement, concrete properties will be affected on both sides positive and negative, which can be listed below.

Positive effects [93]

- It can increase the workability of fresh concrete.
- It can reduce sweating in fresh concrete.
- It reduces the hydration rate of concrete.
- Reduces the amount of water permeability in hardened concrete.
- It can increase the resistance of hardened concrete against sulfates.
- It provides the economy.

Negative effects [93]

- It delays the setting time of concrete a little, this is cause problems, especially when casting concrete in cold weather.
- FA causes a delay in gaining strength concrete, especially at early age.
- It causes concrete to cure for a longer time.

1.2. Metakaolin

Metakaolin (MK) is a natural product. It is obtained by the thermal treatment of pure or refined kaolinite clay at such a temperature that was between 650°C and 850°C. After that it is grinding to obtain a finesse of 700-900 m^2/kg. It has a high-quality pozzolanic material, which is mixed with cement to develop the durability of concrete. When added to concrete, it will block the void space between cement particles that made concrete more impermeable. MK is a comparatively new material in the concrete manufactures. When MK blended with cement, concrete becomes more strength, less sulfate attack and improving the air void network. Pozzolanic reactions modify and change the structure and the chemistry of hydration products of cement by consuming the released porlandit. Then, it forms additional calcium silicate hydrate, thus, developing improved strength and lower porosity causing more durable concrete [94]. It is important to remind when using MK, the concrete becomes greener because it involves no CO_2 production and lower temperature. Moreover, it is possible to develop concrete performance when using MK. It has been known for more than a decade that MK improves durability, but as kaolin deposits vary in composition and purity each one needs to be tested for supplementary cementing material (SCM) qualities [95]. However, depending on the kaolin source, the proportion of the silica phase and

alumina phase can vary from 8% and 10%, respectively. It is a common assertion that metakaolin has the general form of $Al_2O_3.SiO_2$ [29]. MK generally contains Al_2O_3 (40-45%) and SiO_2 (50-55%). Different other oxides, including CaO, MgO, Fe_2O_3, and TiO_2 can also be present in smaller amounts in MK [96]. The formation and properties of MK are shown in Figure 1.5. The properties of MK presented in Table 1.4 and 1.5

Fig.1.5. Formation and appearance of metakaolin [94]

Table 1.4 Chemical properties of metakaolin [94]

Chemical composition	Metakaolin %
Silica (SiO_2)	54.3
Alumina Al_2O_3	38.3
Calcium oxide CaO	0.39
Ferric oxide Calcium oxide (Fe_2O_3)	4.28
Magnesium oxide (MgO)	0.08
Potassium oxide (K_2O)	0.50
Sulphuric anhydride (SO_4)	0.22
LOI	0.68

18

Table1.5 Physical properties of metakaolin [97]

Specific Gravity	2.40 to 2.60
Physical Form	Powder
Color	Off white, Gray to Buff
Brightness	80-82 Hunter L
BET	15 m2/gram
Specific Surface	8 – 15 m2/g.

1.2.1. Types of Clay

Clay is a natural material (soil or rock) comprising one or more minerals with little amounts of metal oxides and organic materials. Clay is a fine-grained. Depending on the composition of the original materials, geologic clay is generally composed of phyllosilicate minerals. Clay has various colors, orange, white, brown, gray or red. Clay minerals are created by weathering of a diversity of minerals. Through two main processes clay is made. That may involve chemical and physical modifications or decomposition and re-crystallization [98]. Table 1.6 represents the various groups of clay minerals.

Table 1.6 Clay mineral groups [99]

Group	Type of Chemical Formula
Kaolinite	$[Si_4]Al_4O_{10}(OH)_8.nH_2O$ (n=0 or 4)
Ilite	$Mx[Si_{6.8} Al_{1.2}]Al_3Fe.025Mg_{0.75}O_{20}(OH)_4$
Vermiculite	$Mx[Si_8]Al_{3.2}Fe_{0.2}Mg_{0.6}O_{20}(OH)_4$
Smectite	$Mx[Si_8]Al_{3.2}Fe_{0.2}Mg_{0.6}O_{20}(OH)_4$
Chlorite	$(Al(OH)_{2.55})4[Si_{6.8}AlO_{1.2}]Al_{3.4}Mg_{0.6})20(OH)_4$

1.2.2. Sources of Kaolin Clay

Kaolin mines, can be found in various countries including; South East Asia, Indian, South America, China, North America, Australia, also many European countries. Chinese clay can be considered to be very pure, among the different sources of kaolin.

Clay is composed chiefly from the mineral Kaolinite, it occurs in the deposits of China clay rock, a mixture of 15% china clay and 10% mica, and the remainder is quartz [98].

.2.3. Thermal Treatment of Kaolin Clay (Metakaolin)

MK is different from other cement replacement materials (SCMs) as it is not completely natural, and it is not obtained from industrial waste. The kaolinite clay mineral is the source of MK, and it can be processed for several applications and uses including cementitious purposes. The calcination (thermal treatment, temperature ranges from 600-800°C) is mainly used to produce MK [99]. For the production of highly reactive pozzolanic materials, the treatment process of calcination is extremely important. The mineral structure collapses due to the fact that the water is dried off from the kaolinite clay ($Al_2O_3.2SiO_2.2H_2O$) that resulted in a water-free amorphous alumino-silicate ($Al_2O_3.2SiO_2$) which is commonly known as metakaolinite or MK see Figure 1.6 and 1.7. The process of driving off the water molecule is known a de-hydroxylation and could be explained through the following equation [99].

$$Al_2O_3.\ 2SiO_2.\ 2H_2O \rightarrow Al_2O_3.\ 2SiO_2 + 2H_2O\uparrow$$

Because of its importance and usefulness, the focus point of several types of research is the thermal conversion of kaolinite. The major influencing parameters that can change the de-hydroxylation process are ambient conditions, cooling rate, heating duration and rate, and heating temperature. It is worth to mention that the total loss of mass due to de-hydroxylation (14% H_2O, 46.5% SiO_2, and 39.5% Al_2O_3,) is about 14% of ambient atmosphere [99].
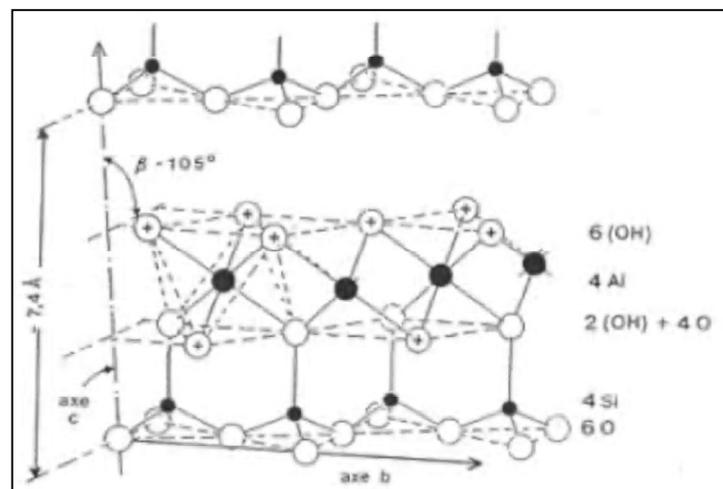
Figure 1.6 The chrystalochemical structure of kaolinit [100]
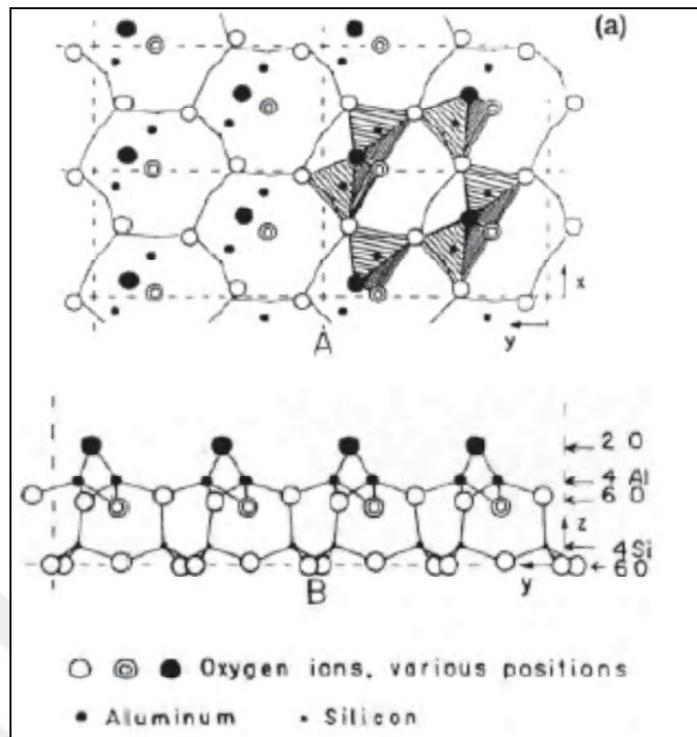
Figure 1.7 Lattice of metakaolinite [100]

1.2.4. Advantages From Using Metakaolin

When using MK as pozzolanic admixtures can be obtained many of the advantages. Some of these advantages are as follows:

- It is possible to finish concrete surfaces easily by smoothing and rubbing due to the reduction of stickiness of concrete to the tools.

- When using MK can be reduce the amount of cement in the manufacture of concrete, chiefly in concrete which need the high requirements to water resistance.

- MK can significantly increase the residual strength of refractory concrete after firing; typically lose 50% of its strength after heating to $800^{o}C$.

- Can increase the durability and strength of concrete.

- The initial setting of concrete can accelerate by using MK

- MK increases compressive strength of concrete by 20 %.

- MK can safely reduce the areas of structural members, thus saving in concrete amount and also can be economically used in dams, high rise buildings, bridges, and so on.

- It Imparts improved water-tightness, so safely used for water retaining structure, offshore structure etc.

- MK has high early strength, therefore, allows quicker reuse of formwork, and thus improves the production rate.

- Eco-friendly.

- MK increases resistance to chemical attack and prevention of Alkali-Silica Reaction.

- MK able to reduce autogenous shrinkage.

- MK show more facility and less dusting in the mixer.

- MK decrease the hydration heat that leading to good ratre of shrinkage and less cracks.

- Good sprayability

- Lesser rebound so used in shotcrete with reduced wastage [97].

1.3. Geopolymer

The material 'geopolymer' can be used as several materials, including cement, adhesive coating, and binder. During the search for a fire-resistant material, in the 1970s, Davidovits first invented the geopolymer. Extensive development and research in the area of engineering and science discover the potential of geopolymer as an alternative cementitious material to ordinary Portland cement [101].

1.3.1 Terminology

Geopolymer is a generic term commonly used for a broad range of aluminosilicate products manufactured with different formulations under heat or ambient curing regimes. Geopolymer technology is an emerging technology in various applications comprising cosmetics, pharmacology, agriculture, ceramics, insulation and concrete infrastructure [102]. In the context of concrete technology, a geopolymer is considered as emerging cement-less and sustainable alternative binder to OPC purported to provide significant environmental advantages. Geopolymer refers to a class of largely X-ray amorphous aluminosilicate binder materials [103], synthesized from a wide range of source materials (precursors) that are rich in silica and alumina at different curing conditions. Industrial by-products such as FA and slag, or geological materials such as calcined clays are examples of aluminosilicate source materials. Geopolymer concrete

has gained great interest in the recent years since sustainability and concern for environmental impacts are nowadays becoming major considerations in the construction industry and geopolymer concrete is believed to have considerably less environmental impacts and potentially beneficial engineering properties and commercial features compared to conventional OPC concrete [102].

The term geopolymer was initially introduced by Davidovits [5] representing a wide range of inorganic materials. According to Davidovits [104], among nine different classes of geopolymers, geopolymer cement and concrete are of particular interest comprised of aluminosilicate materials that could potentially be used to completely replace the Ordinary Portland Cement (OPC) and conventional concrete in transportation infrastructure applications.

The largest amount of energy is needed for the manufacture of OPC. That energy is consumed to reach the very high temperatures necessary for the burning of clay and lime ($CaCO_3$) mixtures. This leads to the release of large amounts of CO_2 from the limestone into the air. As a rule of thumb, almost one ton of CO_2 is emitted due to manufacturing one ton of OPC, half of which is attributed to the energy needed to burn the limestone at $1800^{\circ}C$ and the rest of the emissions is attributed to the chemical release of CO_2 from $CaCO_3$ to make CaO [105]. In contrast, the production of an FA-based geopolymer is reported to consume almost 60% less energy than that needed for the production of OPC, which results in less carbon emission into the atmosphere [106]. In addition according to Duxson et al. [107], at least 80% less CO_2 emission is resulted from the production of an FA-based geopolymer compared to the manufacture of OPC. The environmental advantages of geopolymer cement and concrete are mainly due to the fact that the burning of limestone is not involved in the manufacturing process, and therefore much less energy is needed for the production of geopolymers.

In addition, the fact that geopolymer materials are often synthesized from already existing waste products (by-products) such as FA and slag, results in better use of natural resources, along with added environmental benefits due to the reduced need for disposal of these waste materials [102].

1.3.1. Background Information About Geopolymer

It was Davidovits who first introduced polysialate or geopolymer as the three-dimensional semi-crystalline to amorphous aluminosilicates. It is important to note that the geopolymer is formed by a tetrahedral AlO_4 and SiO_4 where all the oxygen atoms are connected and shared. Positive ions such as Ca^{2+}, Li^+, K^+, and Na^+ are required in the system in order to balance the negative charge of Al^{3+} in IV^- fold coordination of the network. The network configuration is shown in Figure 1.8.
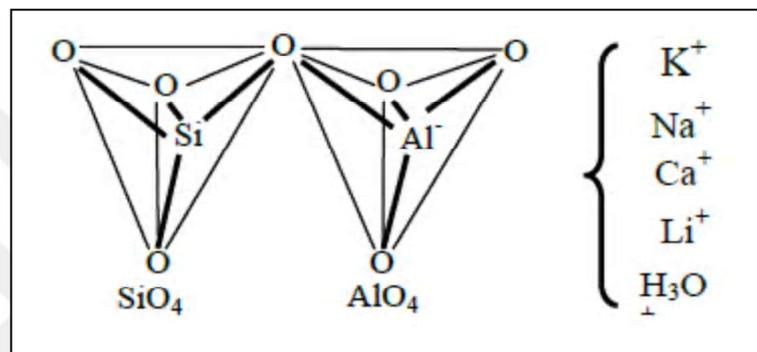
Figure 1.8 Tetrahedral configuration of sialate, ionic concept [101]

It is important to note that there are generally three types of polysialate such as polysialate-disiloxo (PSDS), polysialate-siloxo (PSS), and polysialate (PS). The pragmatic formula of polysialate was determined by the following equation:

$Mn(-(SiO_2)_z-Al-O)_n, wH_2O$

Where n = degree of polymerization, z = 1, 2, 3, - = bond, and Mn = alkaline element.

The availability of the source material driving the development of the type of geopolymer. During the early development of the geopolymers, MK was the investigated material by different researchers throughout the world [108-110]. It is important to note that even in the case seawater environment, the geopolymer from MK performed with excellent durability, fire resistance, and mechanical properties [111-113]. There are mainly two reasons that the use of MK is limited only in the research purpose:

a) It requires a large amount of liquid to make it workable,

b) it involves huge expenses in the production process. Therefore, it is necessary to develop other materials that are cheap to produce and can be used in practical settings and can be served as a substitute for MK.

In case, the FA and slag can serve as an alkaline activator to activate Al_2O_3 and SiO_2 enriched materials [114, 115]. It is important to mention that both the materials are the industrial byproducts, therefore, by using them, the initial cost involved in the production of geopolymer can be reduced drastically. FA and slag produce different final products, namely aluminosilicate and Calcium Silicate Hydrate (CSH), respectively. In order to make the FA and slag derived geopolymer more suitable in real applications, currently, there are many types of research ongoing for both materials.

It is vital to point out that during the development of a geopolymer, various terminology used by different researchers could cause confusion. Different materials, including rice husk, waste mud, fly ash, slag, and metakaolin that can be activated by several kinds of activators slightly changed the original terminology.

It is important to note that the definition of geopolymers describes as geopolymers is a division of alkali-activated materials and inorganic polymers that are able to produce aluminosilicates as a final product. The source material is usually alkaline activators from silicate or alkali metal hydroxide and low calcined clays and calcium fly ash. Alkali activated slag with a final product called Calcium Silicate Hydrate (CSH), is included in the inorganic polymers. The inorganic polymers are part of the alkali-activated materials that have disordered the silicate network as the final product. Geopolymers can be broadly defined as any binding system that is derived from an alkaline salt reaction with a solid silicate powder.

1.3.2 Constituent Materials of Geopolymer

The two main constituent materials used for preparing geopolymer materials include the source materials and the alkaline activators. The source materials are also known as feedstock or precursors or raw materials, and the alkaline activators could be in the form of solution or powder, which need to be dissolved in water.

2.3.2.1 Source Materials

According to Xu and Van Deventer [116], the source materials should contain a high amount of silicon (Si) and aluminum (Al) in amorphous form. The source materials can have geological origins (natural minerals) such as kaolinite and calcined kaolinite (MK) or could be industrial by-products such as FA and slag [117]. There are several factors such as availability, cost, type of application, and specific demand of the end-users, which affect the selection of the source materials for the manufacture of geopolymer [118]. There are several studies available in the literature which investigated the properties and application of geopolymer materials made by using either kaolinite or MK as the source materials [116, 117,119,120]. Similarly, there are extensive research studies on the application and properties of geopolymer material made by using FA [121-123) and slag [124, 125].

1.3.2.2 Alkaline Activators

According to Rowles [126], in terms of alkaline activators, any strong alkaline solution may be used for the manufacture of geopolymers. Davidovits [127] reported that for building the pyramids in ancient days lime solution $Ca(OH)_2$ and volcanic ash were used as the alkaline activator and the source material, respectively. Alonso and Palomo [128] also studied the use of $Ca(OH)_2$ as an alkaline activator for the production of geopolymers. Nowadays, a combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) or potassium hydroxide (KOH) and potassium silicate (K_2SiO_3) solutions are commonly used as the alkaline activators for production of geopolymers [129].

1.3.2. Mechanism of Geopolymerization

Geopolymerization accompanied by an exothermic production, which is extremely complex. It has been suggested by Glukhovsky that alkali-activated mechanism is suitable for the materials that have alumina and silica. Three stages of polymerization have been proposed by him. These stages are as follows-

(a) Stage No.1: Destruction–coagulation;

(b) Stage No.2: Coagulation–condensation;

(c) Stage No.3: Condensation–crystallization.

Figure 1.9 shows a simplified mechanism for geopolymerization including converting solid particles to the gel by using a high alkaline solution. This planning illustrates processing convert aluminum-silicate material to geopolymer, but this process is not simple as shown in planning. The first process (dissolution) converts the raw material (aluminosilicate source) to aluminate and silicate species by using an alkaline solution. This process accompanied by water consumption. Increased surface area of aluminosilicate material and highly alkaline solution, dissolution of amorphous aluminosilicates is rapid at high pH, leads to accelerate the process of geopolymerization. In addition, the liquid phase saturated with aluminosilicate lead to the formation of geopolymer gel. The process of releasing the water leads to condensate the structure. Therefore, water plays a very important role in the reaction and pores formation. By increasing the gel network, the formation of gel continues to reorganize and rearrange, and finally, the three-dimensional aluminosilicate network is commonly attributed to geopolymers [130].
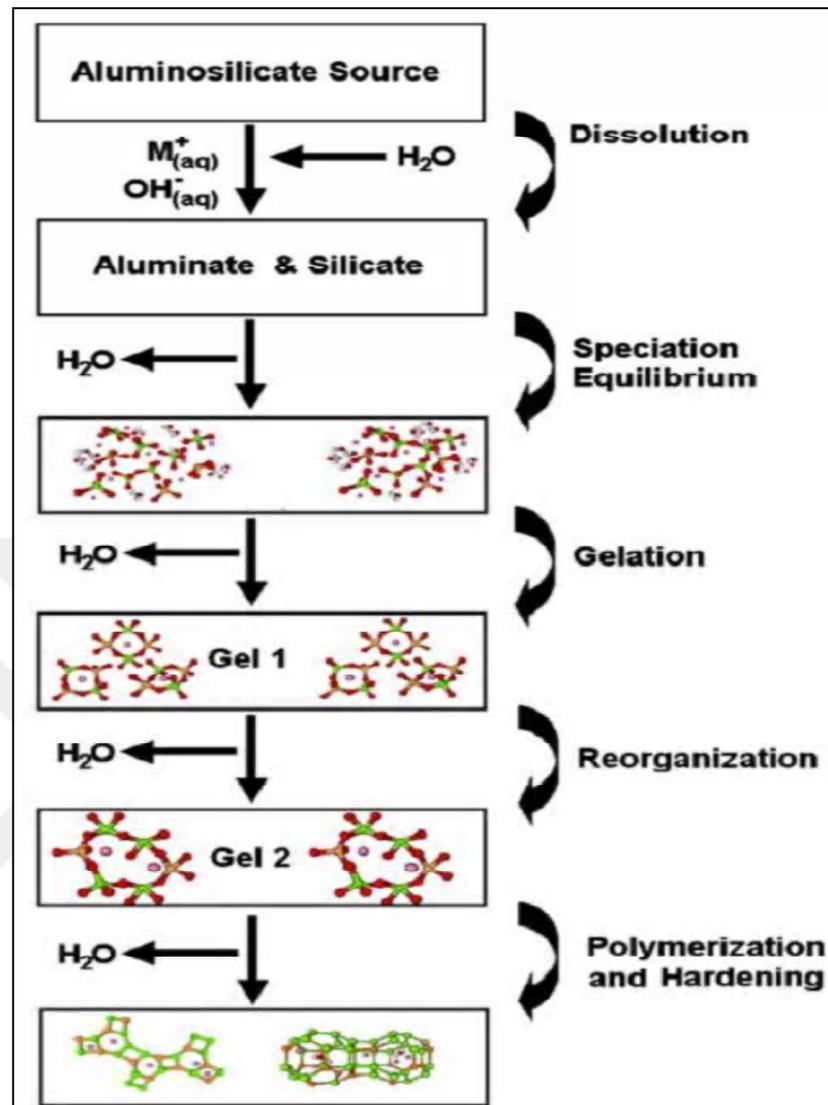
Figure 1.9 Conceptual model for geopolymerization [130].

1.3.3. Advantages of Geopolymers

Geopolymers have many advantages when compared to Portland cement, can be listed at the flowing;

1. Geopolymer has abundant sources of raw materials, pozzolanic compound or silicates or alumino-silicates are solved in alkaline solution by this way production geopolymer

2. Geopolymers save energy and protect the environment. Natural alumino-silicates at 600-800°C heat treatment makes it suitable geopolymeric raw materials, it also uses 3/5 less energy than Portland cement. Also, very little CO_2 is released compared to Portland cement.

3. Geopolymer can be prepared simply. Geopolymer, alumino-silicate materials and strong alkali solutions, and then at room temperature can be easily hardening. Also in a short time, strength can be obtained. Its production is very similar to that of Portland cement concrete.

4. Geopolymers have good volume stability, geopolymers from Portland cement 80% less shrinkage.

5. Geopolymers gain reasonable short-term strength; geopolymer assumed pressure can gain 70% strength in the first 4 hours.

6. Geopolymers are durable, thousands of years without suffering losses.

7. Geopolymer is resistant to high temperatures and has low thermal conductivity. Geopolymers when exposure to temperature from 1000-1200°C didn't show losing and have very low thermal conductivity [131].

Several advantages are offered by fly ashes-based geopolymers which can be a reliable material for the construction system. The advantages are listed below-

1. It improves concrete durability because of the lower level of calcium content in the mixture that can resist sulfate and acid attacks.

2. Greater resistance performance against fire.

3. Performs a low shrinkage concrete when it is cured at high-temperature curing.

4. Produces a high early strength concrete in a relatively short time due to a high-temperature curing method.

5. Adds value to industrial by-products without using a conventional cement binder in the mixture.

1.3.4. Potential Applications of Geopolymers

Until recent days, there are very few availabilities of information regarding the application of geopolymer concrete. It is important to note that different trial projects are focusing on the use of fly ash-based geopolymer concrete that has been applied successfully. These include-

1. Manhole structures and sewer pipes

2. Sewage sewer pipes

3. Structural/non-structural

4. Precast box culvert

5. Reinforced concrete

6. Toxic waste containment

7. Brick lining of steel pickling tanks

1.4. Literature Review

The effects of curing on the characteristics and properties of MK and FA-based geopolymers have been extensively studied by Gökhan Görhan and his colleagues [132]. The authors employed, the FA used as the main material in the production of geopolymer paste and MK was used as a replacement material in different dosages. MK material was made of kaolin clay after thermal treatment at a temperature of 1000°C for 1 hour. The FA replaced by MK at ratio from 10% to 40% in mixtures. In the mixtures, NaOH and sodium silicate solution were used with each other as reactive. The mixtures were molded into cylinder molds with size 25×50-mm, under a 100 bar pressure had been used a hydraulic hand press. After that the samples were put in an oven for heating curing. The samples were subjected to curing at 60°C and 80°C (two different curing temperatures) for 2 h, 4 h and 24 h (three different curing times). After curing, the samples were left in laboratory conditions until the day of tests. Geopolymer paste samples at 7day were tested. They were concluded that optimal curing temperature and time were 60°C and 2 hours. They reported that mixture made with 40% MK replacement provided a better geopolymerization and developed 25.1 MPa compressive strength. Also, they found an increase in the curing temperature lead to increased porosity and water absorption. In addition to when increase MK replacement rate, the water absorption and apparent porosity also decreased. They found increased replacement dosages of MK in geopoylmer lead to increase of bulk density values in parallel

Geopolymer mortar has been prepared using GGBFS and Palm Oil Fuel Ash (POFA) and to select MK as the binder by Kabir and his colleagues [133]. The authors concluded that the addition of MK and POFA significantly decrease the flow tendency due to the porous and spongy characteristics of the POFA microstructure. From their

results, it can be concluded that the flow tendency was decreased by the addition of POFA, MK due to the finer particle size of MK particles and the spongy and porous nature of the microstructure of POFA.

Steinerova [134] investigated the influence of send content on the freezing-thawing ability of the MK-based geopolymer mortar. For this purpose, the author used a special parameter to assess the frost resistance of the MK-based geopolymer mortar containing various quartz contents. Their results indicated that the sand content was involved in limiting the freezing-thawing resistance of the specimens. It is important to note that they found that the critical content of sand was 34 weight% of the geopolymer mortar. The specimens could not endure 25 freezing-thawing cycles if the sand content lower than this critical value.

Abdollahnejad et al. [135] compared the capillarity coefficient and the absorption coefficient of water with different contents of sodium hydroxide and calcined kaolin and fly ash. Because of the similar binder/water ratio, the absorption of water was similar for all mortars. When the geopolymer mortar containing 8% calcined stuff, very high capillary water absorption was found because of the large number of capillary pores.

Yusuf et al. [136] investigated the affected by mixing of MK with silica rich palm oil fuel ash on the strength distribution of geopolymer mortar. They used Weibull distribution. Geopolymer mortar produced from 100% MK, 50% and 70% palm oil fuel ash and cured under room condition. Prismatic and cubic molds were used to casting the mortar for flexure strength and compression strength, respectively at 28 days. The results were resolved using Weibull distribution. They concluded that Weibull distribution is suitable for resolved of the mixed geopolymer. Whilst porous internal structure is fundamentally responsible for failure of flexural, heterogeneity of reactions are responsible for the failure of compression.

Using MK based geopolymers mixtures for modify purposes was investigated by Vasconcelos et al. [137]. They studied geopolymer mixtures as a binding agents or a repairing layer to ensure the adhesion property between carbon fiber reinforced polymers sheets and concrete substrate. Many mixtures of MK geopolymer were studied by using varying sand/binder ratio and the concentration of sodium hydroxide. They found that MK geopolymer mixtures show a high mechanical properties and a

relevant adhesion to the concrete substrate. Moreover, the adhesion strength between carbon fiber reinforced polymers and geopolymer mortars showed to be lower than expected, that may be due to the composition of the geopolymer mixtures were not optimized and as well to the fact that the carbon fiber reinforced polymers used wasn't suitable to this type of application.

The influence of high temperatures (up to 1200°C) on the internal structure and mechanical properties of MK-based geopolymer mortars were studied by Kuenzel and colleagues [138]. They found, internal structure and compressive strength of geopolymer mixtures stay comparatively fixed after exposure to high temperatures up to 800°C. The flexural strength reduced due to the formation of hair cracks at inter facial transition zone. Up 800°C, phase a sodium aluminate crystalline form and the geopolymer phase transform to carnegieite and nepheline on heating to 900°C. Above 1000°C these crystalline phases make tender and partly melt and coarse, closed pores are created in the internal structure that reduces the mechanical properties. Heating MK geopolymer mixtures containing filler particles of fine quartz to 1000°C represent a novel way to prepare polycrystalline nepheline/quartz ceramics.

Muhammad Zahid et al. [139], studied the influence of replacing fly ash with metakaolin on strength development geopolymer mortar. They replaced 5, 10, 15% metakaolin with fly ash. Sodium hydroxide and sodium silicate solution combination was used as an alkaline activator. Geopolymer mortar was cured at 60°C for 24 hours. Their result represented different behavior of metakaolin replacement on compressive strength of geopolymer mortar containing fly ash. Increase in compressive strength was observed with the addition of metakaolin in class F fly ash based geopolymer mixture. However, decrease was observed in compressive strength of metakaolin added class C fly ash based geopolymer up to certain replacement level.

Ping Duan et al. [50] worked on properties of fly ash based geopolymer paste containing from 0% to 20% metakaolin after exposing sulfate attack. Geopolymer were activated with combination of sodium silicate and sodium hydroxide solutions. The results of laboratory work showed that fly ash based geopolymer paste suffer from strength loss due to sulfate attack. They reported that replacement of fly ash by

metakaolin improves the mechanical properties, refines the microstructure and decreases the rate of damage due to sulfate attack.

The shrinkage properties of geopolymer mortars prepared from different concentrations of slag and MK and the effect of relative humidity during the curing time were investigated by Chang et al. [140]. They conducted different research and their results indicate that the geopolymer containing 70% slag and 30% MK showed the lowest drying shrinkage after 28 days of curing in the presence of 50% relative humidity.

The shrinkage behavior and pore structure of the MK-based geopolymer mortars and pastes containing 0 to 30% FA were investigated by Tao Yang et al. [141]. The results of the study indicating that a prolongation of the polymerization stage was resulted due to the decrease of average reactivity of the solid precursors in a partially replaced MK by fly ash. The changes in the volume of MK-based geopolymer pastes and mortars are primarily because of the shrinkage caused by drying but not because of autogenous shrinkage. During the designing geopolymer mortar mixes, the partial use of FA instead of MK resulted in a decrease in the drying shrinkage and may solve the problems regarding the structural stability of the geopolymer pastes and mortars.

The effects of silica fume on the MK-based geopolymer concretes were studied by Khale and Chaudhary [142]. The authors employed 0 percent to 10 percent replacement of SF and cured at room temperature for different time points such as day 1, day 7, day 28, and day 90. The authors concluded that the compressive strength of the geopolymer mortars was increased by increasing the time of curing because increased curing time allows forming a homogeneous and fine structure in addition to hydration was progressive to form CSH. It is important to note that the strength of the geopolymer mortars increased due to the increment of silica fume up to 7%. When using silica fume more than 7%, the strength of geopolymer mortars decrease up to 10 percent. The enhancement in the physical properties like bond strength, abrasion resistance, and compressive strength is due to the pozzolanic activity of silica fume.

MK geopolymer pastes and the effects of different curing regimes were investigated by Liew et al. [143]. The results of the study indicating that the heat is relatively important in the MK geopolymer synthesis because curing at room temperature was not feasible. It is important to note that the dissolution of the MK was slowed by lower curing

temperature which ultimately showed down the geopolymerization process. The authors also concluded that at higher temperatures the chemical reaction of geopolymerization was speeding. At a moderate elevated curing temperature (40°C and 60°C), there was an improvement in the compressive strength of the geopolymer mortars. It is important to note that higher curing temperature resulted in the formation geopolymers with gel with poor structure and quick polymerization which leads to a decreased compressive strength.

The influence of different concentrations of NaOH on MK-based geopolymer paste was investigated by Wang et al. [144]. The effect of NaOH was investigated by employing 8, 10, 12, 14, and 16 M/L of concentrations of NaOH on the geopolymer mortar mixes. The results showed that with the increasing of the concentration of NaOH, the compressive strength of geopolymer mortar and paste was increased at day 7 specimens. It is also important to note that the highest level of compressive strength was observed with a NaOH concentration of 16 M/L.

The effects of various concentrations of NaOH on the geopolymer mortar/concrete made out of Kaolin were studied by Kamarudin et al. [145]. In this experiment, the authors were trying to develop geopolymers with high compressive strength using various concentrations of NaOH (6, 8, 10, 12 and 14M) at a curing temperature of 80°C for the different duration (day 1, day 2, and day 3). The results of the experiments showed that there was no increase in the compressive strength of geopolymer mortars prepared with various concentrations of NaOH when they were cured for 1 and 2 days. It is important to note that the highest compressive strength was observed at day 3 curing when the concentration of NaOH was 12 M. However, with the increase of NaOH concentration, there was an increasing trend of compressive strength of geopolymer mortars was observed due to the quicker activation of binder resulted in stronger geopolymer mortar. The solubility of aluminosilicate enhanced with the increase of NaOH concentrations.

Yana et al. [146] studied properties of geopolymer prepare from FA and MK mixed with sepiolite at ratio 0%, 5%, 10%, 15% and 20% as a replacement material with FA and MK. Flexural strength, compressive strength, abrasion resistance, vickers-hardness internal structures were measured. Before 7 days of curing, they found, there is

noticeable increase in compressive strength. At 1day when compared the reference specimen with various replacement ratio of sepiolit found change in compressive strength. While sepiolite added, compressive strength increases at longer times after 7 days. Sepiolite exhibits positive effect on compressive strength, particularly at longer times of curing. Up to 10% sepiolite addition, shows positive effect on flexural strength regardless of time curing. Sepiolite improves the abrasion resistance. The minimum losing in weight due to abrasion test observed in geopolymer mixtures containing 10% sepiolite. That means it has high resistance to abrasion. Also, they concluded when increasing replacement ratio of sepiolite that vickers-hardness increases. They found all results which obtained from laboratory work (flexural strength, compressive strength, Vickers hardness and abrasion resistance) were compatible. They concluded geopolymer mixtures containing 10% sepiolite have higher compressive and flexural strength, higher abrasion resistance and higher surface hardness.

Raphaëlle Pouhet and Martin Cyr [147] studied carbonation phenomenon in geopolymer produced from MK according to the pore solution these materials. Most total carbonation of the pore solution happened after 14 days in normal condition. Also, the results obtained from work laboratory display a very rapid reduction in the pH, contrast to Portland cement. When sodium carbonate is formed under normal condition of CO_2 it didn't lead to a reduce pH less than 10.5 at one year. Therefore, the risk of corrosion is limiting by depassivation of the reinforcement. While they used accelerated carbonation carry out down 50% of CO_2 they found great amounts of sodium bicarbonate had been formed and it responsible for decrease pH of the pore solution, and a potential risk of corrosion by carbonation.

Mo Bing-hui et al [148] studied the influence of various curing on geopolymerization procedures of MK-based geoplymer. They used Impedance Analyzer to research the influence of various curing temperatures on the dissolution, polymerization, reprecipitation procedures of the geopolymerization reaction. The temperatures used for curing in work were 20 to 100°C. In geopolymer mixtures produced from MK, they were noticed that the rising temperature curing accelerates the dissolution process of MK and polymerization process in the primary geopolymerization reaction. They concluded extend curing time; develop the formation of hardy structure, particularly in the early-step (12 hours) of geopolymerization process. Also found rising temperature

less than 60 °C lead to fast the hardening process and enhance the physical properties of the geopolymer mixtures. Whilst, curing at temperatures 80 and 100°C there were passive effect on physical properties. The ideal curing temperatures of geopolymer is 60°C, because geopolymer mixtures at 60°C show the better mechanical properties.

Huajun Zhu et al [149] investigated the effect of rice husk ash on the reaction kinetics, on MK-geopolymer mixtures. They studied mechanical property, internal structure of MK- geopolymer. Geopolymer pastes prepared from MK as main binder material and different amount of rice husk ash (0%, 10%, 20%, 30%, 40%, and, 50%) as a replacement material with sodium silicate activation. Analytical results display that both MK and rice husk ash are contributory in the geopolymerization. Both materials contributed to the improvement of mechanical properties and forming of internal structure. They found when added rice husk ash to geopolymer mixtures, pore structure of geopolymer samples is compact; therefore display a comparatively high compressive strength. They conclude the ideal ratio of replacement MK by rice husk ash was 20%. The plentiful in amount of gel in geopolymer lead to decrease the pore system. Also, secondary filling contributed to the improvement refinement of pore and enhancement strength.

The effects of the marine environment of MK-based geopolymers were investigated by Xing Li et al [150]. The geopolymer was exposed to air, sea water, wet-dry and heat-cool cycles of seawater (30, 60 and 90 days). They prepared geopolymer mixtures from MK as a main binder. They found increment in compressive strength of geopolymers when exposing to air till to 90 days. Whiles, it reduced as exposing in sea water, dry-wet and heat-cool cycles of seawater. Exposure conditions to sea water, salts and cracks and like halite are created that leading to reduce in compressive strength. Also, they found the sea water environments damp the geopolymerization reactions process therefore less amount of gel forming in geopolymer system.

The effect of rice husk ash on the thermal stability and internal structures of geopolymer were studied by Guangwei Liang et al [151]. They produced geopolymer from MK as a binder material and rice husk ash as substitution material with ratio (0%, 10%, 20%, 30%, and 40%). The results display, the aluminosilicate fractions of rice husk ash were related with the acid-base reaction of geopolymerization, that leading to more formation

of gels. They concluded, when used rice husk ash as a replacement material, the pores system of geopolymer mixtures were re-fined due to filling impact of rice husk ash and more generation of gel phases, which were essential reason for the good thermal stability of geopolymer. They found the ideal ratio of replacement was 30% rice husk ash. It affords the best strength of geopolymer before or after exposure to temperature.

Ruizhe Si et al [152] investigated the effect of waste glass powder as a replacement material (with ratio from 0% to 20%) on geopolymer prepared from MK as a main material. In work they measured nano pore structures, mechanical properties, and drying shrinkage. They used two types of curing; under normal condition at ambient temperature and thermal curing at 60°C. The mechanical properties of the geopolymer mixtures containing low ratio of glass powder (5% and 10%) display improvement in results. Also, they found when used glass powder in geopolymer mixtures, internal structure and nano pore systems became better due to formed gel phase was more intense. At dry condition, the replacement MK by glass powder decreased the water loss rate of the geopolymer samples that lead to decrease drying shrinkage at early time. The quantity of capillary stress formed in geopolymer mixtures containing glass powder was comparable to geopolymer mixtures with 0% glass powder.

CHAPTER TWO

MATERIALS AND METHODS

In this work, we used two types of admixtures MK and FA for the production of Geopolymer mortar. It is important to mention that the Class F of FA used in the current experiments was obtained from Catalagzi thermal power plants in Turkey. MK was obtained from the OTS Company in Turkey. In this work, the white powder-fine, Sodium metasilicate was used as the activator. Natural river sand was used in the mixture. Addition we used Portland cement to predicted normal mortar to compare with the geopolymer normal condition used as curing.

The main objective of the current study is to investigate the influence of MK as a partial replacement on the properties of FA-MK geopolymer mortar which made without any need for curing, or air-curing. In the study, the FA was replaced with MK by weight at the ratio of 0%, 10%, 20%, 30%, 40%, and 50%. The water-binder and sand-binder ratios were 0.50 and 3.0, respectively. Adding to all this we cast Portland cement mortar with water-cement ratio 0.5 to compare with geopolymer. The fresh mortars were cast in prismatic molds with the size of $40{\times}40{\times}160mm^3$ for unit weight and specific gravity, flow workability, compressive strength, flexural strength, ultrasonic pulse velocity, shrinkage, and fire resistance additional to cubes molds with size $71{\times}71{\times}71mm^3$ for abrasion resistance. As mentioned, we used the white powder Metasilicate as the activator. Metasilicate used at constant concentration (10%). Compressive strength and flexural strength were measured at 3, 7, 28, 90, and 180 days to evaluate which one of age gives the best improvement in strength. According to the compressive strength of mortar, other properties tested at 28 days because at this age we obtained the best improvement in strength.

2.1. Materials

2.1.1. Fly Ash

In the current study, we used Class F-FA which was provided by the Catalagzi thermal power plants in Turkey. The physical and chemical properties of the FA had been supplied from Erciyes University Technology Research and Application Center (TAUM). The activity index FA at 28 days was 76%. The results of the analysis are presented in Table 2.1 microstructure of FA as shown in Figure 2.1.

By investigating the FA, it is evident that it contains calcium oxide, iron oxide, alumina, and silica. The content of $SiO_2 + Al_2O_3 + Fe_2O_3$ in FA is more than 70%, while the CaO is 10% for FA. It is found that FA satisfies the chemical requirements for use as a pozzolanic material. This FA can be classified as Class C of FA according to the ASTM C618 [87] classification.

Table 2.1 The chemical composition and physical properties of the fly ash

The Physical and Chemical composition of the FA	Çatalağzı Fly ash	TS EN 450-1 V	ASTM C618 F
SiO_2 (%)	57.34		
Al_2O_3 (%)	22.05		
Fe_2O_3 (%)	7.92		
$SiO_2 + Al_2O_3 + Fe_2O_3$	87.31	≥ 70	≥ 70
K_2O (%)	2.72		
Na_2O (%)	1.70		
MgO (%)	1.79	< 4	
CaO (%)	2.71		
SO_3 (%)	0.57		< 5
TiO_2 (%)	1.05		
P_2O_5 (%)	0.66		
SO_3 (%)	0.57	< 3	≤ 5
SrO (%)	0.11		
BaO (%)	0.10		
MnO (%)	0.07		
ZrO_2 (%)	0.06		
Cl̄ (%)		< 0.10	
Free CaO (%)	0.22	< 2.5	
L.O.I. (%)	1.00	< 5	< 6
Density (g/cm³)	2.36		
Retain on 45 μm sieve (%)	11		< 34
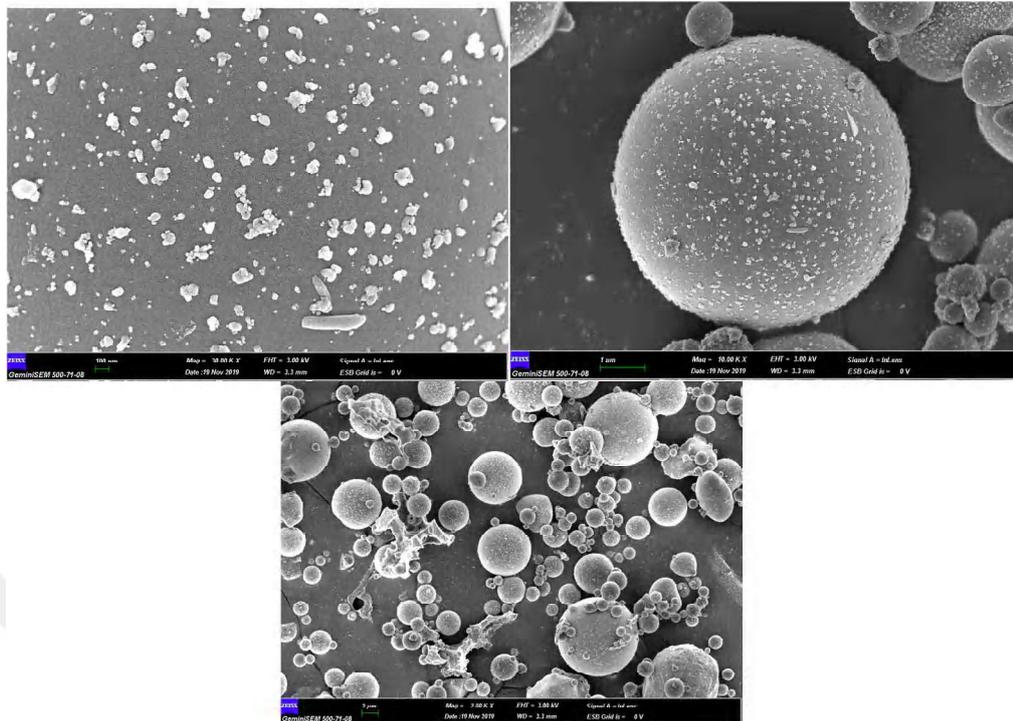
Figure 2.1 Microstructure of fly ash

2.1.2. Metakaolin

MK was obtained from the OTS Company in Turkey. The activity index of MK at 28 days was 124%. The chemical composition and physical properties of the Metakaolin is presented in Table 2.2. The specific gravity of MK is 2.41. The chemical composition of MK comprised nearly 96% of (SiO_2 + AL_2O_3 + Fe_2O_3), which conforms to ASTM C 618 Class N pozzolan [87]. Figure 2.2 microstructure of MK
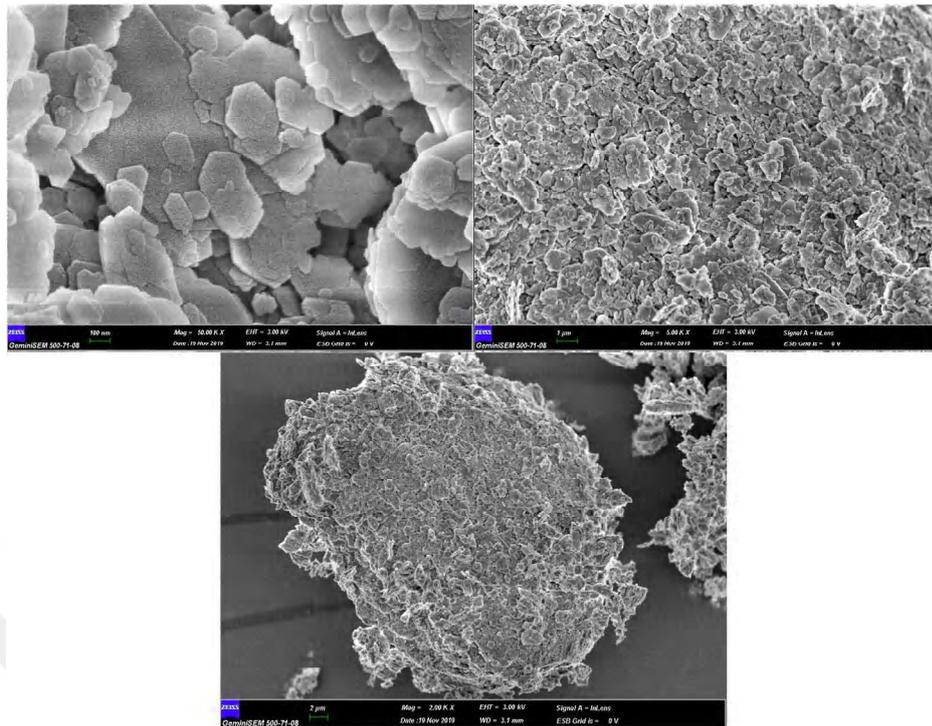
Figure 2.2 Microstructure of metakaolin

Table 2.2 The chemical composition and physical properties of the metakaolin

The Chemical Composition and Physical Properties of MK	Metakaolin	ASTM C618 N
SiO_2 (%)	50.91	
Al_2O_3 (%)	43.49	
Fe_2O_3 (%)	1.44	
$SiO_2 + Al_2O_3 + Fe_2O_3 \geq \%70$	95.84	≥ 70
K_2O (%)	0.62	
Na_2O (%)	0.13	
MgO (%)	0.18	
CaO (%)	0.11	
TiO_2 (%)	1.68	
P_2O_5 (%)	0.09	
L.O.I. (%)	1.10	< 6
Specific Gravity (gr/cm^3)	2.41	
Physical Form	Powder	
Color	Off-white	

2.1.3. Cement

In the current study, Portland cement type CEM I 42,5R, fulfilling the TS EN 197-1 [97] standards and with the trademark of ÇİMSA was used for the production of control samples (Figure 2.30) It has been stored in airtight plastic containers to avoid exposure to atmospheric conditions. The chemical and physical properties of this Portland cement are presented in Tables 2.3 & 2.4 respectively.

Table 2.3 The chemical composition of the cement

The Chemical Composition		Values	TS EN 197 -1	
			Minimum	Maximum
SiO_2	%	19.90	-	-
Al_2O_3	%	5.14	-	-
Fe_2O_3	%	2.80	-	-
MgO	%	2.49	-	5
SO_3	%	3.30	-	4,0
L.O.I	%	3.47	-	5,0
Insoluble Residue	%	0.84	-	5,0
Chloride	%	0.0047	-	0,1

Table 2.4 The physical properties of the cement

The Physical Properties		Values	TS EN 197 -1	
			Minimum	Maximum
2 days compressive strength	MPa	34,1	20,0	-
7 days compressive strength	MPa	43,8	-	-
28 days compressive strength	MPa	54,1	42,5	62,5
Initial setting	Min	180	60	-
Final setting	Min	240	-	-
Volume Expansion	mm	1	-	10
45 micron sieve analysis	%	4	-	-
Specific weight	cm^3/g	3,14	-	-
Specific surface area	g/cm^2	3652	-	-

Figure 2.3 Portland cement which used in the work

2.1.4. Sand

River sand has been used in the study, as a fine aggregate after it has been sieved by sieve size 4mm. It had specific water absorption and a gravity of 4.71% and 2.32 cm³/g, respectively. The grading of fine aggregate was as shown in Table 2.5.

Table 2.5 Grading for fine aggregate used in this work

Sieve Size (mm)	Passing Sand (%)
16	100.0
11.2	100.0
8	100.0
5.6	100.0
4	97.1
2	83.8
1	65.9
0.5	48.4
0.25	17.3
0.15	5.2
0.063	0.7
PAN	0.0

2.1.5. Water

In the case of normal mortar, water is very important to provide workability during mixing and for the hydration of cement. Water also played a crucial role in the curing process. Although there are not many strict rules for water purity, the water should not be highly contaminated and dirty. In the current study, we used the normal tap water.

2.1.6. Activator

In this work, the white powder-fine, Sodium metasilicate (anhydrous) with bulk density =1.1 (g/L) was used as the activator. The chemical formula of it is $Na_2O.xSiO_2.yH_2O$ (x=1 and y=0, 5 or 9) from SILMACO COMPANY as shown in Figure 2.4.

Figure 2.4 Activator material

2.2. Trail Mixes

In this work, we made trail mix through 9 months to obtain the ideal mixtures we faced many problems (Figure 2.5). The difficult part in trail mix whom I can make a mixture by using two materials, MK and FA which have different behaviors toward curing and activator, for example, in general FA in geopolymer using thermal curing and sodium hydroxide while I saw from trail MK unlike the heat and defame silicate.

- We made a trail mix to find which one activator can use, we used Na(OH) with Sodium silicate all so we used Metasilicate (MS). According to compressive strength, MS with contraction 10% and water/binder ratio 0.5 gives better results.

- We made a trail mix with using different types of curing: The first type of curing is using cabin (40°C+90%) for 24 hours after that in the air until test day. The second type is curing in the air without cover nylon. The third type is curing in the air with cover (nylon). The fourth type of curing had been using the oven (100°C) for 24 hours; the fifth type is curing in oven 60°C for 24 hours after that wait in the air until test day. The sixth type of curing, after24hours form casting samples had been curing by using cabin (20°C for 24 h) after that the samples left in water until the test day. The seventh type is curing 24hours in the air after

that in the cabin (20°C for 24 hours) after that in water until test day by using cover. The eighth type is curing in the oven (100°C) after that in the air until test day. The last method of curing, after 48 hours casting samples had been put in water until test day. According to compressive strength, a normal condition in the temperature room gives better results.

- We made a trial mixture by using different construction of MS (10%, 12%, and 14%). All these constructions give result in compressive strength closely. According to the initial setting and workability, 10% give better results.

- We made trail mix by using different dosages of MK as a supplementary material we found the best dosages for compare are 0%, 10%, 20%, 30%, 40%, and 50%, therefore, we used these dosages in our work.

- Also, we made trail mix by using high dosages of MK 60%, and 70% by weight of FA but we couldn't cast due to the high absorbability of the MK. We need to use a high amount of water-reducing (superplasticiser). Superplasticiser was not planned in our work, so these dosages were abandoned.

Figure 2.5 The problems in trail mix

molds with the size of Ø100×200mm for accelerated corrosion, rapid chloride ion penetration show in Figure 2.6. As mentioned, we used the white powder MS as the activator. We first mixed MS at a constant concentration of (Na=10%) with water by hand for 1min, added FA, and then the designated percentage of MK (0%, 10%, 20%, 30%, 40%, and 50%) to the mixture. All these materials mixed for 30sec. After that, we added sand to the mixture and mixed it with a mixer for 3 min. In the mixing procedure, we used the automatic method to produce fresh mortar the type of mixture used shown in Figure 2.7.

Figure 2.6 The types of molds which used in the work

Figure 2.7 Mixer used in the production of samples

2.3.2. Preparation Geopolymer Mortars

The fresh geopolymer paste was cast in prismatic molds with a size of $40{\times}40{\times}160\text{mm}^3$ for unit weight and density, flexural strength, compressive strength, ultrasonic pulse velocity, water absorption and porosity, sorptivity rate water absorption, wetting-drying test, freezing-thawing test, drying shrinkage test, and, high temperature resistance, cubes molds with $71{\times}71{\times}71\text{mm}^3$ for abrasion resistance, fresh mortars were cast in cylinder molds with the size of $\varnothing100 \times200\text{mm}$ for accelerated corrosion, rapid chloride ion penetration and, vibrated to remove entrained air bubbles. The molds were then placed in the air for 2 days. After 2 days of casting, all the specimens were released from the molds and repeated to normal conditions before being subjected to further curing in a standard condition of $20{\pm}1°\text{C}$ and $50{\pm}10\%$ relative humidity up to 28 days. While normal mortar after 24 h from casting the samples removed from modules and put in water until test day show Figure 2.8.

Figure 2.8 Curing of samples.

2.3. Test Methods

In this work, we cast geopolymer mortar and cement mortar as a reference to compare between it and the geopolymer. After we cast them, we made requested curing to obtain strength and tested it. Firstly, the compressive strength and the flexural test were at (3, 7, 28, 90, 180) days done according to TS EN 1015 -11 [153] to evaluate which age give better resulted and chosen the age to use in study durability properties. When we found the best time for curing at 28 days for geopolymer decided to use in this age in the study, therefore, we used 28 days at the age for the normal mortar to compare between normal mortar and geopolymer. We are casting samples by using FA and MK (with replacing 0%, 10%, 20%, 30%, 40%, and 50%) as binder material and MS activate with construction 10%Na. The testing which made were unit weight and density, flow workability, flexural strength, compressive strength, ultrasonic pulse velocity, water absorption and porosity, sortivity rate water absorption, wetting-drying, freezing-thawing, rapid chloride ion penetration, dry shrinkage, abrasion resistance, high temperature resistance and, accelerated corrosion.

2.3.1. Unit Weight and Density Test

This test made according to TS EN 1015-10 [154], after we placed samples 28 days in the air, we take the weight of samples in air, Oven-Dry Mass (W_D) determine the mass of the samples 40×40×160 mm, and a temperature range of 100-110°C in the oven for 24h was used to dry the specimens. After that, the specimens were removed from the oven and allowed to cool them in dry air at an ambient temperature of 20 to 25°C and after that, the mass was determined. After we obtained W_D, Saturated Mass (W_{SSD}) was taken, the specimen was immersed, and after final drying, cooling, and determination of mass, in water at approximately 21°C for 48hours, the surface of the specimen was dried using a towel to remove the surface moisture and finally we determined the mass of the specimen. In the end, we determined, immersed Apparent Mass (W_W) suspend the specimen by a wire and determine the apparent mass in water. We are working to analyze the data and evaluate them to see Figure 2.9. To calculate unit weight and specific gravity, we are using the following equations.

Bulk density dry (g/cm^3) $= W_D / (W_{SSD}-W_W)$ (Equation 2.1)

Bulk density after immersion SSD (g/cm^3) $= W_{SSD}/ (W_{SSD}-W_W)$ (Equation 2.2)

Apparent density (g/cm^3) $= W_D / (W_D-W_W)$ (Equation 2.3)

Apparent Unit Weight (g/cm^3) $= W_D /$ dimension of the sample   (Equation 2.4)

Figure 2.9 Archimedes balance view

2.3.2. Flow Workability Test

The workability of the mixes was measured according to TS EN 1015-3 [155]. A truncated cone mold was filled with freshly mixed mortar and placed on the flow table to determine the initial flow of the mortar. After that, the mold was removed and the flow table was uplifted by 10-mm mechanically and then dropped for 15 seconds at the rate of one per second. The mortar was progressively moved outwards by increasing the diameter of the flow during the test. The diameter of the mortar at the final stage was measured in millimeter for every mix. Figure 2.10 shows the determination of consistency with spreading a table.

Fig 2.10 Determination of flow workability with spreading a table

2.3.3. Flexural Test

The mixtures were cast into molds with size 40×40×160 mm³. The test for the flexural strength was done by the procedures described in TS EN 1015-11 [153], in seven series of mixtures. First, the specimens were tested for the flexural strength which resulted in two halves. A U-TEST testing machine with a capacity of 150 kN in bending and loading speed of 50 N/s, was used to measure the flexural strength. From one mold we could take 3 samples for flexure then we took an average of them as equation (2.5). As shown in Figure 2.11

$$R_f = 1{,}5\frac{F \times l}{b^3}$$
(Equation. 2.5)

Where;

R_f: Strength of flexure, N/mm²

b: The edge length of the square section of the prism, (40 mm)

F: Force applied to the center of the prism, (Newton)

l: Distance between the axis of the support rollers, (100 mm)

Figure 2.11 Flexural strength tests

2.3.4. Compressive Test

The blends were cast into molds with a 40×40×160mm^3. The compressive strength test of the blends was measured in accordance with the procedures described in TS EN 1015-11 [153], in seven series mixtures. At the initial stage, the specimens were first tested for flexural strength which resulted in the specimens into two halves, and then the compressive strength of the specimens was tested. The compressive strength of the specimens was carried out by a U-test testing machine that has a capacity of 250 kN and the loading speed was 500 N/s as is shown in Figure 2.12. From one mold we could take 6 samples for compressive then we were taken average of them.

$$R_c = \frac{F_c}{b^2}$$
(Equation 2.6)

Where;

Rc: Compressive strength, N/mm²

b: Side length of the pressure plate, (40 mm)

Fc: The biggest force in breaking, (Newton)

Figure 2.12 Compressive strength tests

2.2.5 Ultrasonic Pulse Velocity Test

The ultrasonic pulse velocity of the samples we were measured by a Proceq device in Figure 2.13 called Pundit (Portable Ultrasonic Non-destructive Digital Indicating

Tester) according to TS EN 12504-4 [156]. The low-frequency ultrasonic signals sent from the device are detected by the transducers by passing through the sample and thus the time of the ultrasonic signals passing through the sample is accurately measured. The gel was applied to the rough surface of the samples and transducers were placed in the direction of the sample and readings were made from 0.16 m. Transition time T was recorded in µs using the direct transmission method. The transit time of the ultrasonic signals depends on the sample density. During the measurements, the experiments were carried out on 3 ($40\times40\times160mm^3$) prismatic samples and their averages were recorded. Transition time T is converted to microseconds in seconds and the ultrasonic pulse velocity is calculated using equation 2.7 given below.

$$V = \frac{L}{T}$$
(Equation 2.7)

Where:

T = transit time, s

V = pulse velocity, m/s, and

L = distance between centers of transducer faces, m.

Figure 2.13 Ultrasonic pulse velocity test

2.3.6. Water Absorption and Porosity Test

The procedure of this experiment as follows: after we placed samples 28 days in the air, we take the weight of samples in air, oven-dry Mass (W_D) was determined the mass of the samples with dimension $40\times40\times160mm^3$, and dry in an oven at a temperature of 100-110°C for 24 hours in the oven was used to dry the specimens. After the drying

step, the specimens were removed from the oven and allowed them to be cooled in the dry air of ambient temperature of 20 to 25°C and after that, the mass was determined. After we obtain W_D we were taken saturated mass (W_{SSD}), the specimen was immersed, and after final drying, cooling, and determination of mass, in water at approximately 21°C for 48hours, the surface of the specimen was dried using a towel to remove the surface moisture and finally we determined the mass of the specimen. At the end of this step, we determined the immersed apparent mass (W_W) suspend the specimen by a wire and determine the apparent mass in the water as shown in Figure 2.14. We are working to analyze the data and evaluate them. To calculate absorption and volume of permeable pore space voids we are using the following equations.

Voids Ratio, % = [(W_{SSD} - W_D) / (W_{SSD} - W_w)] × 100 (Equation 2.8)

Water Absorption % = [(W_{SSD} - W_D) / (W_D)] × 100 (Equation 2.9)

Figure 2.14 Water absorption and porosity test

2.3.7. Sorptivity Test

The rate water absorption test was performed according to the method described in ASTM C1585-13 [157]. For each mixture, 3 samples with dimension $40 \times 40 \times 160 mm^3$ were produced and the geopolymer samples were cured in the air for 28days, and the Portland cement samples were cured in water for 28 days. All mixtures dried at 105°C for 24hours. The side and top surfaces of the samples were covered with aluminum foil

tape and protected from air humidity. Clearance about 2±1 mm is provided on the side surfaces and it is provided to come into contact with water with the lower surface. By forming a glass pool, the supports were placed at the bottom of the samples in water (Figure 2.15). Samples placed on the supports were allowed to absorb water capillary without contacting each other and the water contact surface was wiped with a paper towel each time it was removed from the water and only the amount of water absorbed as capillary was calculated. For each samples 1, 5, 10, 20, and 30 minutes and 1, 2, 3, 4, 5, and 6 hours and 1, 2, 3, 4, 5, 6, 7, and 8 days we determined the weight of them. To calculate water absorption we can use the following equation:

$$I = mt / (a \times d) \hspace{4cm} \text{(Equation 2.10)}$$

Where:

d = the density of the water in, g/mm^3

a = the exposed area of the specimen, in mm^2,

mt = the change in specimen mass in grams, at the time t, and

I = the absorption, mm

Figure 2.15 Sorptivity test

2.3.8. Wetting–Drying Test

After 28 days of curing, the mortar was cast into molds $40 \times 40 \times 160 mm^3$. We made this test carried out according to the procedures described by ASTM D5313 [158]. Dry each sample in an oven to a constant mass at 110±5°C and record the mass. Begin the wetting sequence by placing each specimen, in a container. Add enough potable water to the container such that the specimen is fully immersed and let stand at room temperature for a minimum of 12hours. Begin the drying sequence by decanting or siphoning the water and placing the container in an oven at a temperature of 65±5°C. Thoroughly dry the specimen for a minimum of 6hours. The completion of the wetting

and drying sequences constitutes one wetting-drying cycle (Figure 2.16). After the drying, the sequence allows the samples to cool to ambient room temperature. Repeat the process of wetting and drying for 80cycles had been made. Upon completion of the 80 cycles, dry the samples in an oven to a constant mass and record the mass after that we did determine the loosing of weight due to the wetting-drying test according to the following equation.

$$\text{Losing of weight } \% = \frac{A - B}{A} \times 100 \qquad \text{(Equation 2.11)}$$

Where:

A = oven-dried mass of the specimen prior to testing

B = oven-dried mass of the specimen slab after testing

Figure 2.16 Wetting-drying test

2.3.9. Freezing – Thawing Test

We made this test according to ASTM C 666 [159]. The procedure of this experiment was specimens of geopolymer shall be cured for 28 days in air for testing. While the specimen of Portland cement mortar cured in water for 28 days. Immediately after the specified curing or conditioning period, bring the specimen to a temperature within -10°C and +4°C of the target thaw temperature that will be used in the freeze-thaw cycle. Start freezing-and-thawing tests by placing the specimens in the thawing water at the beginning of the thawing phase of the cycle. Remove the specimens from the apparatus, in a thawed condition, at intervals not exceeding 100 cycles of exposure to the freezing-

and-thawing cycles, determine the mass of each specimen, measured the ultrasonic pulse velocity of each them and return them to the apparatus as seen in Figure 2.17. After we finished 300 cycles we determine the mass of each specimen, measured the ultrasonic pulse velocity of each them and determined the compressive strength of samples.

Figure 2.17 Freezing-thawing experiment.

2.3.10. Rapid Chloride ion Penetration Test (RCPT)

This test had been made according to ASTM C1202-12 [160]. Cylinder samples of 100 Ø × 200 mm dimensions were produced and 50 mm thick specimens were cut from the middle part of the cylinder by stone cutting machine and made to test standard. Samples cut to 100 mm in diameter and 50 mm in thickness were placed in a desiccator and vacuumed for 3 hours with the help of a pump that produces a vacuum of 50 mm Hg (6650 Pa) as shown in Figure 2.18. The desiccator was then filled with water and vacuum was applied at 1 hour, so that the samples remained in the water. After the vacuum pump was switched off for 18 ± 2 hours, the samples were left in the water. At the end of the preparation period, the samples were removed from the water and fixed between the chloride permeability cells (Figure 2.19). One of the cells was filled with 3% NaCl solution and the other with 0.3% NaOH solution. Pure water was used for the solutions, 4 samples were simultaneously connected to the rapid chloride permeability apparatus and 60 V dc current was transferred from the 50 mm thick samples for 6 hours. The chloride permeability value of the samples was determined in terms of Coulomb depending on the chloride ion penetration resistance.

Figure 2.18 Cutting and vacuuming of samples

Figure 2.19 Rapid chloride ion penetration test

2.3.12. Shrinkage Test

This test made according to TS ISO 1920-8 [161], we used molds with dimension $40\times40\times160$mm^3. After that we removed molds and measured the first reading to samples and continue the reading until 360 days. Portland cement mortars were kept in the mold for 24 hours and then removed from the mold and the first measurement was made. The samples were kept in the laboratory with 20 ± 1°C temperature and $50\pm10\%$ relative humidity during the experiment (Figure. 2.20). During the first 14 days, daily, up to 91 days, weekly and then monthly measurements were made to determine the change in height over 360 day. Measurements were made on a measuring device with a deformation clock of 0.002 mm precision. The change in length in each sample was calculated with the help of equation 2.13 below.

$$\Delta L_X = \frac{CRD - \text{initial CRD}}{G} \times 100$$ (Equation 2.13)

Where:

ΔL_X: a length change of specimen at any age, %,

CRD = difference between the comparator reading of the specimen and the reference bar at any age, mm

Initial CRD: Initial value read at the beginning of the test for reference, mm

G: Distance between measuring points, mm

Fig.2.20 Shrinkage testing

2.3.13. Abrasion Resistance Test

The abrasion resistance of geopolymer mortar samples was determined by applying abrasion to $71 \times 71 \times 71 mm^3$ cube samples on the Böhme abrasion device according to TS 2824 EN 1338 [162]. Böhme abrasion tester and samples used in the study are shown in Figure 2.21. The pressure piston is pressed by the weight suspended on the loading arm. The disc applies an abrasion force of 294 N to the sample. The disc automatically stops after 22 cycles (1 period). The sample is rotated 90° clockwise and new abrasive powder is added to the track. The disc and contact surfaces are cleaned each time. In this way, the second, third and fourth surfaces are also abraded and the first stage is completed after a total of 88 cycles. In the study, 352 cycles were applied to each sample with a total of 16 periods. At the end of 16 periods, weights of the samples which were cleaned by brush were weighed. To find wear losses, the initial weight and the initial volume of each sample were first determined and thus the density of the samples was calculated. Then the difference between the first weight and the weight at the end of the experiment was calculated. The volume loss was calculated by dividing the weight difference by the

density of each sample. Corrosion loss was calculated as equation 2.14 in terms of volume reduction. Wear Loss (ΔV, mm^3 / 5000 mm^2).

$$\Delta V = \frac{\Delta m}{\rho R}$$

(Equation 2.14)

Where;

ΔV: Volume loss after 16 periods, mm^3

Δm: Mass loss after 16 periods, g,

ρR: Density of sample, g / mm^3

Figure 2.21 Abrasion resistance test

2.3.14. High Temperature Resistance Test

Geopolymer and Portland cement samples were produced in dimensions of $40 \times 40 \times 160 mm^3$ and high temperature resistance test was applied. The produced samples were brought to the temperature to be applied 5°C / minute temperature increase in the oven and subjected to high temperature separately at 300, 600, and 900°C for 60 minutes (Figure 2.22). After the experiment was completed in the oven, the samples were allowed to cool to room temperature. A weight had been measured, flexural and compressive strength tests were performed.

Figure 2.22. High temperature resistance test

2.3.15. Accelerated Corrosion Test

Ribbed steel with a diameter of Ø12 was used for the corrosion test. Industrial salt was used in NaCl solution. Cylinder with dimension Ø100×200mm had been used in the test. Reinforcement steel is placed in the center of the cylinder mold 30 mm in height with plastic anti-rust margin components to prevent the reinforcement to touch the mold base. Geopolymer samples were tested after the curing at room temperature for 28 days while the Portland cement samples were cured in water for 28 days after the curing is finishing for all mixtures the test starts. A plastic pool was used for the experimental setup and the metal wire cover was laid on the bottom of the pool and electricity was provided. We used salt solution with a concentration of 5% for the accelerated corrosion test. The positive pole of the direct current source, which applies 12-volt constant voltage to the system, is connected to the upper end of the reinforcement (working electrode) and the negative pole is connected to the metal cover located below (Figure 2.23). Thus, reinforcing rod anode, metal wire cover cathode and NaCl solution also assumed the function of electrolyte. 7 test samples were connected to 7 channels in 4 direct current sources at the same time. After corrosion, weight loss of the reinforcement and adherence loss of the samples was determined.

The pull-out test was performed according to ASTM A944-10 [163] to determine the loss of bond of the samples subjected to corrosion (Figure 2.24). The experiment was applied to the second group of non-corroded samples which we can compare with a group of corroded samples. At the end of the experiment, calculations were made with the help of equation 2.15.

$$\tau = (Bond\ Force)/(\pi \times \theta \times L) \hspace{3cm} (Equation\ 2.15)$$

Where:

Bond Force: the force which needs to pull out reinforcement by the sample, N

Ø: Reinforcement diameter, mm

L: Adherence length (length of reinforcement embedded in the sample), mm

τ: Adherence strength N/mm^2

Figure 2.23 Accelerated corrosion test

Figure 2.24 Bond strength (pullout) test

CHAPTER THREE

RESULTS AND DISCUSSION

In this chapter, 0%, 10%, 20%, 30%, 40% and 50% metakaolin(MK) (M0, M1, M2, M3, M4, and M5 respectively) had been used as a partial replacement with fly ash (FA) as a based material for geopolymer and curing in ambient condition with time, (3, 7, 28, 90, and 180) days for measuring flexural strength and compressive strength to determine which ages using for durability tests. The 28 days give the best results therefore used for the other properties in includes: unit weight and density, flow workability, ultrasonic pulse velocity, water absorption and porosity, sorptivity, wetting-drying, freezing-thawing, rapid chloride permeability, drying shrinkage, abrasion resistance, high temperature resistance, and accelerated corrosion.

3.1. Unit Weight and Density Test Results

The weight of the samples produced in the study was taken at 28 days of curing in the air. Accrediting to TS EN 1015-10 [154], the unit weights and density were calculated. The density and unit weight values of the samples increased in parallel with the increase in the rates of MK substitution used in the preparation of the geopolymer as we have seen in Table 3.1 and Figure 3.1.

The specific weight of MK material is higher than that of the FA, therefore, the density values of the samples increased with an increase in the substitution rates. Also, density is enhanced when MK dosage increased, that means the structure of the samples contains MK is more cohesive and less pores than that samples containing only FA. For example density of M0 mixture containing 0% MK is 2.16 while M5 mixture containing 50% MK is 2.19.

All so we notice, the apparent unit weight of both Portland cement mortar (MC) and mixtures containing 50% MK were 2.11, and 2.10 g/cm^3 respectively very closed. As well, the density of them was 2.22, and 2.19 g/cm^3 respectively. That means the

Amount of water, which absorbed in samples little, maybe because, pores in bodies are decreased when the amount of MK increased that identical with Gökhan et al. [132] was also observed that the apparent porosity and water absorption rates of the samples decreased depending on the increase in the MK substitution rate used in the preparation of the samples. However, what yielded these results was actually the MK having more reactivity than the FA during the polymerization process.

Table 3.1 Unite weight and density of mixtures

Mixtures.	Apparent Density (g/cm³)	Dry Density (g/cm³)	SSD Density (g/cm³)	Unit Weight (g/cm³)
MC	2.45	2.08	2.22	2.11
M0	2.41	2.01	2.16	2.01
M1	2.43	2.02	2.18	2.02
M2	2.45	2.02	2.19	2.04
M3	2.45	2.02	2.19	2.07
M4	2.45	2.02	2.20	2.08
M5	2.44	2.03	2.19	2.10
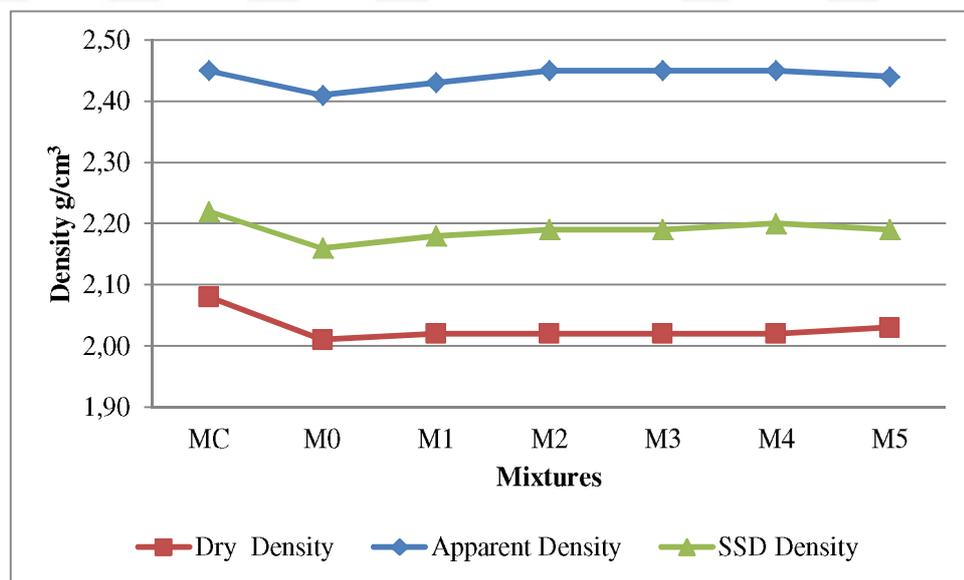
Figure 3.1 Density of mixtures

3.2 Flow Workability Test Results

Flow workability results for each mixture were presented in Table 3.2. It has been observed from Table 3.2 that replacement of MK with FA caused a remarkable decrease in flow workability, as MK replacement increase flow workability was decreased. For

example, flow workability of reference mixture M0 was 257 mm, whilst it was 114 mm for mixture containing 50% MK. This is explained with the specific surface of MK which was very high that absorb mixing water. This result was found to be in agreement with publish results of Sunny A. Jagtap et al [164]. Flow workability Portland cement mortar was 150 mm. Portland cement flowability drops between M3 and M4 mixtures. See Figure 3.2.

Table 3.2 Flow workability test results

Mixture	Flow Workability (mm)
MC	150
M0	257
M1	227
M2	186
M3	163
M4	140
M5	114

Figure 3.2 Workability of Portland cement mortar and geopolymer mortar

3.3. Flexural Strength Test Results

In this work we produced Portland cement mortar samples were cured in water and geopolymer mortar samples were cured at room temperature until the test day, prismatic samples $40 \times 40 \times 160$ mm^3 for each mixture and ages casted. After ages of curing 3, 7,

28, 90, and 180 days, the samples subjected to a single point flexural test. Table 3.3 shows the results of flexural strength of all types of mortar mixes at various ages.

Flexural strength results of all mixtures at ages 3, 7, 28, 90 and, 180 days presented in Figure 3.3. In general, all mixes exhibit continuous increase in strength with increasing in MK contain for all ages.

Table 3.3 Flexural strength of all types of mixes

Mixture	Flexural Strength (MPa)				
	3 days	7 days	28 days	90 days	180 days
MC	5.5	6.6	8.8	9.3	10.3
M0	1.2	1.6	4.8	7.3	9.2
M1	1.5	3.0	5.5	8.1	9.5
M2	2.8	3.3	6.3	8.8	10.8
M3	3.7	5.5	7.8	9.3	11.3
M4	6.9	7.7	8.7	12.3	13.1
M5	9.0	9.4	9.8	12.5	13.3

In age 3days, the strength of mixtures of MC, M0, M1, M2, M3, M4 and M5 were 5.5, 1.2, 1.5, 2.8, 3.7, 6.9, and 9.0 MPa respectively. From the results we can say, the mixtures containing 40% and 50% MK have strength more than Portland cement mortar MC.

Age 7days, the strength of of MC, M0, M1, M2, M3, M4 and M5 were 6.6, 1.6, 3.0, 3.3, 5.5, 7.7, and 9.4 MPa respectively. We notice geopoylmer mixtures incorporating 40%, 50% MK developed flexural strength values than mortar made with only fly ash geopolymer (M0) and Portland cement (MC).

The strength of MC, M0, M1, M2, M3, M4 and M5 were 8.8, 4.8, 5.5, 6.3, 7.8, 8.7, and 9.8 MPa respectively in 28 days. We notice the mixtures with 40% and 50% MK have strength closed to MC.

From the above it is concluded the mixtures containing 40% and 50% MK gets strength at an earlier age compared to cement mortar.

In ages 90 days the strength of mixtures of MC, M0, M1, M2, M3, M4 and M5 were 9.3, 7.3, 8.1, 8.8, 9.3, 12.3, and 12.5 MPa respectively. From the results we can say the mixtures with 40% and 50% MK replacement have strength more than MC.

Ages 180 days, the strength of MC, M0, M1, M2, M3, M4 and M5 were 10.3, 9.2, 9.5, 10.8, 11.3, 13.1, and 13.3MPa respectively. We notice the mixtures with 40% and 50% MK have strength more than MC.

From all mentioned, mixtures with 40% and 50% MK has strength more than cement mortar in all ages curing.

We noticed the flexural strength has increased when MK increased, for example M0 sample strength about 4.8 MPa while in M5 was 9.8 at 28 days as we seen in Figure 3.3. On the other hand the strength of the mixture containing 50% MK in all ages near to strength of cement mortar because the geopolymer mortar exhibits high flexural due to the excellent adherence of geopolymer to the aggregate particles and the remarkable fragility of the geopolymer [165].

Additional the time of curing is an effect on strength until 180 days, improvement continues until 180 days as shown in Fig 3.3. When comparing M5 at 28 days with 180 days we found enhancement in flexural in good rate 9.8 and 13.3 MPa at 28days and 180 days respectively. This increase in the strength of these specimens is due to the continuity of the hydration process.

 At the same time, the mixtures with low ratio of MK 0%, 10%, and 20% ongoing in improved strength with the highest rate, that because the low reactivity and slow setting of the FA hinders the development of resistance. In many cases, FA cannot complete dissolution before the final hardening [166].

At the same time the results of M0, M1, M2, M3 were near to MC at 180 days while in early time, there are big differences between MC and these geopolymer mix, except M4 and M5 have high strength from early ages that mean the high dosages of replacement of MK is very effective in flexural strength at early ages, because, actually the MK is having more reactivity than the FA during the polymerization process [132].
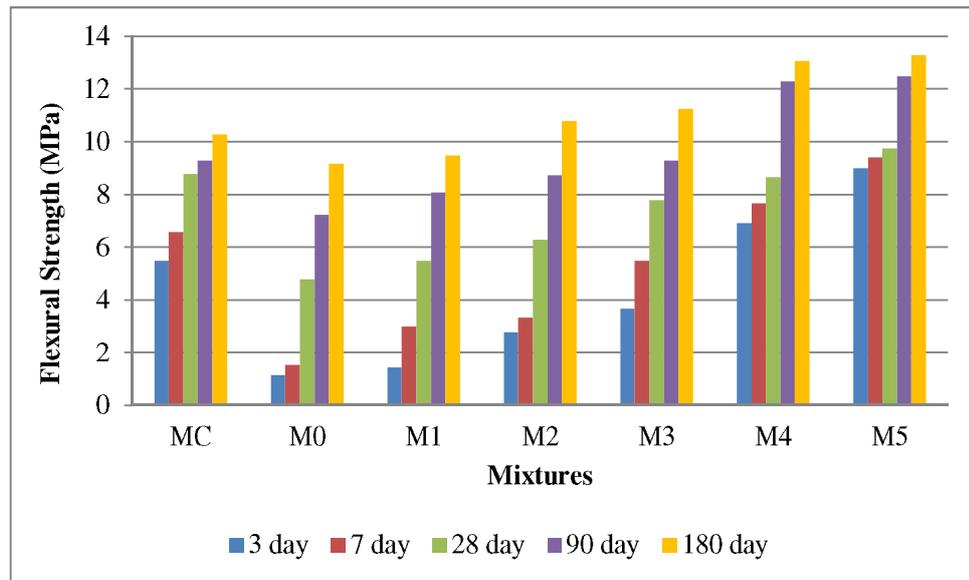
Figure 3.3 Flexural strength for mixtures at all ages

3.4. Compressive Strength Test Results

The Portland cement samples produced in the study were subjected to water cure and compressive strength test was applied to the samples which were divided into bending strength. Geopolymer mortar samples were subjected to the air curing process, then 3 pieces of $40 \times 40 \times 160$ mm^3 prismatic samples were divided into two parts by bending test and each part was subjected to compressive strength test.

As we saw in Table 3.4 MK substitution rate made a significant contribution to the compressive strength values of the samples. Figure 3.4 shows the compressive strength at 3, 7, 28, 90, and 180 days. Strength values increased with an increase in the MK substitution for all ages, the best results obtained with a 50% MK substitution, while the lower values obtained with using 0%MK. These results may be because MK has more reaction than the FA during the polymerization process as Gökhan et al. Mentioned [132].

Table 3.4 Compressive strength of mixtures

Mixture	Compressive Strength (MPa)				
	3 days	7 days	28 days	90 days	180 days
MC	32.3	40.6	53.4	59.4	62.4
M0	4.8	6.5	15.1	21.0	28.4
M1	6.4	10.1	17.0	24.9	33.9
M2	8.9	15.9	26.4	33.2	38.6
M3	18.2	28.3	41.3	41.5	50.4
M4	31.1	41.9	54.7	56.1	56.4
M5	46.8	54.7	60.2	60.5	61.1

In ages 3days the strength of mixtures MC, M0, M1, M2, M3, M4, and M5 were 32.3, 4.8, 6.4, 8.9, 18.2, 31.1, and 46.8 MPa respectively. From the results we can say the mixtures containing 40% MK (M4) is close to Portland cement mortar (MC), however, the mixture containing 50% MK (M5) has strength more than an MC.

Ages 7days, the strength of MC, M0, M1, M2, M3, M4, and M5 were 40.6, 6.5, 10.1, 15.9, 28.3, 41.9, and 54.7 MPa respectively. We notice the mixtures containing 40%MK is near to MC. The strength of M5 is more than an MC.

The strength of MC, M0, M1, M2, M3, M4, and M5 were 53.4, 15.1, 17.0, 26.4, 41.3, 54.7, 60.2 MPa respectively in 28 days. We notice the mixtures with 40%MK and 50% MK have strength closed to Portland cement mortar.

In ages 90 days the strength of mixtures MC, M0, M1, M2, M3, M4, and M5 were 59.4, 21.0, 24.9, 33.2, 41.5, 56.1, 60.5 MPa respectively. From the results we can say the mixtures with 50% MK very near to MC.

Of all the above results, we can notice, compressive strength for high rate replacement of MK, increases dramatically before 28 days of curing, however, the changes in compressive strength are modest with increasing curing ages. Strength at 90 days is near to strength at 28 days. It is noted that the compressive strength develops quickly before 28 days of curing. It can be concluded that early strength of geopolymer increases rapidly and this is consistent with previously reported findings [167-169, 147], which concluded that the compressive strength of geopolymer increased slowly after 28 days of curing and the strength gain beyond this period was insignificant.

Ages 180 days, the strength of MC, M0, M1, M2, M3, M4, and M5 were 62.4, 28.4, 33.9, 38.6, 50.4, 56.4, and 61.1 MPa respectively. We notice the mixtures M5 has strength closed to MC.

From all mentioned, mixtures with 40% and 50% MK replacement has strength more than Portland cement mixture in all earlier ages curing, while in later ages the results of M4 and M5 were insignificant improvement. On the other hand, the low ratio of MK mixtures continues to develop strength until 180 days, that's because the low reactivity of the FA hinders the development of resistance. In many cases, FA cannot complete dissolution before the final hardening [166].

The mixture containing 50%MK has strength more than Portland cement at 28 days nevertheless in ages 180 both have the same strength. This behavior is mean geopolymer contain a high ratio of MK are owing strength very fast in early ages compare with MC which have the highest strength at 180 days. The same time, the best results obtained from geopolymer at 28 days when compare with later ages, curing ages effective in strength after 28 days, but not significant (Figure 3.4). Manjunatha et al. [170] report, the compressive strength values of the samples had an upward trend with an increase in MK amount and the curing times applied to the samples until 28 days.

This higher strength development rate at early ages and lower strength development rate can be explained with the activation energy such that the activation energy of metakaolin is lower than that of fly ash. Sun and Vollpracht [171] reported that the binding material with low activation energy react faster than material with a high activation energy level.
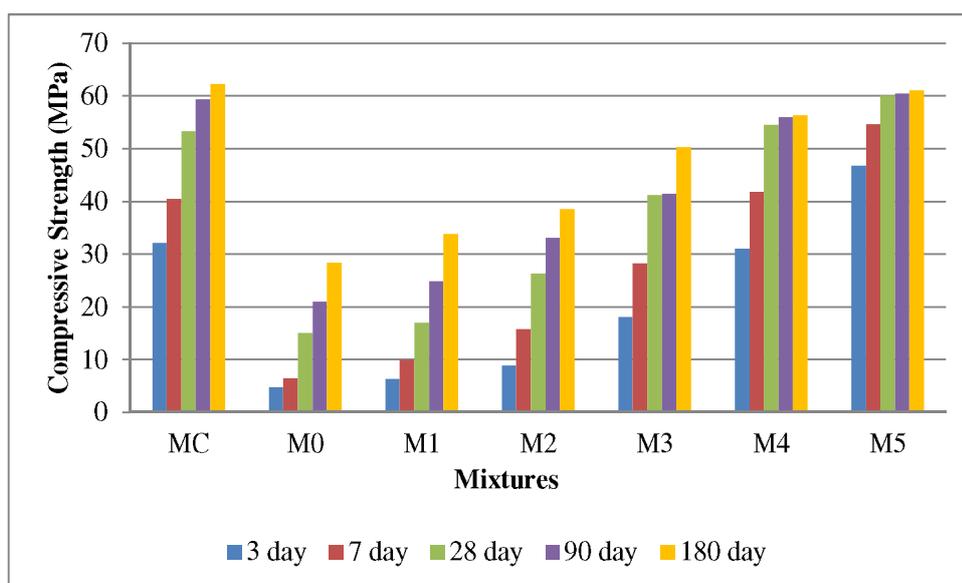
Figure 3.4 Compressive strength for mixtures at all ages

3.5. Ultrasonic Pulse Velocity Test Results

The transition time of ultrasonic sound was measured in dry and saturated surface dry SSD conditions at 28 days in ambient condition for geopolymer mixtures samples. Ultrasonic pulse velocity was calculated by converting the measured times from microseconds to seconds and dividing the sample length of 0.16 m. The ultrasonic pulse velocity values calculated for the dry and saturated dry surfaces are given in Table 3.5 and the graph of changes in ultrasound velocities are given in Figure 3.5. In addition, the ultrasonic pulse velocity of Portland cement samples cured in water for 28 days to compare with geopolymer mortars.

Table 3.5 depicted the impacts of the amount of MK in geopolymer mixture, on the ultrasonic pulse velocity at 28 days of age in saturated surface dry and oven dry case. An increase in the MK content from 0 to 50% could result an improvement in geopolymeric reaction and reduced the porosity by densifying microstructure of specimens, and thereby enhanced the ultrasonic pulse velocity values from 2596 to 3902 m/s and 2404 to 3599 m/s; for saturated surface dry and oven dry case, respectively. The ultrasonic pulse velocity values in the saturated surface dry case were higher than oven dry case. This was explained by the water content of saturated specimens [172].On the other hand, comparisons between ultrasonic pulse velocity values of geopolymer mixtures and Portland cement mixture showed that geopolymer mixture containing 40% and 50% MK as FA replacement developed closer velocity values to Portland cement

mixture. However, M1, M2 and M3 geopoylmer mixtures incorporating 10%, 20% and 30% MK were lower ultrasonic pulse velocity values than that of Portland cement mixture (MC).

Table 3.5 Ultrasonic pulse velocity of the mixtures

Mixture	Ultrasonic Pulse Velocity SSD (m/s)	Ultrasonic Pulse Velocity Dry (m/s)
MC	3912	3789
M0	2596	2404
M1	3057	2883
M2	3321	3218
M3	3583	3334
M4	3810	3461
M5	3902	3599
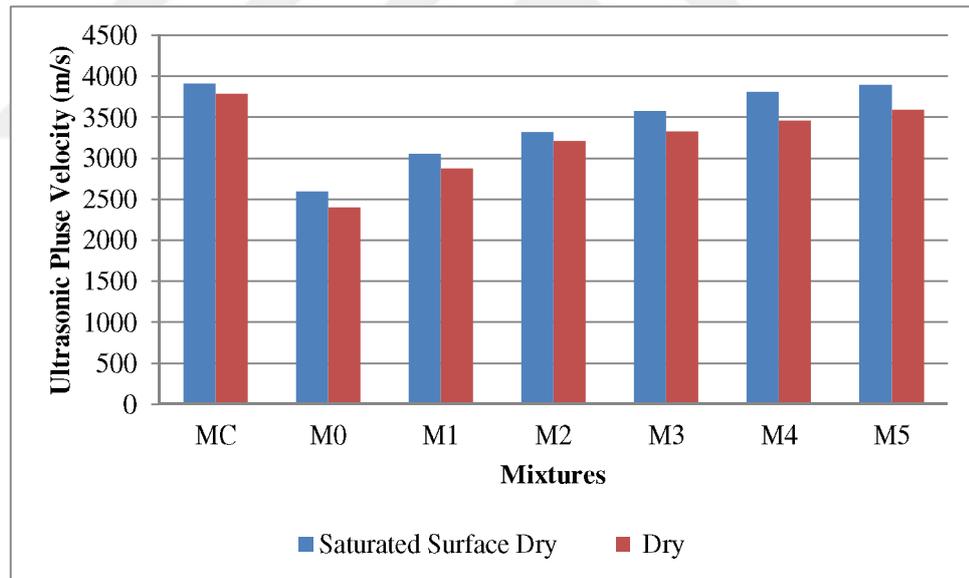
Figure 3.5 The Ultrasonic pulse velocity of the Mixtures

3.6. Water Absorption and Porosity Test Results

Geopolymer mixtures cured in ambient condition for 28 days, then these samples drying in oven for 24 hours at 100°C, after that the geopolymer samples and Portland cement samples weight at room temperature measured that was dry weight. For saturated surface dry weight the samples kept in water for at least 24 hours. Water absorption and

porosity were determined using the measured weights. The evolution of the amount of water absorbed and porosity is reported in Table. 3.6

Table 3.6 The water absorption and void ratio of the mixtures

Mixture	Absorption (%)	Porosity (%)
MC	7.4	15.4
M0	8.9	17.9
M1	8.7	17.3
M2	8.7	17.5
M3	8.7	17.6
M4	8.1	16.6
M5	8.0	16.2

The evolution of the amount of water absorbed is shown in Figure 3.6. The water absorbed of geopolymer varies from 8.0% to 8.9 % of specimens while for MC was 7.4% cured in water for 28 days. The maximum water absorption was recorded at M0 mixture (8.9%) while the minimum water absorption was recorded at M5 (8.0%). MK no longer significant and remains almost constant at ratio replacement of MK 10%, 20%, and 30%. See Figure 3.6

In general the effect MK on FA geopolymers varied, as confirmed by Shadnia, et al [173], show that there is an obvious variation in specific gravity of the geopolymer mortars with various dosages of phase change material, and the unit weight decreases with more incorporation of phase change material.
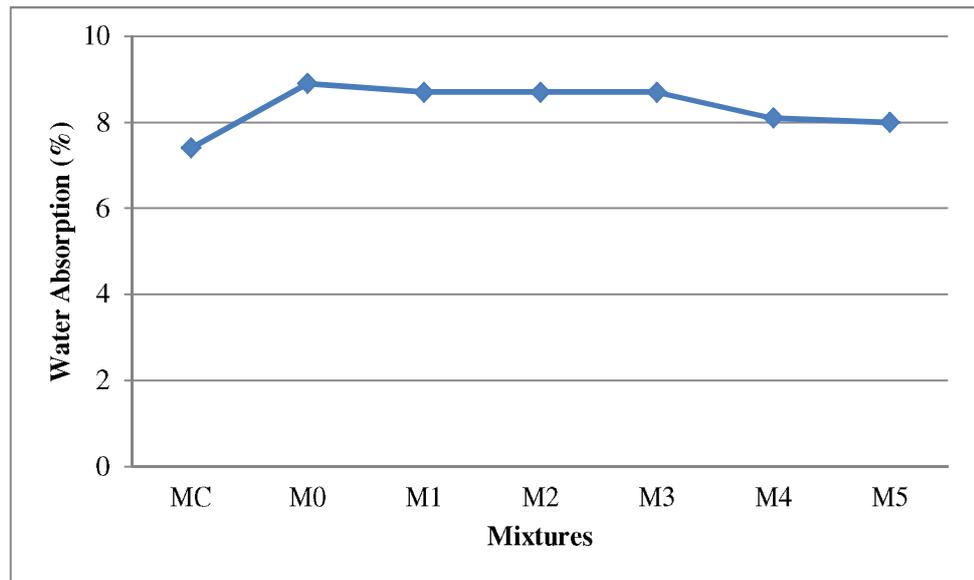
Figure 3.6 The water absorption of the mixtures

The percentage of porosity is shown in Figure 3.7. The porosity varies from 16.2% to 17.9% of geopolymer specimens cured at ambient condition and 15.4% of MC specimens cured in water. The maximum porosity was recorded at mixture containing 0%MK (17.9%) while the minimum water absorption was recorded at M5 which containing 50%MK (16.2%).
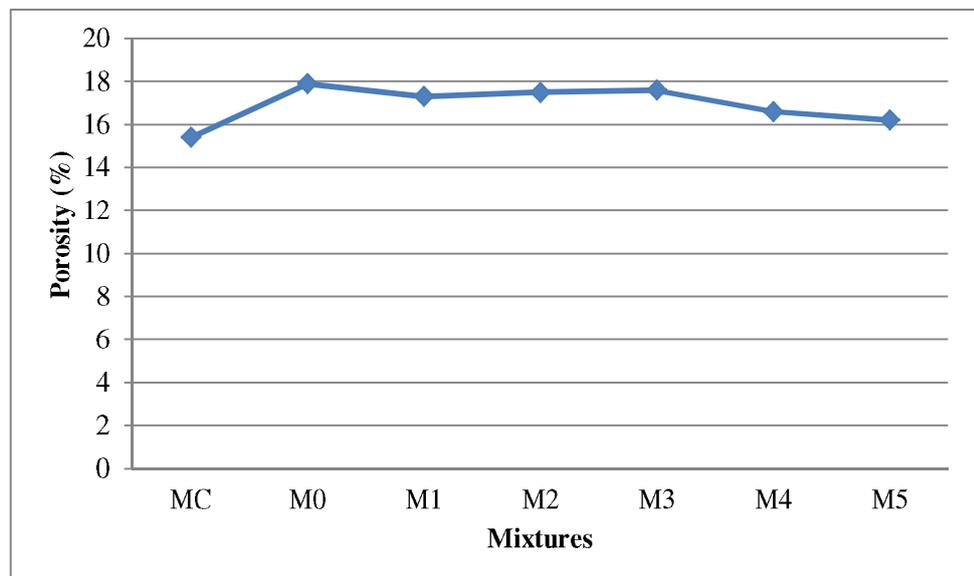
Figure 3.7 Porosity of the mixtures

3.7. Sorptivity Test Results

Portland cement samples and geopolymer samples dried in the oven, we measured the weight of them, then we made the sorptivity test according to ASTM C1585 [157]. The weight of samples at 1, 5, 10, 20, 30 minutes and 1, 2, 3, 4, 5 and 6 hours measured, from the weights of the samples, through these times, initial rate water absorption coefficient was calculated. To calculate secondary rate water absorption coefficient the weights of samples measured at 1, 2, 3, 4, 5, 6, 7 and 8 days. The results are given in Table 3.7 and graphically in Figure 3.8 and 3.9.

The initial rate water absorption coefficients of M0, M1, M2, M3, M4, and M5 geopolymers were 0.0515, 0.0505, 0.0490, 0.0487, 0.0465 and, 0.0423, respectively. Secondary rate water absorption coefficients were calculated as 0.0005, 0.0005, 0.0003, 0.0003, 0.0003, and 0.0003 respectively.

The initial and secondary rate water absorption coefficient value of the Portland cement mortar cured in water for 28 days were 0.0103 and 0.0048, respectively.

When the MC and the geopolymer samples compared, there is a big difference between them in the results for the initial rate water absorption coefficient. However, MK positively effects on the results test of geopolymer (Figure 3.8).

In general, the best value had been obtained in geopolymer at mixture containing 50%MK (M5), that mean MK have positive effects on initial rate water absorption coefficients from 0% to 50% MK replacement with FA.

Secondary rate water absorption coefficients were very close to each other in mixtures of geopolymer. The secondary rate water absorption coefficient of MC samples (0.0048) was higher than all types geopolymer samples (Figure 3.9).

Table 3.7 Initial & secondary rate water absorption coefficients

Mixture	Initial Rate of Water Absorption Coefficients $(mm/s^{1/2})$	Secondary Rate of Water Absorption Coefficients $(mm/s^{1/2})$
MC	0.0103	0.0048
M0	0.0515	0.0005
M1	0.0505	0.0005
M2	0.0490	0.0003
M3	0.0487	0.0003
M4	0.0465	0.0003
M5	0.0423	0.0003
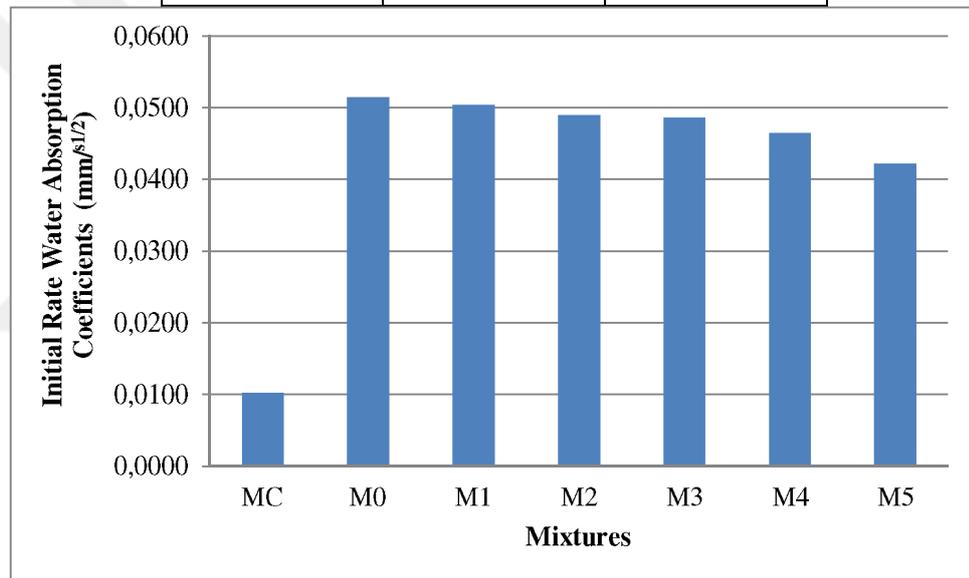
Figure 3.8 Initial rate water absorption coefficients of mixtures
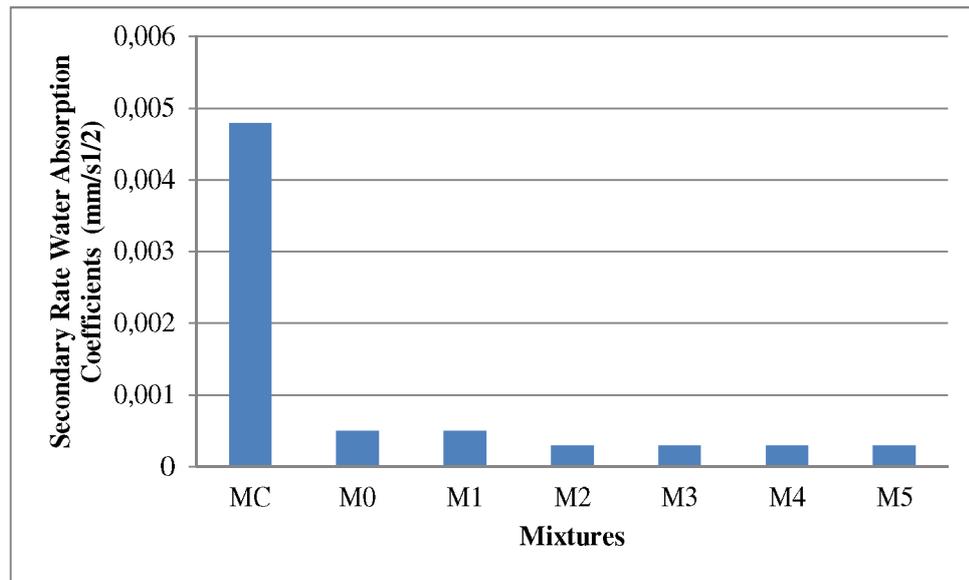
Figure 3.9 Secondary rate water absorption coefficients of mixtures

3.8. Wetting-Drying Test Results

All samples were dry in oven for 24 hours at 100°C to obtain constant weight. According to ASTM D5313 [158] the weight losses were determined. After 80 cycles of wetting-drying we measured the weight, flexural and compressive strength of samples. It was examined by taking pictures at the end of 80 cycles (Figure.3.10)

Figure.3.10 Wetting-drying test

When visually examined during the wetting-drying cycle, the samples did not suffer any major part losses during the entire cycle. However, M0 produced samples, especially in the corner parts of the parts began to break. Already, 0% MK all samples suffered the most weight loss (Table 3.8). It's also worth noting that no visual deterioration was observed on the surface of all specimens after 80 cycles. All this shows that FA based geopolymer mortars, FA-MK geopolymer and Portland cement mortar are stable under drying and wetting cycles, and can be used accordingly in severe hot and dry climate.

Table 3.8 Weight of samples in wetting-drying test

Mixture	Weight Before Test (g)	Weight After Test (g)	Weight Loss (%)
MC	538.6	542.3	-1
M0	516.7	504.2	2
M1	514.8	508.3	1
M2	530.6	525.1	1
M3	532.8	526.1	1
M4	538.8	534.5	1
M5	528.6	523.6	1

The compressive strength of geopolymer mortars during wet and dry conditions is reported in Table 3.9 and. The strength before the test was 53.4, 15.1, 17.0, 26.4, 41.3, 54.7and 60.2 MPa. After 80 cycles of test strength were 52.8, 14.6, 28.7, 43.1, 52.6, 60.8 and 62.6 MPa to MC, M0, M1, M2, M3, M4, and M5 respectively. Such condition didn't have any effect on geopolymer mortar and cement mortar. The behavior of samples in case of compressive strength is opposite of their flexural behavior.

The flexural strength of geopolymer mortars during wet and dry conditions is reported in Table 3.9 and Figure 3.11. It can be seen that, the decreasing strength were 26, 79, 59, 21, 26, 31, 21 to MC, M0, M1, M2, M3, M4, and M5 respectively. From the data, such condition, reduces strength, but, this negative effect reduced when MK increase.

Table 3.9 Strength before and after wetting-drying test

Mixture	Compressive Strength			Flexural Strength		
	Before Test (MPa)	After Test (MPa)	Decreasing (%)	Before Test (MPa)	After Test (MPa)	Decreasing (%)
MC	53.4	52.8	1	8.8	6.5	26
M0	15.1	14.6	4	4.8	1.0	79
M1	17.0	28.7	-69	5.5	2.2	59
M2	26.4	43.1	-63	6.3	5.0	21
M3	41.3	52.6	-27	7.8	5.8	26
M4	54.7	60.8	-11	8.7	6.0	31
M5	60.2	62.6	-4	9.8	7.7	21
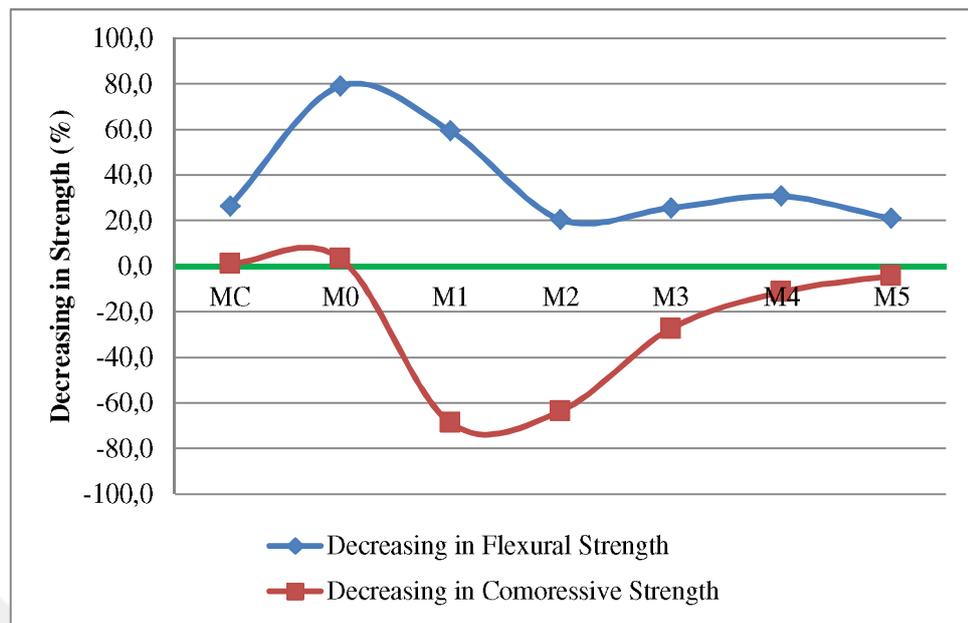
Figure 3.11 Strength in wetting-drying test

It's also worth noting that no visual deterioration was observed on the surface of all specimens after 80 cycles. All this shows that FA-MK based geopolymer mortars are stable under dry and wetting cycles, and can be used accordingly in severe hot and dry climate.

3.9. Freezing-Thawing Test Results

The alkaline activated FA-MK geopolymer mortar samples produced in this study were subjected to ambient condition curing process and Portland cement had been cured in water until 28 days. Then 3 pieces of $40 \times 40 \times 160$ mm^3 prismatic samples from each mixture saturated with water were placed in the freeze thaw test cabinet. The test specimens were frozen by reaching -18ºC and then thawed by reaching to 4ºC and subjected to a total freezing and thawing cycle. The experiment needs about 10 weeks for a total of 300 cycles. Weights and ultrasonic pulse velocity of the samples were measured after every 100 cycles. Weight losses, decrease in ultrasonic velocity and strength losses was determined at the end of 300 freeze thaw cycles. The samples after the experiment are shown in Figure 3.12.

Weight loss after freezing-thawing were calculated and given in Table 3.10. Ultrasonic pulse velocity changes (%) are calculated and given in Table 3.11.

Figure 3.12 The samples after the 300 cycles of freezing-thawing

The weight decrease resulting from the freeze-thaw of the MC sample produced with Portland cement was 0%. The weight decrease of M0, M1, M2, M3, M4, and M5 were 54%, 20%, 21%, 17%, 15%, and 15% respectively.

Table 3.10 Decreasing in weight after freezing-thawing

Mixture	Weight Before Test (g)	Weight After 300 Cycles (g)	Decreasing in Weight (%)
MC	589.0	589.0	0
M0	563.0	261.0	54
M1	565.0	453.0	20
M2	563.0	445.0	21
M3	588.0	487.0	17
M4	587.0	498.0	15
M5	565.0	482.0	15

The ultrasonic velocity loss caused by freezing-thawing of the MC sample was 0%. The ultrasonic velocity losses of mixtures containing 0%, 10%, 20%, 30%, 40% and 50% MK were NA, 23%, 11%, 4%, 5%, and 3% respectively.

Table 3.11 Ultrasonic pulse velocity changes after freezing-thawing

Mixture	Ultrasonic Pulse Velocity Before Test (m/s)	Ultrasonic Pulse Velocity After 300 Cycles (m/s)	Decreasing in Ultrasonic Pulse Velocity (%)
MC	3912	3902	0
M0	2596	NA	NA
M1	3057	2363	23
M2	3321	2971	11
M3	3583	3448	4
M4	3810	3626	5
M5	3902	3783	3

From results can be concluded when MK dosages increased the decreasing of both weight and ultrasonic pulse velocity due to freezing are decreased.

Decrease of flexural strength after freezing and thawing of M0, M1, M2, M3, M4, and M5 geopolymers were 73%, 33%, 38%, 20%, 24%, and 18% respectively. While the MC sample produced with Portland cement was 2% (see Table 3.12 and Figure 3.13).

Table 3.12 Flexural strength after freezing - thawing

Mixture	Flexural Strength Before Test (MPa)	Flexural Strength After Test (MPa)	Decreasing Flexural Strength (%)
MC	8.8	8.6	2
M0	4.8	1.3	73
M1	5.5	3.7	33
M2	6.3	3.9	38
M3	7.8	6.2	20
M4	8.7	6.6	24
M5	9.8	8.0	18
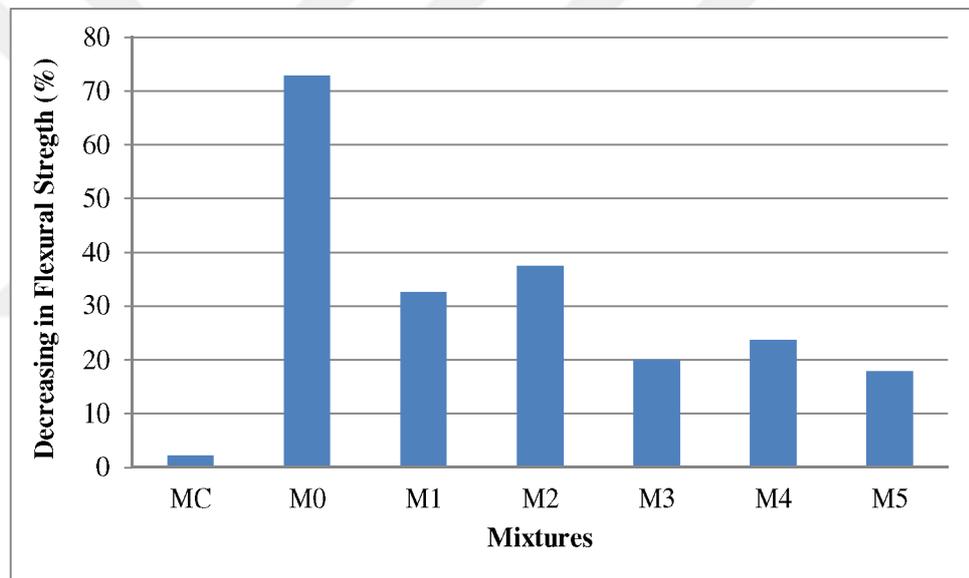
Figure 3.13 Decreasing in flexural strength after freezing - thawing

Decrease of compressive strength after freezing and thawing of geopolymer containing 0%, 10%, 20%, 30%, 40% and, 50% MK were 89%, 64%, 62%, 63%, 60% and, 55%. While the MC produced with Portland cement was 1% (see Table 3.13 and Figure 3.14).

Table 3.13 Compressive strength after freezing - thawing

Mixture	Compressive Strength Before Test (MPa)	Compressive Strength After Test (MPa)	Decreasing in Compressive Strength (%)
MC	53.4	52.8	1
M0	15.1	1.6	89
M1	17.0	6.2	64
M2	26.4	10.0	62
M3	41.3	15.3	63
M4	54.7	22.0	60
M5	60.2	27.1	55
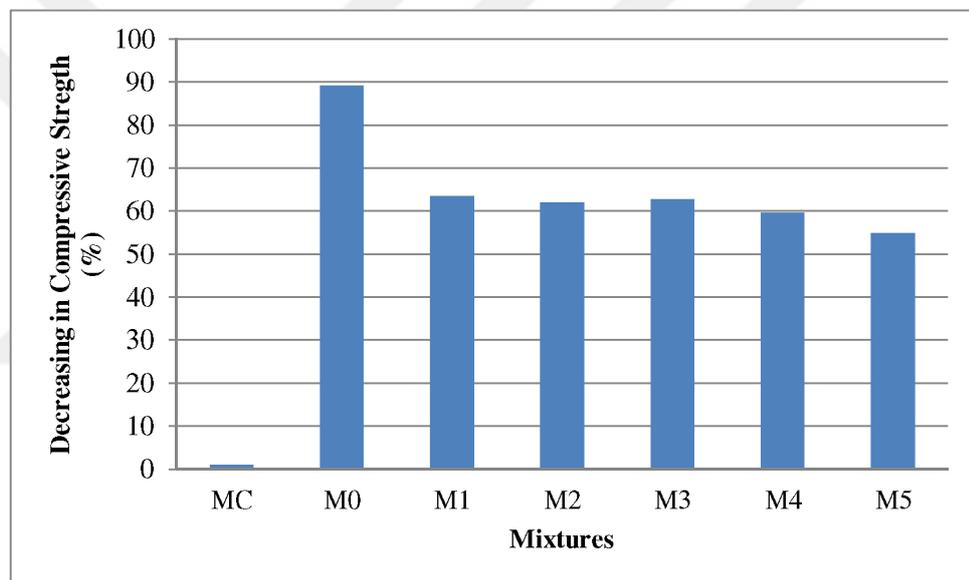
Figure 3.14 Decrease of compressive strength after freezing - thawing

From results can be concluded when MK dosages increased the resistance to freezing-thawing, all so increased. That are identified with the results of compressive and flexural strength which obtained through normal condition in this studying.

The greater abundance of C-S-H gel greatly improves the microstructure of geopolymer mortars [174]. As a result, it can be concluded that geopolymer mortars with a high ratio of MK have good durability under the condition of very low temperatures compared with low ratio of MK geopolymer mortars.

Again, it can be said that the decreases in both flexural and compressive strengths aren't having the same behavior toward frost condition because the loss of compressive more

than flexural, that may be because the geopolymer mortar exhibits high flexural due to the good bond of geopolymer to the aggregate particles and the remarkable fragility of the geopolymer [165].

3.10. Rapid Chloride Permeability Test Results (RCPT)

In the study, geopolymer mortar samples were cured at ambient condition $20\pm1°C$ for 28 days. Portland cement samples were cured in water for 28 days. The test specimens which cut at 50 mm thickness and Ø100 mm diameter in stone cutting machine, then they were subjected to rapid chloride permeability test in accordance with ASTM C1202 standard [160]. Maximum values of Coulomb, of the samples at the end of 2 hours (except Portland cement samples, the test continues to 6 hours) were shown in Table 3.14. The results of chloride permeability graphically in Figure 3.15.

The rapid chloride permeability values of the samples of geopolymer with 0%, 10%, 20%, 30%, 40% and 50% MK replacement were measured as 8125, 7724, 7539, 7212, 6749, and 5666 Coulomb, respectively. The rapid chloride permeability value of the MC samples was determined as 5628 Coulomb at 6 hours while at 2 hours was1514 Coulomb. According to ASTM C1202 standard, the all geopolymer mixtures and cement samples are in high chloride permeability class since they exceed the 4000 Coulomb limit.

In general mixtures containing 40% and 50% MK are lower than samples with 0% and 10% MK. From the results, the content of MK has a positive effect on the rate of chloride permeability although all mixtures of geopolymer classified high according to ASTM 1202 but there is a reduction in Coulomb when increased in MK dosages for example mixture with 0%MK was 8125 while mixture containing 50% MK was 5666.

All so we noticed, the test of the geopolymer samples doesn't last more than 2 hours because the temperature of device reach to $82\pm1°C$ was self-stop while, MC samples continue for 6 hours.

Table 3.14 The results of chloride ion permeability

Mixture	Chloride Ion Permeability (Coulomb)
MC	1514
M0	8125
M1	7724
M2	7539
M3	7212
M4	6749
M5	5666
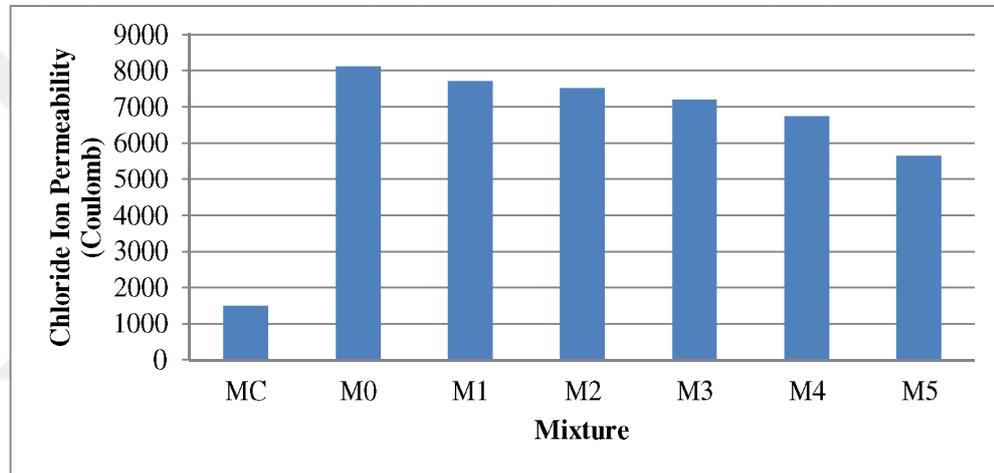
Figure 3.15 The results of chloride ion permeability for all mixtures.

3.11. Drying Shrinkage Test Results

The mortar of geopolymer samples was removed from molds, immediately the first measurement was made. The samples were kept in the laboratory with $20\pm1°C$ temperature and $50\pm10\%$ relative humidity during the experiment. In order to calculate the change in length due to contraction, TS ISO 1920-8 [161] standard was taken as reference, and the change in length was determined by measuring every day for the first 14 days, every week for up to 91 days and every month for 360 days as we seen in Table 3.15.

Drying shrinkage is usually considered as a significant durability parameter for concrete and cement mortar because it suggests the formation of potential cracks in the hardened cementitous materials.

The shrinkage of the geopolymer mortar and Portland cement mortars represented in Figure 3.16. This shrinkage behavior is due to the evaporation of internal water from pore network of the binder to the external environment with relatively low humidity level. During the drying process, a capillary stress is formed in the capillary water with menisci, resulting in the shrinkage strain. Most of the drying shrinkage takes place within the first day, because of the rapid internal relative humidity loss from the freshly formed surface of the specimens after demoulding.

The results of drying shrinkage reported in Table 3.15, the shrinkage values of M0, M1, M2, M3, M4, and M5 were 0.65%, 0.58%, 0.45%, 0.14%, 0.12%, and 0.11%, respectively at 14 days, while after 360 days were 0.71%, 0.63%, 0.50%, 0.19%, 0.16% and 0.15% respectively. MC samples underwent 0.13% length change after 14 days and 0.16% after 360 days.

The changes in length were clearly influenced by MK ratios. At the end of 360 days, the samples of MC, M4 and M5 showed the same values while the maximum changes were observed samples of M0, M1, and M2. In all samples, the change in length became constant after 56 days.

From the results, the geopolymer mortar has low drying shrinkage when MK contain increase may be due to enhancement in structures of mortar as seen in the results of density.

These results which obtained from work were corresponded with Kouamo [175], studied the impact of different dosage of MK on the linear shrinkage of geopolymer mortar prepared with volcanic ash. They found the linear shrinkage of the mortar samples is increasing with the increase of curing days, and the mortar sample incorporating higher dosage of MK shows much lower linear shrinkage than the samples containing lower MK content because the gel resulted in by high dosages of MK is much thicker. Tao Yanga et al [141], the replacement of FA for MK in designing geopolymer mixes, shows a possibility of decreasing the drying shrinkage strain and resulting structural stability problem of the geopolymer products.
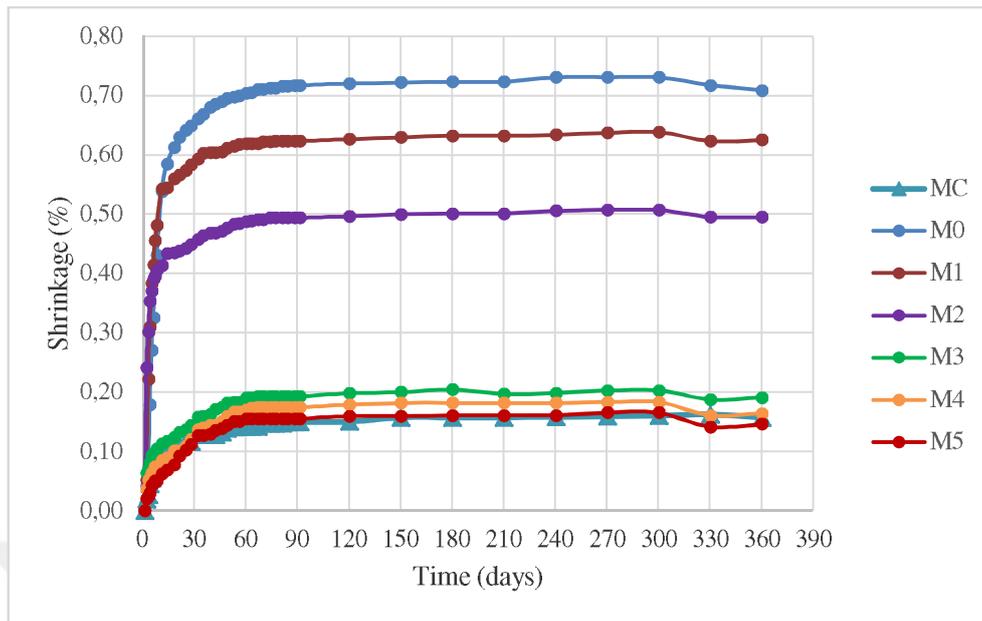
Figure 3.16 The change length to all samples

Table 3.15 The change length to all samples

| Sample Age (Days) | Normal Mixture | Geopolymer Mixtures | | | | | |
| | MC | M0 | M1 | M2 | M3 | M4 | M5 |
	Length Change (%)	Length Change (%)	Length Change (%)	Length Change (%)	Length Change (%)	Length Change (%)	Length Change (%)
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	0.02	0.04	0.05	0.24	0.05	0.04	0.02
3	0.03	0.05	0.22	0.30	0.07	0.05	0.03
4	0.05	0.18	0.31	0.35	0.08	0.06	0.03
5	0.06	0.27	0.38	0.37	0.09	0.06	0.04
6	0.06	0.33	0.41	0.39	0.09	0.06	0.05
7	0.07	0.40	0.46	0.40	0.10	0.07	0.05
8	0.09	0.43	0.48	0.41	0.10	0.07	0.05
9	0.10	0.54	0.54	0.41	0.11	0.09	0.06
10	0.11	0.59	0.54	0.43	0.11	0.09	0.07
11	0.11	0.61	0.56	0.44	0.12	0.10	0.08
12	0.12	0.63	0.57	0.44	0.12	0.10	0.09
13	0.12	0.64	0.57	0.44	0.13	0.11	0.10
14	0.13	0.65	0.58	0.45	0.14	0.12	0.11

21	0.13	0.66	0.59	0.46	0.15	0.14	0.13
28	0.13	0.67	0.60	0.46	0.15	0.14	0.13
35	0.13	0.68	0.60	0.47	0.16	0.14	0.13
42	0.13	0.69	0.60	0.47	0.16	0.14	0.14
49	0.14	0.70	0.61	0.48	0.18	0.16	0.14
56	0.14	0.70	0.62	0.49	0.18	0.17	0.15
63	0.14	0.71	0.62	0.49	0.19	0.17	0.16
70	0.15	0.71	0.62	0.49	0.19	0.17	0.16
77	0.15	0.71	0.62	0.49	0.19	0.17	0.16
84	0.15	0.72	0.62	0.49	0.19	0.17	0.16
91	0.15	0.72	0.62	0.49	0.19	0.17	0.16
120	0.15	0.72	0.63	0.50	0.20	0.18	0.16
150	0.16	0.72	0.63	0.50	0.20	0.18	0.16
180	0.16	0.72	0.63	0.50	0.20	0.18	0.16
210	0.16	0.72	0.63	0.50	0.20	0.18	0.16
240	0.16	0.73	0.63	0.51	0.20	0.18	0.16
270	0.16	0.73	0.64	0.51	0.20	0.18	0.17
300	0.16	0.73	0.64	0.51	0.20	0.18	0.17
330	0.16	0.72	0.62	0.50	0.19	0.16	0.14
360	0.16	0.71	0.63	0.50	0.19	0.16	0.15

3.12. Abrasion Resistance Test Results

The abrasion resistance of the samples obtained from activation of FA and MK with MS (10% Na) at 28 days in ambient condition $20 \pm 1°$ C was determined. In addition, the weight loss and volume loss values of the sample which was cured in water for 28 days of the MC produced with Portland cement were determined in order to compare with the geopolymer samples. At the end of the böhme abrasion test, the results based on weight loss and volume loss is given in Table 3.16.

From Table 3.16, abrasion testing results were presented in terms of weight loss and volume loss for all mixtures at 28 days of curing. A close observation reveals that the loss of weight decreased with increasing replacement levels of MK. The lowest abrasion

values were obtained from Portland cement mixture. The weight loss and volume loss of Portland cement mixture were 31.5 g and 15077 $mm^3/5000\ mm^2$, respectively. They were changed from 46 g to 39 g and 21581 to 18552 $mm^3/5000\ mm^2$, respectively, for geopolymer mixture made with 0% to 50% MK replacement with FA. Although all geopolymer mixtures showed lower abrasion resistance than that of Portland cement mixture, higher replacement of MK with FA result with higher abrasion resistance in comparison to mixture containing the lower amount of MK. Development in abrasion resistance of MK containing geopolymer mixture with an increase in amount of MK seemed to get an asimptot a value, when replacement ratio becomes 30% or beyond. Moreover, it can be seen from Table 3.17 that there was a good relation between weight loss and volume loss for all mixtures, the lower weight loss corresponded to the lower volume loss. This was explained with the changes of mechanical properties, the higher compressive or flexural strength corresponded to higher abrasion resistance.

Table 3.16 Abrasion results for all samples

Mixtures	Decreasing in Abrasion Weight (g)	Decreasing in Volume (mm³/5000mm²)
MC	31.5	15077
M0	46.0	21581
M1	45.0	21040
M2	41.5	19775
M3	40.0	18953
M4	40.5	18938
M5	39.0	18552

3.13. High Temperature Resistance Test

To investigate the effect of high temperature, samples of geopolymer mortar were cured at ambient condition at 20±1°C for 28 days. Cured in water for 28 days for Portland cement samples. The oven temperature was subjected to a test temperature of 60 minutes at 300°C, 600°C, and 900°C with a temperature increase of 5°C / min. The appearance of the samples after high temperature at 300°C and 900°C is as in Figure 3.17, and 3.18 respectively. After cooling the samples to room temperature, flexural and compressive strength test was applied. Flexural strength as a result of high temperature effect is given in Table 3.17 and compressive strength is given in Table 3.18

The flexural strength of the mixtures, MC, M0, M1, M2, M3, M4, and M5 at 300°C were 8.3, 4.1, 5.8, 7.2, 8.0, 7.7 and 9.0 MPa. For 600°C the strength were 3.7, 2.3, 2.1, 3.7, 3.9, 4.3 and 4.8 MPa respectively. While the flexural strength at 900°C were 0.6, 3.6, 2.5, 2.5, 2.3, 2.2, and 2.3 MPa respectively

The compressive strengths which obtained after exposure to high temperature at 300°C, 600°C, and 900°C, for MC, M0, M1, M2, M3, M4, and M5 were 57.1, 22.1, 23.2, 32.4, 49.2, 56.6, and 63.4 MPa at 300 °C respectively. At 600°C were 34.9, 15.8, 16.7, 28.1, 32.8, 42.4, and 43.9 MPa respectively. While in 900°C strength were 10.9, 23.9, 19.3, 20.3, 21.6, 20.2, and 20.8 MPa respectively.

The results of geopolymer samples aren't affected in 300°C that mean this degree didn't cause any damage to the microstructure of samples, on the contrary, there is improved in compressive strength, for example the strength of M0 and M5 at 20°C were15.1MPa and 60.2MPa, while in 300°Care 22.1MPa and 63.4 MPa respectively. That improvement may be due to changes in phase of mortar structures, the same principle of brick making when exposed to high temperature.

The degree 600°C, geopolymer samples show losing in both strength (flexural and compressive), but in 900°C, there are improving in compressive strength in mixtures containing 0% and 10% MK while the other mixtures there were losing in strength.

According to the results of Pan et al. [176], the compressive strength of geopolymer mortars prepared using two types of FA sometimes increased, but at other times decreased when the specimens were exposed to the temperature of 800 °C. Kuenzel [139] studied the mechanical performance of geopolymer mortar containing MK after exposure to high temperature, and concluded that the microstructure, porosity and strength of the specimens were not greatly influenced by the temperature up to 800 °C, and the using of silica sand improved the mechanical behavior of the geopolymer mortar exposure to temperature up to 1000°C show Figures (3.19 and 3.20) .

Figure3.17 The appearance of the samples at 300℃

Figure3.18 The appearance of the samples after 900℃

Table 3.17 Flexural strength change after high temperature

Mixture	High Temperature Flexural Strength (MPa)			
	20ºC	300ºC	600ºC	900ºC
MC	8.8	8.3	3.7	0.6
M0	4.8	4.1	2.3	3.6
M1	5.5	5.8	2.1	2.5
M2	6.3	7.2	3.7	2.5
M3	7.8	8.0	3.9	2.3
M4	8.7	7.7	4.3	2.2
M5	9.8	9.0	4.8	2.3

Table 3.18. Compressive strength change after high temperature

Mixture	High Temperature Compressive Strength (MPa)			
	20ºC	300ºC	600ºC	900ºC
MC	53.4	57.1	34.9	10.9
M0	15.1	22.1	15.8	23.9
M1	17.0	23.2	16.7	19.3
M2	26.4	32.4	28.1	20.3
M3	41.3	49.2	32.8	21.6
M4	54.7	56.6	42.4	20.2
M5	60.2	63.4	43.9	20.8
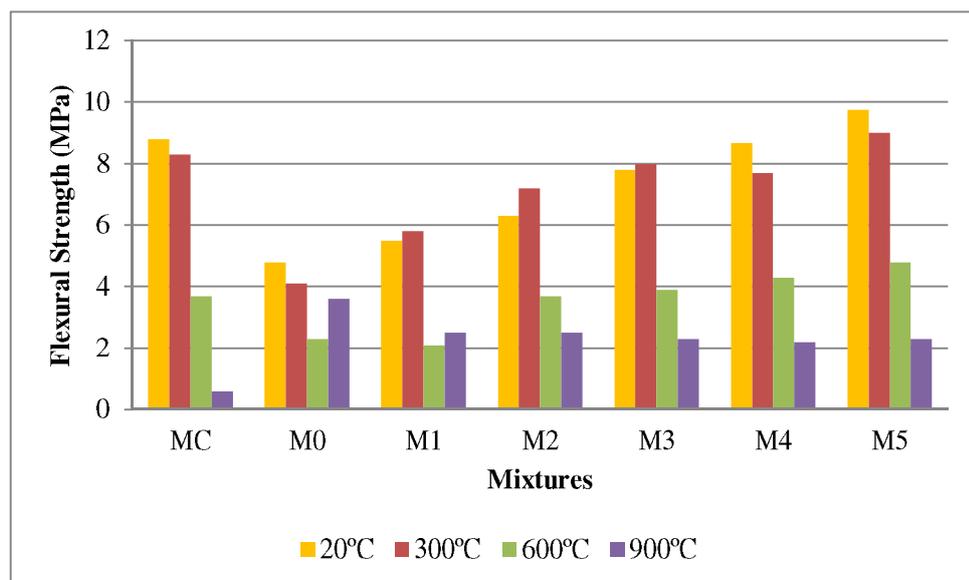
Figure 3.19 Flexural strength change after high temperature
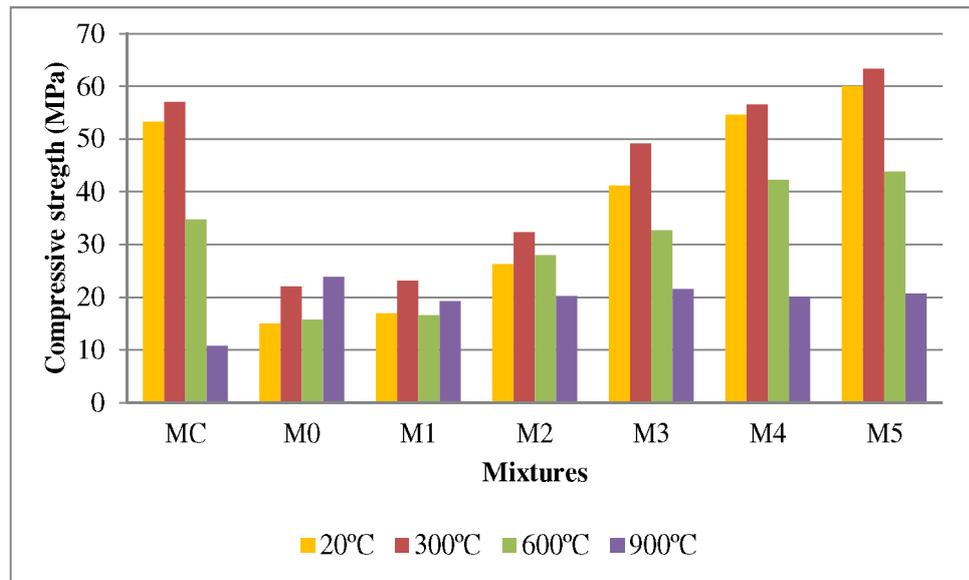
Figure 3.20 Compressive strength change after high temperature

3.14. Accelerated Corrosion Test Results

In order to investigate the corrosion and reinforcement bond of geopolymer samples and compare with Portland cement mortar. Samples of geopolymer cured in ambient condition for 28 days before the start of the test. Portland cement samples were cured in water for 28 days and prepared for the experiment. The weight decrease was determined by taking the weight before corrosion and after corrosion of the reinforcement. Bond test was performed to determine the decrease of bonds of the reinforcement which was subjected to accelerated corrosion test and located in the middle of cylinder samples $100\emptyset \times 200mm$ (Figure 3.21). The reinforcement was stripped off from the geopolymer and Portland cement mortar samples, the maximum force to remove the bar from the sample was read from the device and the bond strength was determined (Table 3.19).

Figure 3.21 The samples after accelerated corrosion test

Table 3.20 Accelerated corrosion test

Mixtures	Weight of Steel Bar Before Corrosion (g)	Weight of Steel Bar After Corrosion (g)	Decreasing in Weight (%)	Bond Strength Before Corrosion, (MPa)	Bond Strength After Corrosion, (Mpa)
MC	452.5	312.6	31	6.7	0.0
M0	447.5	327.7	27	37	0.0
M1	453.5	346.0	24	3.9	0.0
M2	440.0	428.4	3	4.2	2.4
M3	440.5	436.4	1	4.4	2.8
M4	443.5	442.7	0	6.6	3.2
M5	447.0	446.7	0	7.5	6.3

The least weight loss in steel bar after corrosion happened in M2, M3, M4 and M5 mixtures were 3%, 1%, 0%, and 0%. While in MC, M0 and M1 were (31%, 27%, and 24%) higher weight loss. See Figure 3.22.

Bond strength of corroded of MC, M0, M1, M2, M3, M4, and M5 were 0.0, 0.0, 0.0, 2.4, 2.8, 3.2, 6.3 MPa, respectively. Before corrosion, bond strength was 6.7, 3.7, 3.9, 4.2, 4.4, 6.6, 7.5 MPa respectively.

The highest bond resistance was obtained with 50%MK after corrosion as we have seen in Figure 3.25, this corresponds to weight loss which was 50%MK. However, the bond resistance in MC, M0, and M1 were zero and the biggest weight loss happened to them.
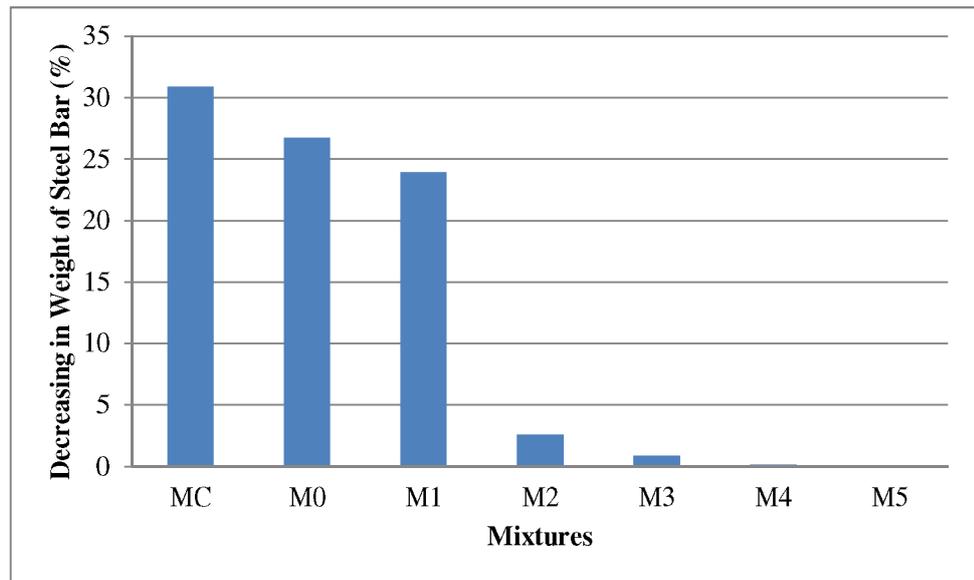
Figure 3.22 Weight losing of steel bar steel
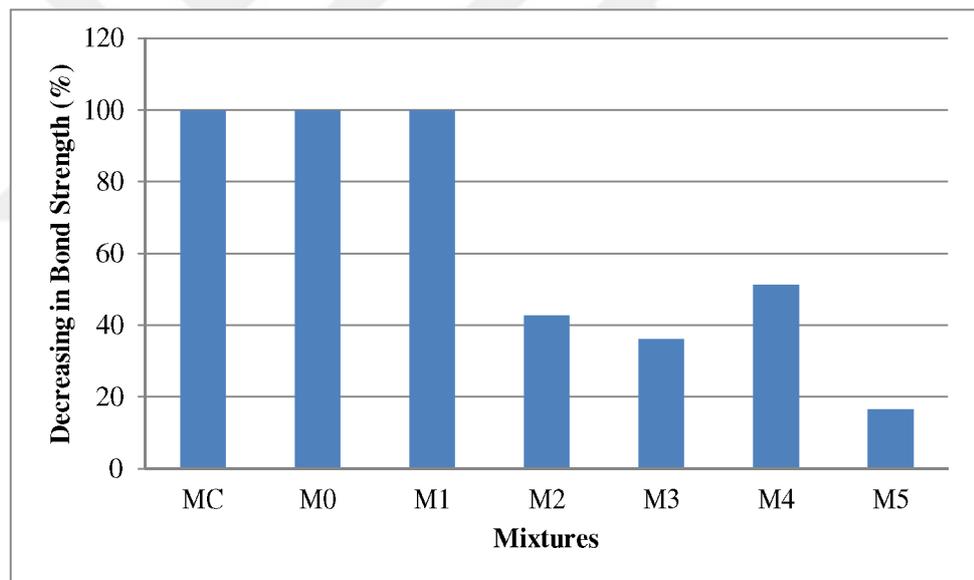
Figure 3.23 Decreasing in bond strength bar steel

CHAPTER FOUR

CONCLUSIONS AND RECOMMENDATIONS

4.1. Results

In this study, strength tests were performed in order to reach high strength values. In the second stage, durability tests were performed with the parameters determined as a result of strength tests. The aim of this study is produce GP without need to curing and to determine the effect of MK on the durability properties of F class fly ashes the geopolymer .The results obtained from strength and durability tests are evaluated and the results are explained below.

4.1.1. Unit Weight and Density Results

• The unit weight of the MK-fly ash geopolymer mortars activated with MS was between 2.01 and 2.10 g / cm^3. The Portland cement samples mortars have a unit weight was 2.11 g / cm^3.

• It was observed that the increase in the MK dosages increased the unit weights.

• It was seen that the increase in MK content slightly increased the apparent densities of the hardened mortar of geopolymer mixtures and slightly increased the dry and saturated surface dry densities.

• It was observed that the unit weight of the mortars produced with Portland cement was higher than the geopolymer mortars excepting 50%MK very closed to it, but the apparent density values were close to each other.

• It was observed that the dry density of the mortars produced with Portland cement was higher than the geopolymer mortars, but saturated surface dry densities values of geopolymer and Portland cement samples were close to each other.

4.1.2. Workability Results

• Flowability values of mortars produced by fly ash and MK with dosages (0%, 10%, 20%, 30%, 40%, and 50%) were measured between 114-257 mm.

• It was observed that the increase in MK dosages tended to reduce the fresh mortar consistency very little due to clay nature that makes it water absorbed in large quantities.

• The consistency of fresh mortar produced with cement was measured as 150 mm. The water / binder ratio of the cementitious mortars was 0.50, which resulted in higher flowability than 40%MK and 50% MK geopolymer mortars.

4.1.3. Flexural Strength Results

• Portland cement has a compressive strength of 53.4 MPa and a flexural strength of 8.8 MPa as a result of curing at 20 ° C for 28 days in water. In Durability tests, this standard mixture was produced as Portland cement sample and used to compare with geopolymer mortars.

• It was observed that the flexural strengths were generally increased by increasing the MK dosages from 0% to 50% at 28 days. In addition, the flexural strength of geopolymer mortars increased with the increase of time curing from 3 days to 180 days.

• The height flexural strength obtained was 13.3 MPa, achieved by using 50%MK for 180 days. For MC samples were 10.3 at the same age of curing.

• Although the geopolymer samples produced fly ash geopolymer without MK show low flexural strength, but through the time this results improvement, the highest strength was achieved by using MK with fly ash. This shows that MK enhance the properties of geopolymer and have a positive effect on it.

4.1.4. Compressive Strength Results

• It was observed that the compressive strengths were generally increased by increasing the MK dosages from 0% to 50% at 28 days. In addition, the strength of geopolymer mortars increased with the increase of time curing from 3 days to 180 days.

• Longer curing time does not significantly affect the improvement of strength. Most resistance obtained at 28 days.

• The height compressive strength obtained was 61.1 MPa, achieved by using 50%MK for 180 days. For MC samples were 62.4 at the same age of curing. This shows that MK enhance the properties of geopolymer and have a positive effect on it.

4.1.5. Ultrasonic Pulse Velocity Speed Results

• Ultrasonic pulse velocity speed results were observed that the results were generally increased by increasing the MK dosages from 0% to 50% at 28 days.

• It was observed that the ultrasonic pulse velocity values of geopolymer mortars measured at the saturated dry surface were lower than the dry state.

• Among the geopolymers produced with fly ash and MK, the highest ultrasonic pulse velocity values were found to be 50% MK in SSD case.

• Ultrasonic pulse velocities of the geopolymer obtained by 50% MK was 3599 m / s while the ultrasonic pulse velocity of the MC sample in the dry state was 3789 m / s respectively.

• Ultrasonic pulse velocities of the geopolymer obtained by 50% MK was 3902 m / s while the ultrasonic velocity of the MC sample in the SSD case was 3912 m / s, as we seen the results of both very close.

4.1.6. Water Absorption and Porosity Results

• Water absorption and void ratio values of Portland cement mortar mixture cured in water for 28 days as control sample was found to be 7.4% and 15.4%, respectively. When compared, MC sample and geopolymer, we found MC samples have water absorption and void rate less than the results which obtained from all types of geopolymer.

• Activation of the geopolymer with MS yielded the lowest water absorption of 8.1% and8.0%, the porosity was 16.6% and 16.2% with 40% MK and 50% respectively. In general the effect of MK on geopolymer samples that the increase in MK ratio decreased the water absorption and void ratio values of geopolymers

• In addition, we can say that geopolymers produced with MK are better in terms of water absorption and void rates.

4.1.7. Sorptivity Results

• The best value of the initial rate water absorption coefficient value was reached by 40%MK and 50%MK. All samples obtained with fly ash and MK activated by using MS (10% Na), have high rate water absorption values than MC samples.

• Secondary rate water absorption value of geopolymer samples is higher than MC samples. The best value of the secondary rate water absorption value was reached by 40%MK and 50%MK.

• Due to the increase in MK ratios, rate water absorption values in both cases initial and secondary were improved in all samples.

4.1.8. Wetting-Drying Results

• In the wetting-Drying experiment, the weight decrease in each mixture of geopolymer activated with MS after 80 cycles were higher than the Portland cement samples.

• Weight decrease in mixtures M1, M2, M3, M4,and M5 were the same value (1%) while Portland cement mortar was -1% that means there no losing in weight of MC.

• The flexural strength decrease percentage of the geopolymer samples after the wetting-drying cycle were decrease when MK contain increase. While the decreasing of MC was higher than M5

• The compressive strength of the geopolymer samples were improved after 80 cycles of wetting-drying, except 0%MK showed losing in strength but not significant. That means, the geopolymerization reactions stayed going during the experiment in samples.

• The Portland cement samples had water curing properties; they did not lose much of their compressive strength(1%). Since the drying temperature in the wetting-drying cycle was 65 ± 5ºC, the temperature effect deterioration of the MC samples remained at low levels.

4.1.9. Freezing-Thawing Results

• Weight decrease results were not significant in the evaluation of freeze-thaw resistance.

• When the changes in ultrasonic pulse velocities are examined, it is seen that in M3, M4 and M5 were close to each other, while the loss of pulse velocity in 0%, 10%, and 20%MK ratio is high. Ultrasonic pulse velocities of the mixtures of geopolymer higher than MC mixtures.

• It has been observed that weight losing decreased with increase in the MK ratio of geopolymers activated by MS (10%Na), after freezing-thawing. While Portland cement samples didn't show any losing in weight.

• It has been observed that the increase in the MK ratio of geopolymers activated by MS (10%Na), flexural and compressive strength losing decreased after freezing thawing.

• In general, losing in flexural and compressive strength of the mixtures of geopolymer higher than control mixtures.

4.1.10. Rapid Chloride Permeability Results

• Chloride transition is very poor for all types of geopolymer samples activated by MS (10%Na).

•In all MK ratios (0%, 10%, 20%, 30%, 40%, and 50%) the temperature increases before the experiment completes for 6 hours, due to high chloride transition. Also, the chloride passages are high in the MC samples.

• Portland cement samples have high chloride permeability even if they complete the experiment in 6 hours.

• The lowest chloride permeability was achieved with 40%MK and 50%MK. The mixtures of geopolymer with MK content of 40% and 50% samples give better results when compare with other mixtures of geopolymer M0, M1, M2, and M3.

4.1.11. Shrinkage Test Results

• At the age of 360days, the shrinkage value of the Portland cement samples were 16%. This value is close to the values of the samples obtained from used MK with 30%, 40%, and 50% ratio.

• The change length in geopolymers was close to each other in mixtures containing 30%, 40%, and 50% MK. The highest change length was observed in the samples M0

• The mixtures of geopolymer samples containing 0%, 10%, and 20% MK showed more shrinkage than mixtures containing 30%, 40% and 50% MK. That means, when the dosages of MK increased the change in length was decreased.

• The water in the Portland cement samples decreases with time therefore loses weight and changes in length were happened. However, the geopolymer samples were cured in ambient condition at 20 ± 1 °C and humidity at $55\pm10\%$, a slight increase in weight was observed during the shrinkage test with the effect of moisture in the laboratory environment.

• After 56 days in geopolymer and Portland cement samples, the change length which occurs is very small levels; we can say the change was constant.

• Portland cement samples showed behavior in length change, similar to the behavior of mixtures containing 30%, 40%, and 50%MK.

4.1.12. Abrasion Test Results

• The abrasion resistance was generally decreased by increasing the MK content from 0% to 50%. Both weight loss and volume loss volume were reduced.

• It has been found that the wear resistance of the geopolymer samples was the best in mixtures containing 40% and 50% MK. Even the wear resistance the mixture with 50% MK is close to the samples produced with Portland cement.

• The worst results of abrasion test obtained in mixtures containing only FA (0%MK) and 10% MK in both weight loss and volume loss volume.

4.1.13. High Temperature Resistance Results

•Strength properties of all mortars after exposure to 300°C were not decreased, in general, but even increased. Portland cement mortar illustrated the worst performance while fly ash geopolymer mortar showed the best performance, and geopolymer mortar containing metakaolin represented intermediate performance at elevated temperature.

•Flexural and compressive strength losses increased at each stage of increase of temperature to 600°C and 900°C in geopolymer mixtures and Portland cement mixtures.

• The decrease in strength properties for geopolymer mixture containing 20%, 30%, 40% and 50% MK were happened at 600 °C. While, at the same temperature geopolymer containing 0% and 10% MK were increased.

•The strength properties of geopolymer mixture containing 20%, 30%, 40% and 50% MK at 900 °C were decrease. While, geopolymer mixtures containing 0% and 10% MK showed increase in strength.

• Significant reductions in flexural and compressive strength at 600°C and 900 °C in Portland cement mortar.

• High temperature resistance was found to be better at low MK ratio for compressive strength. However, in flexural strength showed different behavior, at high MK ratio, high temperature resistance was found to be better.

4.1.14. Accelerated Corrosion Results

• All samples subjected to corrosion tests lost bond strength at the end of the test. However, there was no significant reduction in the weight of the bars, except in Portland cement mixtures, 0%MK and 10%MK.

 • Bond strength increases when MK ratio increased. Samples produced by using 40% and 50% MK have higher bond strength than those produced with Portland cement.

• The corrosion resistance of the samples obtained by activating the MK with a 50% ratio is very close to those which didn't expose to corrosion. That means geopolymer with a 50% ratio of MK as a replacement material has good resistance toward the corrosion.

4.2. Suggestions

Further works will focus on improving and developing the properties of FA-MK geopolymer mortar. The following suggestions are made for future studies:

• It can be used in the site because it didn't need to cure, by this way can encourage more use of geopolymer concrete.

• Investments can be made on reducing the production costs to be an alternative to traditional concrete production.

• Studies can be made on the use of chemical additives to increase the using of geopolymers and reduction waste materials.

• Investigations can be made to improve the properties such as freezing-thawing and wetting-drying.

• Research on improving tensile properties by producing fibrous geopolymer concrete.

• Further work is required to investigate the use of other locally available materials rather than that used in this study to produce geopolymer Concrete.

• A study is recommended to examine the durability of metakaolin Geopolymer concrete.

REFERENCE

1. A.Hasanbeigi, C. Menke, L. Price, 2010. The CO_2 Abatement Cost Curve For The Thailand Cement Industry, **J. Clean. Prod.** 18:1509–1518.

2. C. Chen, G. Habert, Y. Bouzidi, A. Jullien, 2010. Environmental Impact Of Cement Production: Detail Of The Different Processes And Cement Plant Variability Evaluation, **J. Clean. Prod.** 18:478–485.

3. M.Schneider, M.Romer, M.Tschudin, H.Bolio, 2011. Sustainable Cement Productionpresent and Future, **Cem. Concr. Res**. 41 (7): 642–650.

4. C.Gunasekara, D.W.Law, S. Setunge, J.G. Sanjayan, 2015. Zeta Potential, Gel Formation and Compressive Strength of Low Calcium FA Geopolymers, **Constr. Build Mater**. 95:592–599.

5. J. Davidovits, 1991. Geopolymers: Inorganic Polymeric New Materials, **J. Therm. Anal. Calor.** 37:1633–1656.

6. H.Y. Zhang, V. Kodur, B. Wu, L. Cao, F. Wang, 2016. Thermal Behavior and Mechanical Properties of Geopolymer Mortar after Exposure to Elevated Temperatures, **Constr. Build. Mater.** 109:17–24.

7. L. Assi, S. Ghahari, E. Deaver, D. Leaphart, P. Ziehl, 2016. Improvement of the Early and Final Compressive Strength of Fly Ash-Based Geopolymer Concrete at Ambient Conditions, **Constr. Build. Mater.** 123:806–813.

8. C. Shi, A. Fernandez-Jimenez, A. Palomo, 2013. New Cements for the 21st Century: The Pursuit of an Alternative to Portland Cement, **Cem. Concr. Res.** 41:750–763.

9. K.H. Yang, J.K. Song, K.I. Song, 2013. Assessment of CO_2 Reduction of Alkali-Activated Concrete, **J. Clean. Prod.** 39:265–272.

10. P.K. Sarker, S. Kelly, Z.T. Yao, 2014. Effect of Fire Exposure on Cracking, Spalling And Residual Strength Of FA Geopolymer Concrete, **Mater. Des.** 63 (11):584–592.

11. M. Shojaei, K. Behfarnia, R. Mohebi, 2015. Application of Alkali-Activated Slag Concrete in Railway Sleepers, **Mater. Des.** 69:89–95.

12. A. Gharzouni, L. Vidal, N. Essaidi, E. Joussein, S. Rossignol, 2016. Recycling Of Geopolymer Waste: Influence On Geopolymer Formation and Mechanical Properties, **Mater. Des.** 94:221–229.

13. X. Ma, Z.H. Zhang, A.G. Wang, 2016. The Transition of Fly Ash-Based Geopolymer Gels into Ordered Structures and the Effect on the Compressive Strength, **Constr. Build. Mater.** 104:25–33.

14. M. Soutsos, A.P. Boyle, R. Vinai, A. Hadjierakleous, S.J. Barnett, 2016. Factors Influencing The Compressive Strength of FA Based Geopolymers, **Constr. Build. Mater.** 110:355–368.

15. C.D. Atis, E.B. Gorur, O. Karahan, C. Bilim, S. Iikentapar, E. Luga, 2015.Very High Strength (120 Mpa) Class F Fageopolymer Mortar Activated at Different NAOH Amount, Heat Curing Temperature and Heat Curing Duration, **Constr. Build. Mater.**96:673–678.

16. F.N. Okoye, J. Durgaprasad, N.B. Singh, 2016. Effect of Silica Fume on the Mechanical Properties of FA Based-Geopolymer Concrete, **Ceram. Int.** 42 (2): 3000–3006.

17. H.K. Tchakoute, C.H. Rüscher, J.N.Y. Djobo, B.B.D. Kenne, D. Njopwouo, 2015. Influence of Gibbsite and Quartz in Kaolin on the Properties of Metakaolin-Based Geopolymer Cements, **Appl. Clay Sci.** 107:188–194.

18. H.Y. Zhang, V. Kodur, S.L. Qi, L. Cao, B. Wu, 2014. Development of Metakaolin-FA Based Geopolymers for Fire Resistance Applications, **Constr. Build. Mater.** 55:38–45.

19. P. Duan, C.J. Yan, W.J. Luo, W. Zhou, 2016. A Novel Surface Waterproof Geopolymer Derived from Metakaolin by Hydrophobic Modification, **Mater. Lett.** 164:172–175.

20. M. Ardanuy, J. Claramunt, R.D.T. Filho, 2015. Cellulosic Fiber Reinforced Cement-Based Composites: A Review Of Recent Research, **Constr. Build. Mater.** 79:115–128.

21. Atabey İsmail İsa, 2107. F Sınıfı Uçucu Küllü Geopolimer Harcının Durabilite Özelliklerinin Araştırılması, Erciyes Üniversitesi, Fen Bilimleri Enstitüsü, Doktora Tezi, Kayseri.

22. Zhang Z, Wang H, Zhu Y, Reid A, Provis JL, Bullen F, 2014. Using FA To Partially Substitute Metakaolin In Geopolymer Synthesis. **Appl Clay Sci.** 88-89: 194-201.

23. Little MR, Adell V, Boccaccini AR, Cheeseman CR., 2008. Production Of Novel Ceramic Materials From Coal FA And Metal Finishing Wastes. **Resour Conserv Recycl.** 52(11):35-1329.

24. Riahi S, Nazari A, Zaarei D, Khalaj G, Bohlooli H, Kaykha MM. 2012. Compressive Strength Of Ash-Based Geopolymers At Early Ages Designed By Taguchi Method. **Mater Des.** 37:9-443.

25. Ahmaruzzaman M., 2010. A Review On The Utilization Of Fly Ash. **Progr Energy Comb Sci.** 36(3):63-327.

26. Kumar S, Kumar R., 2011. Mechanical Activation Of Fly Ash: Effect On Reaction, Structure And Properties Of Resulting Geopolymer. **Ceram Int.** 37:533-41.

27. Zhang, Z., Yao, X., Zhu, H., 2010. Potential application of geopolymers as protective coatings for marine concrete. I. Basic properties. **Appl. Clay Sci.** 49: 1 -6.

28. Duxson, P., Provis, J.L., Lukey, G.C., MallicApple S.W., Kriven, W.M., Van Deventer, J.S.J., 2005. Understanding The Relationship Between Geopolymer Composition, Microstructure And Mechanical Properties. **Colloids Surf. A.** 269:47-58.

29. Provis, J.L., Duxson, P., Van Deventer, J.S.J., 2010. The Role Of Particle Technology In Developing Sustainable Construction Materials. **Adv. Powder Technol.** 21 (1), 2-7.

30. P. Duan, C.J. Yan, W. Zhou, W.J. Luo, C.H. Shen, 2015. An Investigation Of The Microstructure And Durability Of A Fluidized Bed Fly Ash-Metakaolin Geopolymer After Heat And Acid Exposure, **Mater. Des.** 74:125-137.

31. V. Kannan, K. Ganesan, 2014. Chloride and Chemical Resistance Of Self Compacting Concrete Containing Rice Husk Ash And Metakaolin, **Constr. Build. Mater.** 51:225-234.

32. O. Kele§temur, B. Demirel, 2015. Effect Of Metakaolin On The Corrosion Resistance Of Structural Lightweight Concrete, **Constr. Build. Mater.** 81:172-178.

33. Andini S, Cioffi R, Colangelo F, Grieco T, Montagnaro F, Santoro L., 2008. Coal FA as Raw Material for the Manufacture of Geopolymer-Based Products. **Waste Manag.** 28(2):23-416.

34. Bakharev T., 2005. Durability of Geopolymer Materials in Sodium and Magnesium Sulfate Solutions. **Cem Concr Res.**35:46-1233.

35. Rattanasak U, Chindaprasirt P., 2009. Influence of NaOH Solution on the Synthesis of FA Geopolymer, **Min Eng.**22:8-1073.

36. Winnefeld F, Leemann A, Lucuk M, Svoboda P, Neuroth M., 2010. Assessment of Phase Formation In Alkali Activated Low and High Calcium Fly Ashes in Building Materials. **Constr Build Mater** 24(6):93-1086.

37. Aydın, S. , 2010. Alkalilerle Aktive Edilmiş Yüksek Fırın Cürufu Bağlayıcılı Lifli Kompozit Geliştirilmesi, Dokuz Eylül Üniversitesi Fen Bilimleri Enstitüsü, Doktora Tezi, İzmir, 317 s.

38. The European Cement Association (Cembureau), Activity Report 2015, Brussels, 46 s.

39. Köleli, Y., 2015. TR 63 Bölgesi Çimento Sektör Raporu 2015, Doğu Akdeniz Kalkınma Ajansı, 26 s.

40. Najabat Ali1, Abbas Jaffar, Muhammad Anwer, Shazada Khurram Khan Alwi,Muhammad Naeem Anjum, Najaf Ali,Muhammad Riaz Raja, Adil Hussain8& Xu Ming,2015. The Greenhouse Gas Emissions Produced by Cement Production and Its Impact on Environment: A Review of Global Cement Processing. **International Journal of Research** (IJR).e-ISSN: 2348-6848, p- ISSN: 2348-795X Volume 2, Issue 2, Feb. 2015.

41. (https://cembureau.eu/cement-101/key-facts-figures/)

42. J.S.J. Van Deventer, J.L. Provis, P. Duxson, Technical and Commercial Progress in the Adoption of Geopolymer Cement, **Miner. Eng**. 29 (2012) 89–104.

43. L.K. Turner, F.G. Collins, Carbon Dioxide Equivalent (CO_2) Emissions: A Comparison between Geopolymer and OPC Cement Concrete, **Constr. Build**. Mater. A. Mehta, R. Siddique, An overview of geopolymers derived from industrial byproducts,

44. Constr. Build. Mater. 127 (2016) 183–198. [5] J.M. Mejía, R.M. De Guitiérrez, C. Montes, Rice Husk Ash and Spent Diatomaceous Earth as a Source of Silica to Fabricate a Geopolymeric Binary Binder, J. Clean. Prod. 118 (2016) 133–139.

45. S. Hanjitsuwan, S. Hunpratub, P. Thongbai, S. Maensiri, V. Sata, P. Chindaprasirt, Effects of NaOH Concentrations on Physical and Electrical Properties of High Calcium Fly Ash Geopolymer Paste, **Cem. Concr. Compos**. 45(2014) 9–14.

46. T. Yang, X. Yao, Z. Zhang, H. Wang, Mechanical Property and Structure of Alkali-Activated Fly Ash and Slag Blends, **J. Sustainable Cem. Mater**. 1 (2012) 167–178.

47. M. Jin, Z. Zheng, Y. Sun, L. Chen, Z. Jin, Resistance of Metakaolin-Mswi Fly Ash Based Geopolymer to Acid and Alkaline Environments, **J. Non-Cryst**. Solids 450 (2016) 116–122.43 (2013) 125–130.

48. P. Duxson, G.C. Lukey, J.S.J. Van Deventer, Thermal Evolution of Metakaolin Geopolymers: Part 1-Physical Evolution, **J. Non-Cryst**. Solids 352 (2006) 5541– 5555.

49. Z. Zhang, X. Yao, H. Zhu, Potential Application of Geopolymers as Protection Coatings for Marine Concrete. I. Basic Properties, **Appl. Clay Sci**. 49 (2010) 1–6[12]

50. P. Duan, C. Yan, W. Zhou, Influence of Partial Replacement of Fly Ash by Metakaolin on Mechanical Properties and Microstructure of Fly Ash Geopolymer Paste Exposed to Sulfate Attack, **Ceram. Int**. 42 (2016) 3504–3517.

51. P. Duxson, J.L. Provis, Designing Precursors for Geopolymer Cements, **J. Am.Ceram**. Soc. 91 (2008) 3864–3869.

52. Z. Zhang, H. Zhu, C.H. Zhou, H. Wang, Geopolymer from Kaolin in China: an Overview, **Appl. Clay Sci**. 119 (2016) 31–41.

53. Y. Ma, J. Hu, G. Ye, The Pore Structure And Permeability of Alkali Activated Fly Ash, Fuel 104 (2013) 771–780.

54. S.A. Bernal, J.L. Provis, V. Rose, R.M. De Guitiérrez, Evolution of Binder Structure in Sodium Silicate-Activated Slag-Metakaolin Blends, **Cem. Concr**. Compos. 33 (2011) 46–54.

55. K. Sagoe-Crentsil, L. Weng, Dissolution Process, Hydrolysis and Condensation Reactions during Geopolymer Synthesis: Part II. High Si/Al Ratio Systems, **J.Mater. Sci**. 42 (2007) 3007–3014.

56. P. Duxson, S.W. Mallicoat, G.C. Lukey, W.M. Krivem, J.S.J. Van Deventer, The Effect of Alkali and Si/Al Ratio on the Development of Mechanical Properties of Metakaolin-Based Geopolymers, **Colloids Surf**. A 292 (2007) 8–20.

57. R.R. Lloyd, J.L. Provis, K.J. Smeaton, J.S.J. Van Deventer, Spatial Distribution of Pores in Fly Ash-Based Inorganic Polymer Gels Visualized By Wood's Metal Intrusion, **Microporous Mesoporous Mater**. 126 (2009) 32–39.

58. J.L. Provis, R.J. Myers, C.E. White, V. Rose, J.S.J. Van Deventer, X-Ray Microtomography Shows Pore Structure and Tortuosity in Alkali-Activated Binders, **Cem. Concr. Res**. 42 (2012) 855–864.

59. Z. Zhang, H. Wang, Y. Zhu, A. Reid, J.L. Provis, F. Bullen, Using Fly Ash To Partially Substitute Metakaolin in Geopolymer Synthesis, **Appl. Clay Sci**. 88–89 (2014) 194–201.

60. Benscheidt, N., vom Berg, W., Feuerborn, H.J., Heinz, D., Hohberg, I., Hugot, A., Lutze, D., Mengede, M., Pierkes, R., Schneider, E., & Wiens, U. 2010. Handbook on FA in Concrete (2nd Ed.). Verlag Bau+Technik GmbH, Duesseldorf.

61. Joshi, R. C., & Lohtia, R. P. (1997). Fly Ash in Concrete: Production, Properties, and Uses. Amsterdam: Overseas Publishers Association.

62. Ramachandran, V. S. (1996). Concrete Admixtures Handbook: Properties, Science, and Technology (2nd Ed.). Park Ridge, New Jersey: Noyes Publications.

63. Meltem tangüler, 2015, Characterization of Fly Ashes from Thermal Power Plants in Turkey, Thesis of Master, Middle East Technical University The Graduate School of Natural and Applied Sciences, pp. 1-16.

64. Blissett, R. S., & Rowson, N. A. (2012). A Review of The Multi-Component Utilisation Of Coal Fly Ash. **Fuel**, 97, 1-23.

65. Yao, Z. T., Xia, M. S., Sarker, P. K., & Chen, T. (2013). A Review Of The Alumina Recovery From Coal Fly Ash, With A Focus In China. **Fuel**, 120, 74-85.

66. Elektrik Üretim A.Ş. (EÜAŞ), (2011). Electricity Generation Company 2011 Annual Report, 1-75.

67. Turkish Statistical Institute, Mineral Wastes Generated By Thermal Power Plants, Turkey, 2008.

68. Tangüler, M., Meral, C., & Gursel, A. P. (2014). Merging Mechanical and Environmental Performance of Turkish Fly Ash-Portland Cement Mortars. In 11th International Congress on Advances in Civil Engineering, 21-25 October, İstanbul.

69. ASTM C618, 1998. Standart Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete, Annual Book of ASTM Standarts, No.4. 148

70. TS EN 197-1, 2002. Çimento-Bölüm 1: Genel Çimentolar-BileǦim, Özellikler ve Uygunluk Kriterleri, Türk Standartları Enstitüsü.

71. RILEM Committee 73-SCB, 1998. Final Report on Siliceous by-Products for Use in Concrete, Materials and Structures, 21 (121):69-80.

72. ACI Committee 232., 2003. Use of Fly Ash in Concrete. Detroit, MI: American Concrete Institute.

73. Annual Book of ASTM Standards, C618-03, 319-321.

74. Nalbantoglu, Z., 2004. Effectiveness of Class C Fly Ash as an Expansive Soil Stabilizer, **Construction and Building Materials**, 18: 377-381.

75. Naik, R.T., Ramme, W.B. and Tews, J.H., 1994. Use of High Volumes of Class C and Class F Fly Ash in Concrete, Cement, Concrete and Aggregates, 16: 12-20.

76. Gikunoo, E., 2004, Effect of Fly Ash Particles on the Mechanical Properties and Microstructure of Aluminium Casting Alloy A534, Master of Science, University of Saskatchewan, The College of Graduate Studies and Research, Saskatchewan, Canada

77. Tokyay, M., & Erdoğdu, K. (1998). Türkiye Termik Santrallerinden Elde Edilen Uçucu Küllerin Karakterizasyonu. Ankara: TÇMB / AR-GE / Y 98.3.

78. Malhotra, V.M., 1990. Durability of Concrete Incorporating High-Volume of Low Calcium (ASTM Class F) Fly Ash, **Cement & Concrete Composites**, 12: 271-277.

79. ACI 232.2R, 2003. Use of FA in Concrete. American Concrete Institute, Farmington Hills, MI, USA .

80. Smith, F. 1999. Industrial Applications of X-Ray Diffraction. Boca Raton, FL: CRC Press.

81. ACI, Use of Fly Ash in Concrete Reported by ACI Comittee 232. NCHRP Synthesis of Highway Practice, 1986.

82. Bosbach, D., Michael, E., 1998. Microphotography of High Calcium Fly Ash Particle Surfaces, **Advances in Cement Research,** vol. 10, pp. 17–24.

83. Diamond, S., 1986. Particle Morphologies in Fly Ash, **Cement and Concrete Research**, vol 16, pp. 569-579.

84. Tanosaki, T., et al., 1998. Characterization of Incineration Ashes in Japan, **Journal of Research Chichibu Onoda Cement Corporation**, vol. 49, pp. 145–154.

85. Türker, P., Erdoğan, B., Katnaş, F., Yeğinobalı, A., 2009. Türkiye'deki Uçucu Küllerin Sınıflandırılması ve Özellikleri, Türkiye Çimento Müstahsilleri Birliği.

86. ASTM C 618, 2012. Standard Specification for Coal FA and Raw or Calcined Natural Pozzolan for Use in Concrete.

87. Siddique, R., 2007. Waste Materials and By-Products in Concrete. **Springer Science & Business Media.**

88. Wesche, K., 2004. FA in Concrete: Properties and Performance (Vol. 7). CRC Press.

89. Kosmatka, S. H., Kerkhoff, B., & Panarese, W. C., 2002. Design and Control of Concrete Mixtures. Skokie, IL: Portland Cement Association.

90. (www.enerjiatlasi.com/komur) (Erişim tarihi : Ağustos 2019)

91. Aruntaş, H. Y., 2006. Uçucu Küllerin İnşaat Sektöründe Kullanım Potansiyeli, **Journal of the Faculty of Engineering and Architecture of Gazi University.**, vol. 21, pp. 193–203.

92. Karahan, O., 2006. Liflerle Güçlendirilmiş Uçucu Küllü Betonların Özellikleri," Çukurova Üniversitesi Fen Bilimleri Enstitüsü, Doktora Tezi, Adana, 272 s.

93. Erdoğan, T., Beton, 5th ed., 2015. Ankara, Turkey: ODTÜ Yayıncılık.

94. M.Narmatha, Dr.T.Felixkala Metakaolin–The Best Material for Replacement of Cement in Concrete IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE) e-ISSN: 2278-1684, p-ISSN: 2320-334X, Volume 13, Issue 4 Ver. I (Jul. - Aug. 2016), PP 66-71 www.iosrjournals.org

95. Michael Zeljkovic, 2009. Metakaolin Effects on Concrete Durability, Masters thesis, University of Toronto.Canada.p.p1

96. TS EN 197-1. , 2012. Çimento-Bölüm 1: Genel Çimentolar-Bileşim, Özellikler ve Uygunluk Kriterleri, Türk Standartları Enstitüsü, Ankara.

97. Sanjay N. Patil1, Anil K. Gupta, Subhash S. Deshpande, Metakaolin- Pozzolanic Material For Cement in High Strength Concrete ,**IOSR Journal of Mechanical and Civil Engineering** (IOSR-JMCE) ISSN: 2278-1684, PP: 46-49 www.iosrjournals.org

98. Sposito, G (2016), The Chemistry of Soil, 3rd Edition, OxfordUniversity Press, New York. 255 p.p

99. Biljana R, Alexandra A. and Ljiljana R., 2010. Thermal Treatment of Kaoilin Clay to Obtain MK, Institute for Testing of Materials, Belgrade, Serbia, Scientific Paper, Hem. Ind. 64 (4) 351356 (2010), UDC 553.612:66.094.32, DOI: 10.2298/HEMIND100322014I British Standards-BS EN 196-5 (2011), Methods of testing cement. Pozzolanicity test for pozzolanic cement, British Standard Institution.

100. Gabriel Varga, The Structure of Kaolinite and Metakaolinite. http://dx.doi.org/10.14382/epitoanyag-jsbcm.2007.2

101. Monita Olivia, 2011. Durability Related Properties of Low Calcium FA Based Geopolymer Concrete, PhD thesis, Curtin University of Technology.

102. Shayan, A. 2013. Specification and Use of Geopolymer Concrete in the Manufacture of Structural and Non-Structural Components. Austroads Report, Austroads Project No. TS1835.

103. Provis, J. L. 2006. Modelling the Formation of Geopolymers. PhD, University of Melbourne.

104. Davidovits, J. Geopolymer, Green Chemistry and Sustainable Development Solutions: Proceedings of the World Congress Geopolymer 2005. 2005. Geopolymer Institute.

105. Davidovits, J. 1994. Geopolymers: Inorganic Polymeric New Materials. **Journal of Materials Education**, 16, 91–139.

106. LI, V. C., Lepech, M., Wang, S., Weimann, M. & Keoleian, G. Development of Green Engineered Cementitious Composites for Sustainable Infrastructure Systems. Proceedings of the International Workshop on Sustainable Development and Concrete Technology, 2004a. 181-191.

107. Duxson, P., Provis, J. L., Lukey, G. C. & Van Deventer, J. S. 2007. The Role of Inorganic Polymer Technology In The Development Of 'Green Concrete'. **Cement and Concrete Research**, 37, 1590-1597.

108. Alonso S, Palomo A., 2001. Alkaline Activation of Metakaolin and Calcium Hydroxide Mixtures: Influence of Temperature, Activator Concentration and Solids Ratio. **Materials Letters**. 47(1-2):55-62.

109. Van Jaarsveld JGS, Van Deventer JSJ, Lukey GC., 2002. The Effect of Composition and Temperature on the Properties of Fly Ash and Kaolinite-Based Geopolymers. **Chemical Engineering Journal**. 89(1-3):63-73.

110. Barbosa VFF, MacKenzie KJD, Thaumaturgo C., 2000. Synthesis and Characterisation of Materials Based on Inorganic Polymers of Alumina and Silica: Sodium Polysialate Polymers. **International Journal of Inorganic Materials.** 2(4):309-317.

111. Kong DLY, Sanjayan JG, Sagoe-Crentsil K., 2007. Comparative Performance of Geopolymers Made with Metakaolin and FA after Exposure to Elevated Temperatures. **Cement and Concrete Research**. 37(12):1583-1589.

112. Palomo A, Blanco-Varela MT, Granizo ML, Puertas F, Vazquez T, Grutzeck MW.,1999. Chemical Stability of Cementitious Materials Based on Metakaolin. **Cement and Concrete Research**. 29(7):997-1004.

113. Cioffi R, Maffucci L, Santoro L., 2003. Optimization of Geopolymer Synthesis by Calcination and Polycondensation of a Kaolinitic Residue. **Resources, Conservation and Recycling**. 40(1):27-38.

114. Swanepoel JC, Strydom CA.,2002. Utilisation of FA in a Geopolymeric Material. **Applied Geochemistry**. 17(8):1143-1148.

115. Roy DM., 1999. Alkali-Activated Cements: Opportunities and Challenges. **Cement and Concrete Research**. 29(2):249-254.

116. Xu, H. & Van Deventer, J. S. 2002. Geopolymerisation of Multiple Minerals. **Minerals Engineering**, 15, 1131-1139.

117. Davidovits, J. 1984. Synthetic Mineral Polymer Compound of the Silicoaluminates Family and Preparation Process. Google Patents.

118. Hardjito, D. & Rangan, B. 2005. Development and Properties of Low-Calcium Fly Ash-Based Geopolymer Concrete. Research Report GC 1, Faculty of Engineering, Curtin University of Technology, Perth, Australia.

119. Barbosa, V. F. & Mackenzie, K. J. 2003a. Synthesis and Thermal Behaviour of Potassium Sialate Geopolymers. **Materials Letters**, 57, 1477-1482.

120. Cioffi, R., Maffucci, L. & Santoro, L. 2003. Optimization of Geopolymer Synthesis by Calcination and Polycondensation of a Kaolinitic Residue. **Resources, Conservation and Recycling**, 40, 27-38.

121. Fernandez-Jimenez, A. M., Palomo, A. & Lopez-Hombrados, C. 2006. Engineering Properties of Alkali-Activated Fly Ash Concrete. **ACI Materials Journal,** 103, 106-112.

122. Rangan, B. V. 2008. Fly Ash-Based Geopolymer Concrete. Research Report GC4. Curtin University of Technology, Perth, Australia

123. Fernández-Jiménez, A. & PALOMO, A. 2003. Characterisation of Fly Ashes. Potential reactivity as alkaline cements. Fuel, 82, 2259-2265.

124. Cheng, T. & Chiu, J. 2003. Fire-Resistant Geopolymer Produced by Granulated Blast Furnace Slag. **Minerals Engineering**, 16, 205-210.

125. Ismail, I., Bernal, S. A., Provis, J. L., San Nicolas, R., Brice, D. G., Kilcullen, A. R., Hamdan, S. & Van Deventer, J. S. 2013. Influence of Fly Ash on the Water and Chloride Permeability of Alkali-Activated Slag Mortars and Concretes. **Construction and Building Materials**, 48, 1187-1201.

126. Rowles, M. R. 2004. The Structural Nature of Aluminosilicate Inorganic Polymers: A Macro to Nanoscale Study. Ph.D., Curtin University of Technology.

127. Davidovits, J. 1987. Ancient and Modern Concretes: What Is the Real Difference? **Concrete International**, 9, 23-28.

128. Alonso, S. & Palomo, A. 2001. Alkaline Activation of Metakaolin and Calcium Hydroxide Mixtures: Influence of Temperature, Activator Concentration and Solids Ratio. **Materials Letters,** 47, 55-62.

129. Investigation of Geopolymer as a Sustainable Alternative Binder for Fiber-Reinforced Strain-Hardening Composites, 2017, A Thesis Submitted in Fulfillment of the Requirements for the Degree of Doctor of Philosophy by Behzad Nematollahi Faculty of Science, Engineering and Technology Swinburne University of Technology Hawthorn, VIC, 3122 Australia January.

130. Duxson, P.A., Jimenez, A.F., Provis, J.L., Lukey, G.C., Palomo, A. and Van Deventer, J.S.J., 2007. Geopolymer Technology: the Current State of the Art. **Journal of Materials Science** Vol. 42: pp. 2917–2933.

131. Li, Z., Ding, Z., Zhang, Y., 2004. Development of Sustainable Cementitious Materials, Int. Work. Sustain. Dev. Concr. Technol.

132. Gökhan Görhan, Rıdvan Aslaner, Osman Şinik, 2016. The Effect of Curing on the Properties of Metakaolin and Fly Ash-Based Geopolymer Paste. **Elsevier Ltd. Composites Part B** 97 :329-335.

133. Kabir SMA, Alengaram UJ, Jumaat MZ, Sharmin A, Islam A., 2015. Influence of Molarity and Chemical Composition on the Development of Compressive Strength in Pofa Based Geopolymer Mortar. **Adv Mate sci Eng.** 1-15

134. Steinerova M., 2011. Mechanical Properties of Geopolymer Mortars in Relation to their Porous Structure. **Ceramics.** 55(4):72-362.

135. Abdollahnejad Z, Pacheco-Torgal F, Aguiar JB, Jesus C., 2015. Durability Performance of FA based One-Part Geopolymer Mortars. Key Eng Mater. 634:20-113.

136. Yusuf TO, Ismail M, Uaman J, Noruzman AH., 2014. Impact of Blending on Strength Distribution of Ambient Cured Metakaolin and Palm Oil Fuel Ash Based Geopolymer Mortar. **Adv Civ Eng.** 1-8.

137. Vasconcelos E, Fernandes S, Barroso de Aguiar JL, Pacheco-Torgal F., 2011. Concrete Retrofitting Using Metakaolin Geopolymer Mortars and CFRP. **Construct Build Mate.** 25:21-3213.

138. Kuenzel C, Grover LM, Vandeperre L, Boccaccini AR, Cheeseman CR., 2013. Production of Nepheline/Quartz Ceramics from Geopolymer Mortars. **J Eur Ceram Soc.** 33:8-251.

139. Muhammad Zahid1, Nasir Shafiq, Mohd Fadhil Nuruddin1, Ehsan Nikbakht, Asif Jalal, 2016. Effect of Partial Replacement of Fly Ash by Metakaolin on Strength Development of Fly Ash Based Geopolymer Mortar, **International Journal of Advanced Research**, Volume 4, Issue 7, 1690-1696.

140. Chang TP, Chen ZC, Yang TR., 2014. Shrinkage Behavior of Composite Geopolymer Mortar Cured at Different Relative Humidities. **Adv Mater Res.** 1064:95-100.

141. Tao Yang , Huajun Zhu , Zuhua Zhang, 2017. Influence of FA on the Pore Structure and Shrinkage Characteristics of Metakaolin-Based Geopolymer Pastes and Mortars. **Construction and Building Materials, Elsevier Ltd.** 153: 284–293

142. Khale, D. and Chaudhary, R., 2007. Mechanism of Geopolymerization and Factors Influencing its Development: a Review. **Journal of materials science**. Vol. 42, pp. 729–746.

143. Liew, Y.M., Kamarudin, H., Al Bakri, A.M.A., Bnhussain, M., Luqman, M., Nizar, I.K., Ruzaidi, C.M. and Heah, C.Y., 2013. Effect of Curing Regimes on Metakaolin Geopolymer Pastes Produced from Geopolymer Powder. **Advanced Materials Research**. Vol. 626, pp. 931-936.

144. Wang, J., Zhang, C., Xu, J., Qu, P., Zhou, Y. and Han, H., 2012. The Effect of Alkali on Compressive of Metakaolin Based Geopolymeric Cement. **Advanced Materials Research**. pp. 327-330.

145. Kamarudin, H., Al Bakri Mustafa, A.M., Binhussain, M., Ruzaidi, C.M., Luqman, M., Heah, C.Y. and Liew, Y.M., 2011. Preliminary Study on Effect of NaOH Concentration on Early Age Compressive Strength of Kaolin-Based Green Cement.

146. Bing Yana, Ping Duana,b, Daming Ren 2017,Mechanical Strength Surface Abrasion Resistance and Microstructure of Fly Ash-Metakaolin-Sepiolite Geopolymer Composites ,**Ceramics International** 43 (2017) 1052–1060.

147. Raphaëlle Pouhet, Martin Cyr,2016, Carbonation in the Pore Solution of Metakaolin-Based Geopolymer, **Cement and Concrete Research** 88 (2016) 227–235.

148. Mo Bing-hui, He Zhu, Cui Xue-min, He Yan, Gong Si-yu, 2014, Effect of Curing Temperature on Geopolymerization of Metakaolin-Based Geopolymers. **Applied Clay Science** 99 (2014) 144–148.

149. Huajun Zhu, Guangwei Liang, Zuhua Zhang, Qisheng Wua, Jianzhou Du, 2019, Partial Replacement of Metakaolin with Thermally Treated Rice Husk Ash in Metakaolin-Based Geopolymer. **Construction and Building Materials** 221 (2019) 527–538

150. Xing Li, Feng Rao, Shaoxian Song, Qinyong Ma, 2019. Deterioration in the Microstructure of Metakaolin-Based Geopolymers in Marine Environment, **J Mater Res Technol**.8(3):2747–2752

151. Guangwei Liang, Huajun Zhu, Zuhua Zhang, Qisheng Wu, 2019. Effect of Rice Husk Ash Addition on the Compressive Strength and Thermal Stability of

Metakaolin Based Geopolymer. **Construction and Building Materials** 222 (2019) 872–881.

152. Ruizhe Si, Qingli Dai, Shuaicheng Guo, Jiaqing Wang, 2019. Mechanical Property, Nanopore Structure and Drying Shrinkage of Metakaolin-Based Geopolymer with Waste Glass Powder. **Journal of Cleaner Production** 242 (2020) 118502.

153. TS EN 1015-11, 2000. Mortar Testing Method, Part 11. Measurement of Compressive and Flexural Tensile Strength of Mortar. Ankara: TSE.

154. TS EN 1015-10/A1, Methods of Test for Mortar for Masonry - Part 10: Determination of Dry Bulk Density of Hardened Mortar. Turkish Standard, Ankara.2013.

155. TS EN 1015-3., 2000. Kagir harcı- Deney metotları- Bölüm 3: Taze Harç Kıvamının Tayini (yayılma tablası ile), Türk Standartları Enstitüsü, Ankara.

156. TS EN 12504-4, 2012. Testing concrete - Part 4: Determination of Ultrasonic Pulse Velocity. Ankara: TSE.

157. ASTM C1585-13. Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes, Annual Book of ASTM Standarts.

158. ASTM D5313. Evaluation of Durability of Rock for Erosion Control Under Wetting and Drying Conditions, Annual Book of ASTM Standarts.

159. ASTM C666/C666M-15. Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing, Annual Book of ASTM Standarts.

160. ASTM C1202-12. Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration, Annual Book of ASTM Standarts.

161. TS ISO 1920-8:2009, Testing of Concrete -- Part 8: Determination of Drying Shrinkage of Concrete for Samples Prepared in the Field or in the Laboratory, Turkish Standard, Ankara.2011.

162. TS 2824 EN 1338, 2005. Zemin Döşemesi için Beton Kaplama Blokları- Gerekli Şartlar ve Deney Metotları, Türk Standartları Enstitüsü, Ankara.

163. ASTM A944-10, Comparing Bond Strength of Steel Reinforcing Bars to Concrete Using Beam-End Specimens, Annual Book of ASTM Standarts.

164. Sunny A. Jagtap, Mohan N. Shirsath, Sambhaji L. Karpe, Effect of Metakaolin on the Properties of Concrete, **International Research Journal of Engineering and**

Technology *(IRJET)* e-ISSN: 2395-0056, Volume: 04 Issue: 07 July -2017, p-ISSN: 2395-0072

165. Cyr M, Idir R, Poinot T., 2012. Properties of Inorganic Polymer (Geopolymer) Mortars Made of Glass Cullet. **J Mater Sci**. 47:97-2782.

166. Nath SK, Kumar S. Influence of Iron Making Slags on Strength and Microstructure of FA Geopolymer. **Constr Build Mater** 2013;38:924-30.

167. M.M. Yadollahi, A. Benli, R. Demirboga, The Effects of Silica Modulus and Aging on Compressive Strength of Pumice-Based Geopolymer Composites, **Constr. Build. Mater**. 94 (2015) 767–774.

168. N. Ranjbar, M. Mehrali, A. Behnia, U.J. Alengaram, M.Z. Jumaat, Compressive Strength and Microstructural Analysis of Fly Ash/Palm Oil Fuel Ash Based Geopolymer Mortar, **Mater. Des**. 59 (2014) 532–539.

169. A. Islam, U.J. Alengaram, M.Z. Jumaat, Bashar II, The Development of Compressive Strength of Ground Granulated Blast Furnace Slag-Palm Oil Fuel Ash-FA based Geopolymer Mortar, **Mater. Des.** 56 (2014) 833–841.

170. Manjunatha GS, Radhakrishna, Venugopal K, Maruthi SV., 2014. Strength Characteristics of Open Air Cured Geopolymer Concrete. **Trans Ind Ceram Soc**. 73(2):56-1496.

171. Zengqing Sun, Anya Vollpracht, Isothermal Calorimetry and in-Situ XRD Study of the NaOH Activated Fly Ash, Metakaolin and Slag, **Cement and Concrete Research** .103 (2018) 110–122.

172. Uldis Lencis, Aigars Udris, Aleksandrs Korjakins, Moisture Effect on the Ultrasonic Pulse Velocity in Concrete Cured under Normal Conditions and at Elevated Temperature, DOI:10.2478/cons-2013-0011, October 2013.

173. Shadnia R, Zhang L, Li P., 2015. Experimental Study of Geopolymer Mortar with Incorporated PCM. **Construct Build Mater**. 84:95-102.

174. Peng Zhanga, Yuanxun Zhenga,*, Kejin Wangb, Jinping Zhanga, 2018.A Review on Properties of Fresh and Hardened Geopolymer Mortar, **Composites Part B 152** (2018) 79–95

175. Tchakoute Kouamo H, Mbey JA, Elimbi A, Kenne Diffo BB, Njopwouo D. Synthesis of Volcanic Ash-Based Geopolymer Mortars by Fusion Method: Effects of Adding Metakaolin to Fused Volcanic Ash, **Ceram Int**. 39(2013)1613-2.

176.Pan Z, Sanjayan JG, Rangan BV., 2009. An Investigation of the Mechanisms for Strength Gain or Loss of Geopolymer Mortar after Exposure to Elevated Temperature. **J Mater Sci**. 44:80-1873.

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