JANUARY 2018

M.Sc. in Civil Engineering

OMAR HAMID FARHAN AL JUMAILI

UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES

MECHANICAL PROPERTIES OF SLAG BASED GEOPOLYMER EXPOSED TO CHEMICAL ATTACKS

M. Sc. THESIS
IN
CIVIL ENGINEERING

BY
OMAR HAMID FARHAN AL JUMAILI
JANUARY 2018

Mechanical Properties Of Slag Based Geopolymer Exposed To Chemical Attacks

M.Sc. Thesis
in
Civil Engineering
University of Gaziantep

Supervisor
Prof. Dr. Abdulkadir ÇEVİK
Co-Supervisor
Assist. Prof. Dr. Ahmet Emin Kurtoğlu

by
Omar Hamid Farhan AL JUMAILI
January 2018

REPUBLIC OF TURKEY
UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES
CIVIL ENGINEERING DEPARTMENT

Name of the thesis: Mechanical Properties of Slag Based Geopolymer Exposed to Chemical Attacks

Name of the student: Omar Hamid Farhan AL JUMAILI

Exam date: January 15, 2018

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Ahmet Necmeddin YAZICI
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Hanifi ÇANAKCİ
Head of Department

This is to certify that we have read this thesis and that in our consensus, it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Assist. Prof. Dr. Ahmet Emin Kurtoğlu
Co-Supervisor

Prof. Dr. Abdulkadir ÇEVİK
Supervisor

Examining Committee Members	Signature
Prof. Dr. Abdulkadir ÇEVİK	....
Assist. Prof. Dr. Hasan Erhan YÜCEL	....
Assist. Prof. Dr. Mehmet Eren GÜLŞAN	....

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and proper conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Omar Hamid Farhan AL JUMAILI

ABSTRACT

MECHANICAL PROPERTIES OF SLAG BASED GEOPOLYMER EXPOSED TO CHEMICAL ATTACKS

AL JUMAILI,Omar Hamid
M.Sc. in Civil Engineering
Supervisor: Prof. Dr. Abdulkadir ÇEVİK
Co-Supervisor: Assist. Prof. Dr. Ahmet Emin Kurtoğlu
January 2018
71 Pages

This study presents an investigation on the durability of geopolymer concrete produced with ground granulated blast furnace slag (GGBFS) and alkaline activators. Three groups of specimens were submerged in solutions for up 4 weeks and were categorized according to solution types in which they were submerged: 5% sulphuric acid, 5% magnesium sulphate and 3.5% salt water. Ordinary Portland Cement (OPC) concrete was also used for quality control specimens for comparison purpose. Main parameters studied were the weight change, compressive strength, splitting tensile strength, and fracture toughness. The performance of geopolymer concrete under solution exposure was superior to that of normal concrete produced using ordinary Portland cement (OPC) concrete. Significant strength reduction, however, was observed in some of the geopolymer concrete samples with activators such as sodium silicate and sodium hydroxide. GGBFS-based geopolymer concrete exhibited the best performance among all specimens due to its high resistance capacity against chemical attack**.**

Keywords: Geopolymer concrete, ground granulated blast furnace slag, ordinary Portland cement, durability.

ÖZET

KİMYASAL SALDIRILARA MARUZ YÜKSEK FIRIN CÜRUFU TABANLI JEOPOLİMER MEKANİK ÖZEL LİKLERİAL

JUMAILI Omar Hamid
Yüksek Lisans, İnşaat Müh. Bölümü
Tez Yöneticisi: Prof. Dr. Abdulkadir ÇEVİK
Yardımcı Tez Yöneticisi: Yard. Doç. Dr. Ahmet Emin Kurtoğlu
Ocak 2018
71 sayfa

Bu çalışma öğütülmüş granüle yüksek fırın cürufu (GGBFS) ve alkali aktivatörler kullanılarak üretilen jeopolimer betonun dayanıklılığı üzerine bir incelemeyi sunmaktadır. Üç grup numune hazırlanmış ve bu numuneler ayrı ayrı çözeltilerde 4 hafta bekletilmiş olup numuneler bekletildikleri çözeltilere göre (%5 sülfürik asit, %5 magnezyum sülfat ve % 3,5 tuzlu su) kategorize edilmiştir. Karşılaştırma amacıyla kalite kontrol numuneleri için OPC (Ordinary Portland Cement) beton da kullanılmıştır. Çalışılan başlıca parametreler; ağırlık değişimi, basınç dayanımı, çekme mukavemeti ve kırılma tokluğudur. Çözelti maruziyeti altında jeopolimer betonun performansının, sıradan Portland çimentosu (OPC) kullanılarak üretilen normal betonun performansından daha üstün olduğu gözlemlenmiştir. Bununla birlikte, sodyum silikat ve sodyum hidroksit gibi aktivatörler ile jeopolimer beton numunelerinin bazılarında belirgin mukavemet azalması gözlenmiştir. GGBFS tabanlı jeopolimer beton, kimyasal saldırılara karşı yüksek direnç kapasitesi nedeniyle tüm numuneler arasında en iyi performansı sergilemiştir.

Anahtar Kelimeler: jeopolimer beton, öğütülmüş granüle yüksek fırın cürufu, sıradan Portland çimentosu, dayanıklılık

To My

Father and mother which they span there live for me and my sisters and my wife who give the time and support to reach this level from knowledge

ACKNOWLEDGEMENTS

First of all, praise be to Allah, the Cherisher and the ustainer of the World. A thesis work is a product of collective efforts and guidance. A work has a life and spirits of its own. I believe that no work can achieve its ultimate objectives without proper guidance and support from others. I wish to express my heartiest thanks to my respect guides **Prof. Dr. Abdulkadir ÇEVİK**, Department of Civil Engineering, University of Gaziantep, Gaziantep-Turkey, who devoted their valuable time and provided enthusiast guidance, advice and continuous encourgement, which were the constant source of inspiration for the completion of this thesis work.I cannot forget to recall with my heartiest feelings, the ending heartfelt stream of caring and blessings of my **father** and **mother**, to support me with everything since my early childhood till reach high education, They were always denying themselves for supporting and pushing me to every success.

TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS/ABREVIATIONS

GGBFS	Grand Granular Blast Furnace Slag
OPC	Ordinary Portland Cement
AAR	Alkali Aggregate Reaction
ACI	American Concrete of Institute
W/C	Water/Cement ratio
FA	Fly Ash
ASTM	American Society for Testing Materials
SSD	Saturated Surface Dry
MK	Meta-Kaolin
HSC	High Strength Concrete
RC	Reinforced Concrete
CMOD	Crack Mouth Opening Displacement
FA-F	Fly Ash- Class F
CH	Calcium Hydroxide
ACC	Autoclaved Cellular Concrete
SEM	Scanning Electron Microscope
GPC	Geopolymer Concrete
GGBFS-GPC	Slag Based Geopolymer Concrete
FA-GPC	Fly Ash Based Geopolymer Concrete
f_s	splitting tensile strength

C-S-H	Calcium-Silica-Hydrated (Gel)
G_F	Fracture energy
Kic	Critical stress intensity factor
f_{flex}	Net flexural strength
ƍ	Compressive Strength

CHAPTER 1

INTRODUCTION

1.1 Background

Concrete is the mainstream material used in construction. Mostly, Ordinary Portland Cement (OPC) is used as a binder in concrete worldwide. Approximately 4 gigaton of OPC was manufactured in 2013 [1]. Annual production amount of OPC is supposedly to increase by 25% over the next 10 years. The stone reserve will also face a severe shortage after 25 to 50 years as it constitutes one of the main materials in OPC production. OPC requires large amounts of fuel and raw materials and it is responsible for approximately 7% of total greenhouse gas emissions [2] which is approximately 820 kg of CO_2 per one ton of OPC [3] and a great quantity of OPC is produced each year. OPC requires much more energy as compared to that of other materials such as aluminum and steel [4].

Researchers introduced a new type of binder material namely as geopolymers or alkali-activated cement. Geopolymers are one of the polymeric binding materials synthesized from alkaline activation of different aluminosilicate materials such as FA, GGBFS, and metakaolin etc. Geopolymer concrete is superior to OPC concrete in terms of mechanical characteristics, fire impedance, and acid resistance [4], [5].

During the OPC production, amount of CO_2 emitted to the atmosphere is approximately 80% more than it is when producing GPC, making Geopolymer an environmentally friendly construction material [6].

The alternative option is using the industrial product alkalies such as sodium silicon and sodium hydrooxide as a binder (pillow, 1989; glory, 1989). Furthermore, the most industrial production used in geopolymer concrete is fly ash (FA) and ground granulated blast furnace slag (GGBFS). Ordinary Portland cement has been a replacement GGBFS, while the Pozzolanic material used FA to enhance the physical properties, chemical composition and the strength of concrete [7].

Geopolymers are family members of organic sodium-silicate polymer from alkaline activation of various sodium silicate solutions or an industrial product such as FA, GGBFS, and metakaolin etc. [8]. The geopolymer and natural zeolitic materials have similar chemical composition, the microstructure of geoplolymer, however, is amorphous. The source materials and alkaline activators influences the final products of geopolymerisation based on chemical microstructure [9]. The process of polymerization is mostly accelerated by temperature. Strength gain of fly ash based geopolymer in early days is lower in ambient temperature as compared to heat-cured specimens [10].

Good strength and durability are the desired properties in construction materials. Although OPC possesses good strength, previous studies show that it exhibits poor performance against high temperature and severe environmental conditions such as acid or sulfate attack. Geopolymer was first introduced by Davidovits in 1978. This new material attracted great attention by engineers and chemists as it is considered one of the conceivable alternatives to OPC binders due to its several advantages such as resistance against chemical attack, shorter setting time and environmentally friendly nature [11].

A limited number of studies have been carried out on durability concerns of geopolymer concrete. For instance, Davidovits found that, when GPC samples are exposed to 5% sulfuric acid and hydrochloric acid solutions, a mass loss of 5%-8% is observed in GPC whereas OPC samples are entirely deteriorated in the same environment [12].Bakharev discussed the durability of FA based on GPC that exposed to 5% acid solution for 5 months and found that the GPC samples possesses superior resistance as compared to OPC counterparts [13]. Wallah and Rangan found that GPC specimens possess superior durability characteristics. [14].

1.2 Research Significance

Geopolymer concrete is considered as possible replacement for Ordinary Portland Cement (OPC) in concrete manufacture. Geopolymer concrete has significant superior characteristics, making it more efficient than the (OPC) and it can play important role when the environmental and sustainability issues are concern.

The major objectives of this research are as follows:

- Determining the durability and hence the applicability of alkaline-activated GGBS-based geopolymer exposed to acid environments.

- Studying the mechanical and durability properties of geopolymer concrete and comparing with ordinary Portland cement concrete by determination of fracture toughness, compressive strength, splitting tensile strength and changes in weight after exposure to sulphuric acid solution, magnesium sulphuric solution, and salt water.

1.3 Outline of the Thesis

Chapter 1 Introduction: Aim and objectives of the thesis are introduced
Chapter 2 Literature Review and Background: Literature review of geopolymer concrete and the effect of fly ash and slag based geopolymer concrete as a binder and the suitability of geopolymer materials resistance to chemical attacks.
Chapter 3 Experimental Study: Materials, mixtures, casting, curing conditions, and test methods are described.
Chapter 4 Test Results and Discussions: Indication, evaluation, and discussion of test results are presented.
Chapter 5 Conclusions: Conclusions of the thesis are given.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

GPC has a substantial role when environmental and sustainability issues are concern. As a result of cement manufacturing, about 7% of carbon dioxide is released into the weather globally. According to Roy & Idorn, concrete production with other type of binders such as GGBFS reduces the greenhouse gas emissions approximately by 80% [15]. Duxson et al. also said that using FA as binder reduces cement production-induced greenhouse gas emission by 80% to 90% [16]. Therefore, scientists have found it necessary to utilize geopolymer concrete due to its advantages such as good acid resistance, high thermal stability, low CO2 emission and good mechanical properties. This chapter presents a summary of the terminology and chemistry of geopolymers as well as the previous. Supplemental review of GPC technology is available elsewhere [17].

2.2 Pozzolanic materials

Pozzolan is a siliceous aluminous material that can form compounds possessing cementitious properties after reacting with the calcium hydroxide at ambient temperature [18]. Fly ash, silica fume and blast furnace slag are the most commonly used pozzolanic materials. The replacement of the cement by pozzolans can deduce the early-age strength of concrete. However, it can enhance various age properties of concrete.

2.3 Geopolymer concrete

The geopolymer was introduced in the late 1970s and was discovered by french scientist Joseph Davidovits. Through the 1980s and 1990s, the use of geopolymer for non-structural applications has increased. The geopolymer is manufactured by two aluminosilicate polymers with an amorphous microstructure and created in an alka line environment. The traits of GPC are structure of a two- to three-dimensional Si-O-Al.

2.4 Constituents of Geopolymer concrete

2.4.1 Ground Granulated Blast Furnace Slag (GGBFS)

GGBFS is a partly transparent material produced from iron metal smelting. It generally includes a mixture of silicon dioxide and metal oxides. GGBFS can be utilized for many purposes including helping temperature control through minimizing and smelting the ultimate liquid product before the molten metal. [19]. It is also utilized in the making of concrete and cement manufacture.

Replacing OPC with slag results in various benefits such as better workability of the fresh concrete and reducing life-cycle costs [19]. Other advantages of using slag instead of OPC includes resistance against severe environments and higher compressive strength [19].

Small particles dominate slag in alkali activating systems and cement mixture. The particles larger than 20 µm commonly interact slowly, whilst particles smaller than 2 µm interact fully during 24 hours. Consequently, when the slag is utilized in geopolymerisation, accurate control of the particle size should be ensured to control the strength of the bonds [20].

Ground granulated blast-furnace slag (GGBFS), basically written as “slag”, is a grainy industrial material and is produced via the water cooling of fluid blast-furnace slag. The content of GGBFS is silicates and aluminosilicates of calcium and different bases that has improved in a molten condition at the same time with the materials of iron inside a blast furnace.

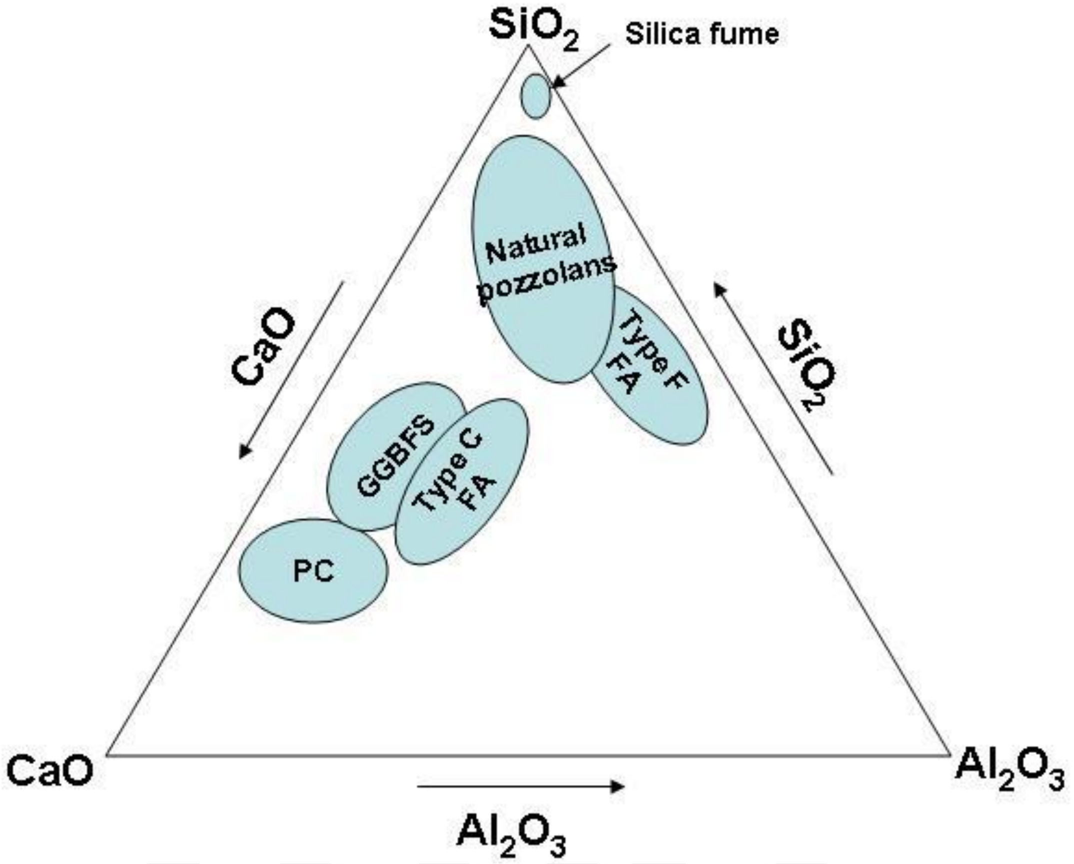


Figure 2.1 The structure of Pozzolanic cementations [21]

The elevated cementations of GGBFS are Al2O3 8-24%, SiO2 28-38%, CaO 30-50% and MgO 1-18%. The sophisticated content of CaO in slag generally leads to a improvement in compressive strength of concrete. The chemical mixtures remain moderately continuous as compared to FA for a given base of GGBFS. Figure 2.1 shows the comparative mixtures of cementations. Moreover, using concrete with GGBFS has more advantages such as lower hydration heat.

2.4.2 Use of slag in concrete

It is well known that using GGBFS in concrete as a replacement of cement in ambient temperatures lead to strength enhancements at a lower rate as compared to concrete prepared with Portland cement [22], [23]. This degree of decline because of a number of variables such as slag activity [24], [25] the proportioning method in addition to content of the slag of the mix. During the mixture of Portland cement and water, a chemical reaction called hydration is initiated and calcium hydroxide (CH) and the creation of calcium-silicate-hydrate (CSH) are formed. CSH stands for a material of gel that prompts the strength development in Portland cement pastes. CSH is a gel that contributes to strength development in OPC. CH, on the other hand, is a resultant material of hydration process and does not have a significant in strength. Silicates in slag combine with CH to form additional CSH. That can lead to harder binder and denser that can raise the final strength as it is compared to Portland cement systems of 100%.

It is known that the definition of Slags to be by-products of metallurgical industry and it includes calciummagnesium aluminosilicate glass. The iron and steel industry can give most produced slags called ground granulated blast-furnace slag (GGBFS). It is made by the latent hydraulic property of GGBFS to be suitable for geopolymer binder.

Such this material of slag by adding a source of alkali falls through the alkaline-alkali earth system as by [26] Me_2O-MeO-Me_2O_3-SiO_2-H_2O. We can use GGBFS by itself as a source material for geopolymer binders. Anyway,we have to notice that the high CaO content of GGBFS can give the rapid setting of the binder that impossiple to be suitable binder for the material of concrete.

2.4.3 Alkaline Activators

In general, the alkaline activator utilized for manufacturing GPC is a mixture of potassium hydroxide (KOH) with silicate potassium or sodium hydroxide (NaOH) with silicate sodium [1], [27]–[29].

Palomo et al. explained that the kind of alkaline activator used for activating FA significantly, affects the reaction development. Moreover, they said that high average reaction happens when an alkaline liquid activator solution contains silicate, potassium or sodium silicate, in comparison to using only single alkaline hydroxides [30].
Van Deventer and Xu (2000) explained that the interaction between the alkaline solution and the source material is improved by adding NaOH liquid [29].
The disintegration operation of aluminum and silica, obtainable in FA, is shown in Fig 2.2.

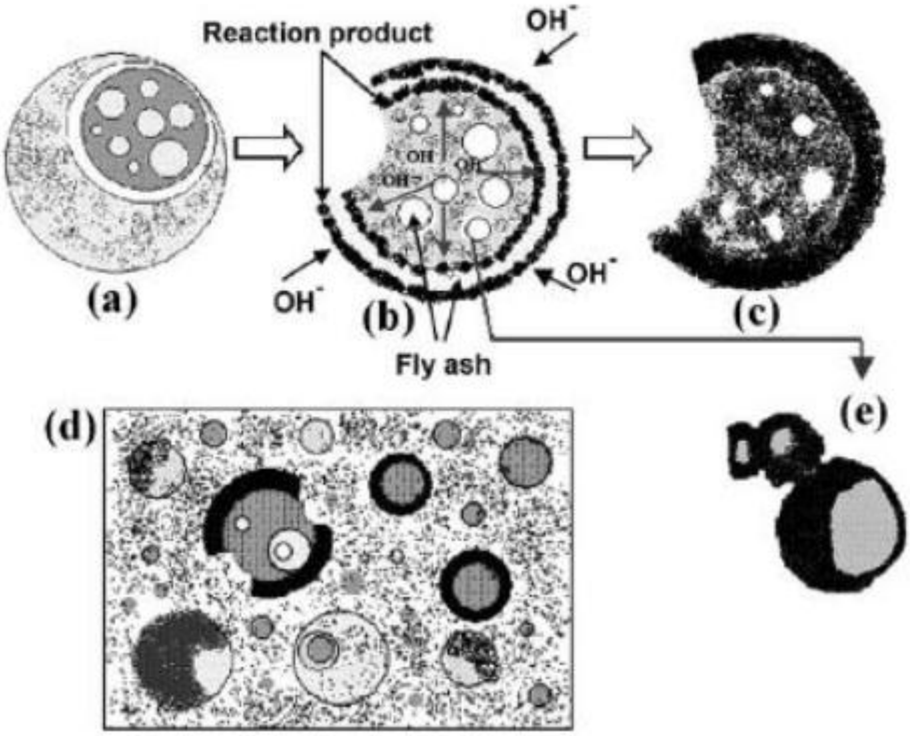


Figure 2.2 Adjective model of the alkali activation of fly ash [31]

Davidovits (1994) mentioned that the polymerization process in fly ash-based geo-polymer requires high alkaline solutions for dissolving the silica and alumina ions in the fly ash. Alkaline liquids are the major components of geopolymer binders. The principle of alkaline activation of blast furnace slag is used first in the 1940s when Purdon published a paper on “The action of alkalis on blast-furnace slag” in the Journal of the Society of Chemical Industry (Belgium) [32].

Recently, various studies are performed using alkaline liquids for the production of geopolymer binders. Sodium hydroxide with sodium silicate solution is the most popular alkaline activator used by many researchers. In fact, van Jaarsveld et al. and Silverstrim et al. (1997) advanced the geopolymeric fly ashbased cements when they combine sodium hydroxide and silicate [8].

It was reported by Davidovits et al. (1999) that using sodium hydroxide solution to attain the polymerization of a kaolinite material. Moreover, many tests result are reported on the development of the source materials, and counducted by and Grutzeck et al. (1999), Palomo et al., Swanepoel, Strydom and Xu and van Deventer (2002), Xu and van Deventer (2001), who used various alkaline activators.

2.5 Effect the chemical attacks of Geopolymer concrete

It was revealed by durability tests on OPC concrete that the materials have a complicated mechanism against sulphate attack. Another reason is the reactions between sulphate-bearing solutions and cement hydration products and it clarifies itself in different manners. The tests of the external sulphate attack upon OPC concrete can clarify reactions involving CH, C–S–H and the aluminate factors of many cement paste [33], [34].

There are results of the reactions that cracking and expansion are directly or indirectly brought about, by ettringite in addition to formation of gypsum, on the other hand , disintegration and softening are brought about by the destruction of C–S–H. Heat-cured-low calcium FA-based geopolymer concretes, on the other hand, shows a strong resistance against sulphate attack. No visual signs of surface deterioration or cracking was observed in specimens exposed to sodium sulphate for up to a year. Also, the compressive strength values remained the same. Moreover, changing the length in geopolymer samples that are exposed in sodium sulphate solution for different periods had little effect which was 0.01% less than that of the first geometry [14]. In addition, in different sulphate solutions, the best performance was showed in the material of geopolymer that prepared with sodium hydroxide and we can cure at temperature that is elevated. The specimens contain 4–12% a high in strength when the immersed through solutions of the sulphate [36].

2.5.1 Acid attacks

It is reported by some authors that the chemical resistance is one of the major advantages of alkali-activated binders upon the Portland cement.
It was used by Glukhovsky that the materials of alkali-activated slag mortars remarking and it was notified increase tensile strength in this stage even after exposed in hydrochloric acid solutions (pH = 3) [37]. The exposure of alkali-activated slag mortars was tested by a lot of researchers during six months in 5% acid solution concentration and reporting for citric acid changes that could be low . It has been noticed because of nitric and hydrochloric acid changing was moderate despite of extreme changes were noticed when they used sulphuric acid [38]. Davidovits et al. reported that, after four weeks of immersion in 5% hydrochloric and sulphuric acid solutions,

alkali-activated binders underwent around the mass losses of 6-7% while Portland cement based concrete suffered mass losses of 78-95% [39].

It was tested by Palomo et al. the metakaolin mixtures activated with the materials of NaOH in addition to waterglass when he submitted it during 90 days towards sea water (pH = 7), sulphuric acid (pH = 3), and sodium sulphate (pH = 6). It was reported by them that a minor flexural strength could be decreased from 7 to 28 days immersion, in the middle of 28 and 56 days flexural strength could rise ,it could go down again from 56 days to 90 [40]. It was also reported by them that behaviour was the same as solutions of the several acid. Unreacted sodium particles according to these authors are impossible to be in the building hardened material and it stayed in condition that could be soluble. When it has a connection with a solution. They can be leached increasing the binder porosity and mechanical strength lesser . After 3 months , on the other hand, strength can rise and indicate that the process of the reaction will be evolving . with the formation of zeolitic precipitates therefore, it can rise strength and lower porosity. It was compared by Stegmann and Shi that the resistance of acid towards several binders; (AASs) that stands for alkali-activated slags in addition to OPC binders, FA /lime binders (FAL) and high alumina cement (AC), when in nitric (pH = 3) is immersed and acetic (pH = 3 e 5) acid solutions [41]. It was told about that OPC binders given higher mass losses than AAS and FAL binders while AC pastes could be fully dissolved. OPC pastes, according to these authors, are more porous than AAS on the other hand, less porous than pastes of FAL, as a result, chemical attack is strongly affected by the nature of hydration materials than from porosity. Also,it was reported by them that low pH acids were charge of the chemical attack.

It was compared by Bakharev et al. the OPC and the resistance of alkali-activated slag concrete towards sulphat attack,reporting that the past showed a little reduction of strength which referred to the binder building chemical differences[13]. It was tested by Bakharev et al. the OPC and slag concretes activated in addition to waterglass and NaOH, It was during one year immersed in an acetic acid solution (pH = 4). A 33% strength loss was reported by them for the privious and for OPC concretes is 47% [42].

The strength loss is influenced by Ca content, that was claimed by them and 64% for OPC concretes and they said that only 39% for alkali-activated slag concretes. In addition to slag compounds contain lower Ca/Si molar ratio in addition to have more stable in acid medium. For OPC concrete calcium compounds, It was hold by them a high of Ca/Si molar ratios and reacted with acetic acid forming acetic calcium compounds that could be soluble.

It was summed up that concretes with less free calcium include a performance that is very higher in acid medium. it was confirmed by work of Song et al. [29] that alkali-activated FA concretes has chemical resistance that is very high, in the time it was during 8 weeks immersed in a 10% concentration sulphuric acid solution, it was showed by them strength losses respectively of 3% and 35% [43]. It was said by Gourley and Johnson that a Portland cement concrete with a service life of 50 years can lose about 25% of its strength in a sulphuric acid solution (pH = 1) after 80 immersions cycles on the other hand, It required for alkaliactivated concrete 1400 immersions cycles in order to lose the same mass .It meant that a service life of 900 years [44]. It was said by Pacheco-Torgal et al. [31] an average mass loss of just 2.6% during 28 days and next of being submitted to the attack of (nitric , hydrochloric and sulphuric) acids, on the other hand , for Portland cement concretes, the mass loss has double value [45].

2.5.2 Magnesium sulfate attacks

Sulphate attack is one of the major concerns for durability of geopolymer materials. Previous tests with OPC suggest that a significant concrete damage occurs when the concrete is immersed in sulfate liquid [46].

Hakkinen (1998) studied the sulfate resistance of OPC and GBFS specimens. The author concluded that, after 2 years of exposure, the geopolymer could demonstrate high stability when exposed to a magnesium sulfate concentration of 1% while 25% decrease was observed in the OPC [47].

2.5.3 Seawater attacks

Concrete might endure various types of attacks in the time that entire immersed in seawater for an enlarged time. The seawater contains 3.5% dissolved salts are composed of sodium chloride and magnesium sulphate. It has been broght about by Sulphate ions a general attack on cement paste by promoting the reactions of chemic that result in spalling and cracking.The reaction in the middle of the sodium sulphate that stands for (Na2SO4) with portlandite that stands for (CH),in this case , the exact mechanism can stay unclear in addition unreacted C3A monosulphate, forms gypsum (CSH) and ettringite (C6AS3H32). Bassuoni and Nehdi. They found out in continuous immersion that erosion and loss of concrete constituents have more control more than expansion because of the ettringite formation. The undesirable cause can reach to concrete deterioration like salt crystallization , erosion of concrete cover, and [49] expansion in the concrete pores. [50]. The process of wetting-drying has a relation with immobilization chloride in addition to moisture throughout the concrete pores under action of cyclic. The degradation of the Surface in the place of salts and a temperature that differs in non-stop immersion and wetting-drying exposure of seawater in the environment ithat ncreases the concrete porosity and the the overall durability will be affected .

There is a new type of concrete like Te GGBFS geopolymer concrete has good engineering properties that are higher than the concrete of OPC. It is said that they claimed that geopolymer is to be durable in some aggressive environments such sulfate and fire [51]. The produc of the reaction , aluminosilicates and the content of low calcium in the geopolymer. They considered the High calcium cement as more prone to the aggressive ions attack. Geopolymer concrete can face resisting in synthetic seawater and do without strength degradation in addition to weight loss that is significant [52]. After 270 days of immersion ,the porosity of the concrete in the seawater will stay low [30]. The FA geopolymer concrete contains low chloride ion diffusion coefficient because of the low permeability coefficient [53]

FA based GPC is a concrete type that exhibits favorable engineering characteristics compared to OPC based concrete. The geopolymer was supposed to be durable in some aggressive environments like fire and sulfate [51], [54].

2.6 Geopolymer Properties

Various studies have been conducted to explore the physical and chemical properties of geopolymer in addition to long term durability tests. Davidovits et al. (1988) has made many tests on physical and chemical properties of geopolymers and clarified that geopolymers can possess exceptional properties such as a early strength and high durability against freeze/thaw cycles, corrosion and sulfate attack [55]. During the initial curing period, strength of geopolymers could reach upto 30 MPa, that was 75% of the final strength. Consequently, in comparison to concrete mortars manufactured with normal Portland cement, geopolymer mortars can obtain their strengths more quickly. The rise in temperature accelerates the reaction in geopolymeric binders, according to Palomo et al. 1999. Higher temperature leads to a quicker strength gain in geopolymer materials. [40].

As compared to OPC materials, geopolymers exhibit superior characteristics considering the heat and fire resistance of geopolymeric binder. (Davidovits 1988 & 1994). Under the temperature exposure up to 300 C, OPC underwent significant deterioration in compressive strength while no significant deterioration was observed in geopolymeric binders at 600 C. Also, geopolymers can demonstrate low shrinkage comparing to OPC [14].

In addition to their mechanical and physical properties, geopolymer materials have also exposed superior chemical properties such as durability against sulfates or acidic medium, seawater attack, and akalisilica reaction [56]. As stated by Comrie et al., the enhanced durability of geopolymers against severe chemical attackes can be attributable to the fact that the lime does not play a significant role in the structure unlike Portland cement. [57].

In OPC concrete deterioration, there is common causes that the alkali-aggregate can give a reaction, which is a chemical reaction in the middle of specific sort of aggregates and alkalis from the Portland cement. The chemical reaction might be either a reaction of alkali-silica or a reaction of alkali-carbonate. Under certain causes, this reaction has results and it can be bad expansion in the concrete structure is cracking. Absent factorslike alkalis in the cement and reactive can stop the chemical process to occure. Davidovits (1994) utilized the standard one.

By demonstrating the alkali-aggregate resistance of geopolymeric cements compared to OPC , they accelerated the Mortar Bar Test, while using much higher alkali content for the geopolymer pastes. The specimens of geopolymer can appear to be healthy, whereas the specimens of the Portland cement did generate alkali-aggregate reaction. Some of them follow many studies on this issue like Palomo ,Fernandez-Jimenez and Garcia-Lodeiro (2007) and they established that alkali-activated FA mortars that is made in addition to sodium silicate solution that expanded less than the 0.1% maximum suggested by the ASTM standard of -94 after 16 days [20].

Resistance to acid attack is a previous tests of appealing property of geopolymer binder that depict the previous one . All of them state that alkali-activated binders can perform a way that is better than OPC in the time that is controled to chemical aggression by acid because of the high calcium content of OPC [14]. It was studied by Silverstrim et al. the behavior of an alkali activated FA specimen that are exposed to 70 vol% nitric acid for about 3 months . they said that the specimen remains its dense microstructure. It was stated by Davidovits et al. that metakaolin-based geopolymer “K-PSS” could clarify just 7% of the mass loss after the specimens were in it submerged for 30 days in 5% solution of sulfuric acid [20]. It was investigated by Bakharev that the materials of the durability of geopolymer manufactured utilizing a class F (FA) and alkaline activators, in the time it is exposed to 5% solutions of acetic and sulfuric acids. It was showed in the results that the materials of a superior performance of the geopolymer in the time is exposed to solutions that is acid and compared to normal Portland cement (OPC) paste. The materials of Geopolymer can be manufactured with sodium hydroxide and cured at elevated temperature that demonstrates a very significance in terms of the performance.

The seawater attack resistance is considered the final chemical property. Usually, in the marine environment, the concrete can be controlled to various chemical reactions that can involve chlorides ,magnesium ions and sulfates by mechanisms of crystallization of expansive salts, precipitation of insoluble compounds and so forth . It was reported by Palomo et al. (1999) the results of experiments that were attained on mortar prisms that was made of alkali-activated metakaolin and sand that was immersed in ASTM seawater and different solutions for some days. They observed that the nature of the aggressive solution contains effect that that has little negative on the evolution of microstructure and the strength of these materials. Similarly, Bakharev (2005), Fernandez-Jimenez et al. (2007), finished by saying that alkaline activated fly ash pastes and mortars perform satisfactorily in the time they were exposed to seawater in addition to sulfates [36], [52].

2.7 Some issues related to the durability of concrete.

The concrete is bound and affected by base substances and acids which appear in wastes . With acids , chemical attack can be specifically strong where the pH will be less than 4 and cause mechanical abrasion.

2.7.1 Drying shrinkage

Drying shrinkage can be defined as the time dependent decrease in volume of concrete. In contrast to creep, drying shrinkage is not effected by the external factors. It has four types that are classified as plastic, chemical, thermal and drying shrinkage [58]. It was reported in the last test that drying shrinkage has result that is direct and of hydration het . It can rise with the increased dosage of waterglass activators [59]. Furthermore, Wallah and Rangan (2006) have reported that heat-cured fly-ash based geopolymer concrete suffers very low drying shrinkage and shrinkage strains altered around the value that is just about 100 microstrain.

2.7.2 Alkali - aggregate reaction

There is a chemical process of Alkali-silica reaction (ASR) between an alkaline solution and the aggregates including alkaline oxides in the cement and forms of reactive silica presented within the aggregate.

The expansion of ASR is a lot of a concern in OPC because of the current of portlandite ($Ca(OH)_2$) in the Portland cement paste. The portlandite can give a reaction with activator alkalis (NaOH, KOH) at favourable humidity which causes by forming a gel which in the end , morphs into a rigid crystalline structure that can cause expansion that is internal in addition to deterioration of the cementitious mass [60].

2.7.3 Heat resistance

Slag based geopolymer concretes have some advantages as compared to normal Portland cements. They have initial higher mechanical strengths and better resistance to chemical attack and better resistance towards the heat. It can be endured by FA based geopolymer concrete by considering high heat of temperature. [61].

2.7.4 Alternate wetting and drying

It is said that the Cyclic drying and wetting can bring about non-stop moisture movement throughout concrete pores [62]. This cyclic effect can cause problems of durability . The water can evaporate and it can rise the concentrations of ions such as other ions and chlorides. The drying of concrete can help it to increase the availability of the oxygen that is required for steel corrosion . . For instance; compared to structures submerged in water permanently, deterioration in concrete structures subjected to wetting and drying exposure is greater [63].

The Fly ash based geopolymers has chemical durability that is greater than normal Portland Cement (OPC) in severe environments that might be attributed to their lower calcium content. The a major component of OPC is Calcium that can react with acids and the aggressive sulphates. To sum up ,[64] heat cured geopolymer concrete has little expansion that can trace exposure to wetting-drying cycles.

2.8 Factors affecting the strength of geopolymer

2.8.1 SiO_2/ Na_2O Ratio

An important parameter is the SiO2 / Na2O ratio in geopolymer design. Variations in the SiO2 / Na2O ratio significantly modifies the degree of polymerization of the dissolved species in the alkaline/silicate solution, deciding overall properties of the synthesized gel product and the mechanics [65].

2.8.2 Water-to-geopolymer concrete ratio

One of the substantial factors influencing the strength of GPC is the water content in the mixture [66]. In geopolymer mixtures, adding any extra water can enhance the workability of the mixtures. In general, the strength of the compressive geopolymer concrete decreases as the ratio of water to geopolymer solids increases [17].This trend is analogous to the well-known effect of water-to-cement ratio on the compressive strength of concrete   of Portland cement.

2.8.3 Temperature and Curing time

One of the biggest challenges in geopolymer design is the setting of curing time and temperatures. Similar to Portland cement, an external heat source can help to achive the geopolymer reaction to promote alkaline reactivity of the material. The temperature of higher curing can give results in high compressive strength for geopolymer concrete [17]. In addition, it can be increased by longer curing [67]. Research shows that longer curing time enhanced the process of polymerization that leads to an improved compressive strength [17].

2.8.4 PH Level

The alteration in the level of PH has a substantial influence on the workability of the GPC. The preferable way to obtain a perfect mechanical strength is the condition which is the PH rate with an interval of 13–14 [68]. The research also showed that the pH and the reaction rate is increased with the denser concentration of alkaline activator. Also, the viscosity and stiffness is decreased with higher pH values.

2.8.5 Sodium silicate-to-sodium hydroxide liquid ratio

Adding sodium silicates to mix design can increase mecahnical properties.. It was indicated by previous studies that the ratio of sodium silicate towards hydroxide of sodium can play an important role upon the development of mechanical properties of geopolymer concrete. The higher the mass ratio of sodium silicate-to-sodium hydroxide liquid and the higher is the compressive strength of geopolymer concrete [2].

2.8.6 Concentration of sodium hydroxide (NaOH) solution

The resulting paste properties are determined by the concentration which is defined by molarity of the activating solution. High NaOH additions depresses the ettringite CH formation and it can accelerate the chemical dissolution [69]. It is known that reducing the content of CH has resulted superior durability performance and strength [70]. Here we can say that higher concentration (in terms ofmolarity) of sodium hydroxide solution can result a higher compressive strength of geopolymer concrete [2]. Using sodium hydroxide as an activator for buffers the pH of pore fluids can organize activity of hydration and affects in a direct way the main form of C-S-H production in pastes of geopolymer. Between NaOH concentration and the heat generation ,we can find a linear relationship [71].

CHAPTER 3

EXPERIMENTAL STUDY

3.1 Introduction

Researchers shows that fly-ash or slag based geopolymer concrete exhibit favorable strength properties under the condition that heat curing conditions must be controlled to obtain desired mechanical properties. Hence, this experimental study focused on GGBFS based geopolymer concrete at ambient curing temperature.

This chapter reports material characteristics used in concrete production, the mixture proportions, the manufacturing and curing processes of the test samples. It also includes the test method in which the specimen types and experimental parameters are explained.

3.2 Description of resources

3.2.1 GGBFS

Ground granulated blast-furnace slag (GGBFS) is a non-metallic material with a smooth and granular nature, containing silicates and alumina silicate of calcium. The chemical compositions of GGBFS used in this research are written in Table 3.1, figure 3.1.

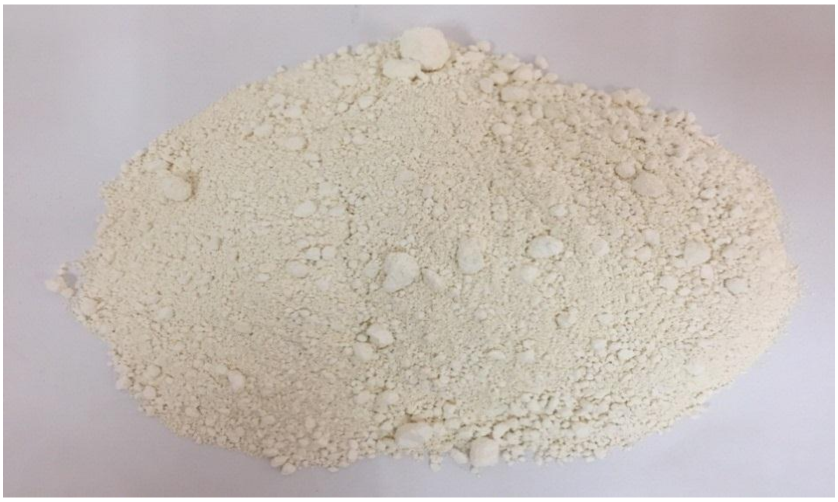


Figure 3.1 The slag used in this study

3.2.2 Ordinary Portland cement

Ordinary Portland Cement (OPC) according to CEM I 42.5 R kind was utilized in this study. Table 3.1 shows the chemical composition of the cement.

Table 3.1 Physical properties and physical properties, Chemical composition of OPC and GGBFS

Chemical analysis	GGBFS	OPC
CaO	34.12	62.12
SiO2	36.41	19.69
Al2O3	10.39	5.16
Fe2o3	0.69	2.88
Mgo	10.26	1.17
SO3	-	2.63
K2O	0.97	0.88
Na2O	0.35	0.17
Loss of ignition	1.64	2.99
Specify gravity	2.79	3.15
Blaine fineness (m^2/kg)	418	394
Surface-volume ratio (m^2/kg)	-	-
Average primary particle size (mm)	-	-
Density (g/cm^3)		
Bulk density (g/cm^3)		
Moisture content (%)		
Particle shape		
Color		Gray
Initial setting time (min)		
Final setting time (min)		

3.2.3 Aggregate

Crush limestone was used as Coarse and fine aggregate, Coarse aggregate size was between 11 mm to 4 mm and fine aggregate less than 4 mm as shown in figure 3.2 ,Table 3.2

(a) (b)

Figure 3.2 Aggregate (a) Coarse aggregate (b) Fine aggregate used in this study

Table 3.2 Mechanical and Physical properties of Gaziantep limestone

Bulk density	1.42 g/cm^3 – 2.62 g/cm^3
water absorption	1.24 % – 26.89 %
Brazilian tensile Strength	0.99 MPa – 15.06 MPa
Direct shear strength	1.36 MPa – 6.20 MPa
friction angle	40^o- 57^o
Cohesion	15 MPa – 2.1 MPa
Residual friction angle	38^o - 54^o
Uniaxial compressive strength	3.75 MPa – 49.8 MPa
Young's modulus	1.76 GPa – 14.62 GPa
Ultrasonic velocity	1950 m/s – 5910 m/s

3.2.4 Alkaline Activators

In our current study, the alkaline solution was formed with a mixture of sodium hydroxide and sodium silicate liquid. Potassium-based solutions was not chosen because it is more costly than sodium-based solutions. The NaOH with 97-98% purity was used in this research and were melted in water at least 6 hours prior to mixing. The properties and the sodium silicate activator (Na2SiO3) composition are written in Table 3.3 as provided by the manufacturer.

Table 3.3 Chemical composition of sodium silicate

Grade	**NA46**
% NaOH (w/w)	14.7
% Na2O (w/w)	11.4
% Si2O (w/w)	30.1
Wt. ratio SiO2/Na2O	2.65
Specific gravity (gm./ml @ 20 ^{o}C)	1.458
Appearance	Viscous clear to light yellow liquid
PH	12.8
Solubility (water)	Soluble
% volatiles	> 60% (water)

3.2.5 Superplasticizer

Workability of GGBFS based- geopolymer mortar was improved by adding superplasticizer (Viscocrete 30) as shown in the figure (3.3). The chemical properties of superplasticizer are shown in the Table 3.4

Figure 3.3 Superplasticizer used in the study

Table 3.4 Properties of Super Plasticizer

Properties	Superplasticizer
Name	Viscocrete 30
Color tone	Dark brown
State	Liquid
Specific gravity (kg/l)	1.07
Chemical description	Modified polycarboxylic type polymer
Recommended dosage	%1-2 (% binder content)

3.3 Experimental details

3.3.1 Mould for casting test specimens

Prism (100x100x500) mm, Cylinder (100Dia&200Ht) mm, Cube (100x100x100) mm were cast for the Fracture toughness. The split tensile and strength compressive strength tests are respectively shown in figure 3.4.

(a) (b)

Figure 3.4 Different types of moulds: compressive strength moulds, Fracture toughness mould, split tensile strength moulds.

3.3.2 Preparation of alkaline solution

The alkali solution was mixed with sodium hydroxide and sodium silicate solutions. Sodium hydroxide with a molarity of 14 the focus was intended by adding water with 177gr. The volume of NaOH solids was determined 14* 41= 574 grams of NaOH liquid with 14 M focus. The alkaline solution was prepared before 24 hours casting the concrete.

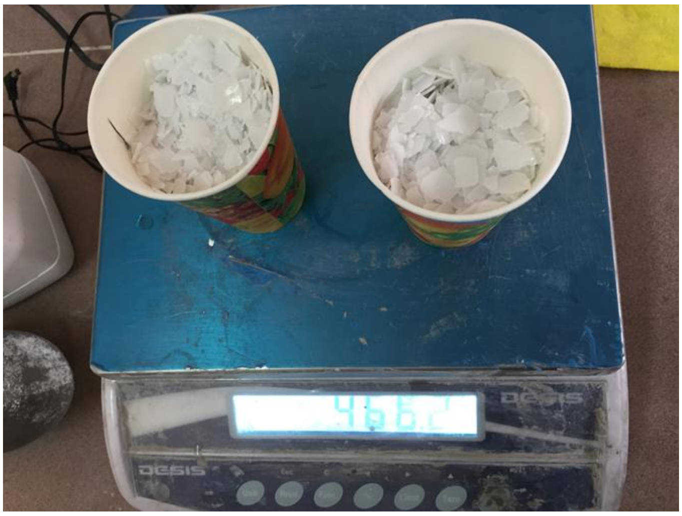
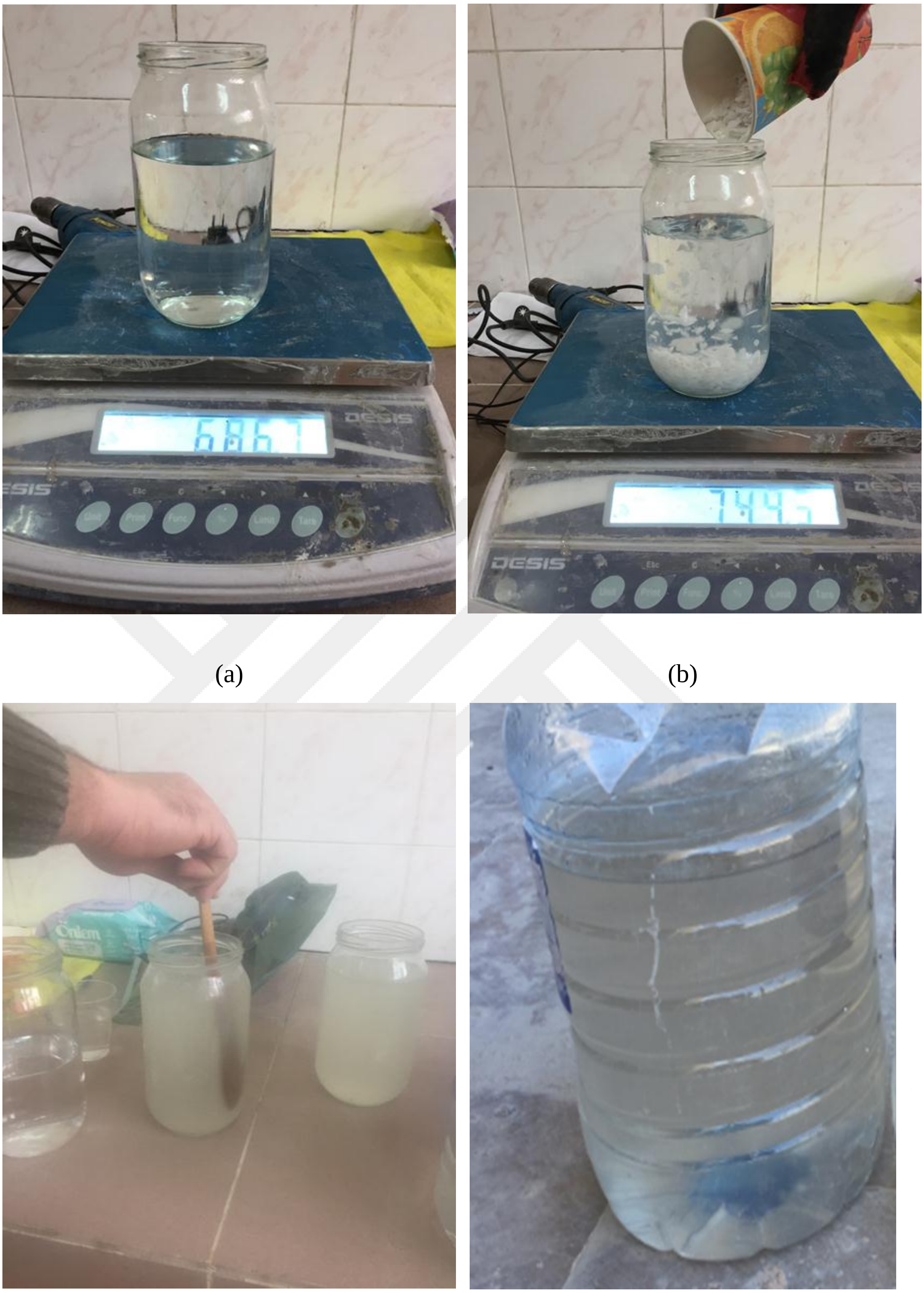


Figure 3.5 Preparation of sodium hydroxide



(a) (b)

(c) (d)

Figure 3.6 a, b, c, d, e Stages of manufacturing alkaline solution

3.3.3 Mix Design

GPC is a concrete that consists of materials such GGBFS instead of cement, Alkaline liquids (Sodium silicate and Sodium hydroxide or Potassium silicate and Potassium hydroxide) instead of water. An alkali solution with a binder proportion of 0.45 to provide perfect strength and microstructure of the GPC. Figure 3.7 shows the process of preparing GPC.

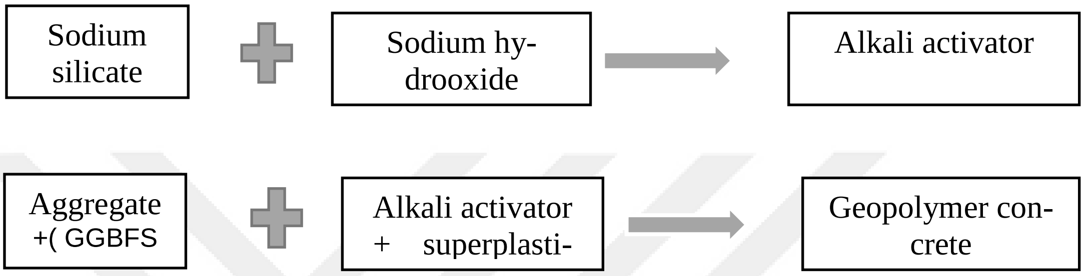


Figure 3.7 Process of preparing Geopolymer Concrete

Table 3.5 Mix design of geopolymer mixtures

Materials		**Mix (kg/m3)**
Coarse aggregate	Coarse Aggregate	1150 kg/m^3
	Fine Aggregate	575 kg/m^3
Na_2SiO_3+NaOH		225 kg/m^3
GGBFS		500 kg/m^3
Superplasticizer (SP)		6.04 kg/m^3
Na_2SiO_3/NaOH		2.5
Fly Ash 0r GGBFS /(Na_2SiO_3+NaOH)		0.45
48 hr Oven curing		70 °C

3.3.4 Geopolymer concrete mix proportion and casting

The basic process for manufacture the GPC mixtures is adopted on Standard mixing method. Aggregates is utilized as a saturated surface dry condition. Firstly, both aggregates in saturated surface dry (SSD) condition were mixed with GGBFS for about 2.5 minutes. Second, the alkaline liquid including sodium silicate and sodium hydroxide with superplasticizer was added to the dry materials and the mixing continued for 3.5 minutes. After that Cube specimen and prismatic were cast and compacted in two layers, whereas cylinder specimens in three layers. Subsequently, compacted in three layers, then vibrated on a vibration table for 10s to eliminate the air voids. After casting, the molds were covered using plastic bags to avoid the vaporization of alkaline solution for 24hr as a rest period as shown in figures (3.8,3.9,3.10,3.11,3.12,3.13).

Figure 3.8 Mixing of aggregates

Figure 3.9 a,b,c Preparation of mixture

Figure 3.10 a,b,c Vibration of concrete for 10s

Figure 3.11 Casting the mixture in the cube & prism mould

Figure 3.12 Casting mixture in the cylinder moulds

Figure 3.13 a,b Covering the moulds with plastic bags

3.3.5 Capping and curing

The concrete samples were opened after for 24hr as rest period on temperature for 23°C, then the specimens with GPC were oven cured at 70 °C temperature for 48hr, as shown in figure 3.14 and then specimens were put in ambient temperature for 28 days at 23°C before exposed in solutions. The specimens with normal concrete cured in water for 28 days. Many factors affected the strength of GPC such as the proportion of GGBFS by mass and the installation of alkaline liquid, also the curing temperature is one of the most substantial factors affecting the GPC. As the curing temperature rises, the strength of concrete decreases. In the polymerization geopolymer concrete during the curing method, it was noticed that, as the temperature rises, polymerization becomes quicker and the concrete can obtain 70% of its strength within 3 to 4 h of heating [72]. GPC needs only temperature curing instead of water curing. The nature of GPC depends on the characteristics, curing temperature and activating alkali activators.

Figure 3.14 a,b GPC specimens oven cured at 70 °C

3.3.6 Preparation of solutions

The concentration of sulphuric acid, Magnesium sulphate and salt water is 5%, 5% and 3.5%, respectively, as shown in figure 3.15 and the solutions were prepared 24hr previues specimen exposure. The initial pH (0.9) of the liquids increased speedily but was held steady at an average final pH of 4.5. Therefore, the solution was prepared 24hr before the immersion of specimens.

Figure 3.15 Solutions in the study

3.3.7 Change in mass

Firstly, the weight of samples were measured and primed with water for 24hr before exposing to liquids .Here , its weight in saturated surface and in dry situation was taken as initial weight. Next , the mass was measured and the specimens were removed from the solutions as shown in figure 3.16, and wiped before the measurement, then, the weights are taken regularly and continuously every 15 days. Weights were measured using a digital balance in a saturated surface dry situation as shown in figures (3.17,3.18). The change of the weight was calculated by the following formula.

Change in weight (%) = [(B-A)/A] x 100 (3.1)

Where A= Initial weight of water primed specimen

B = Weight of specimen after exposure

Figure 3.16 Samples removed from solutions.

Figure 3.17a,b Use of Digital balance in the experiments

(c)

Figure 3.18 Use of Digital balance with cylinder sample

3.3.8 Compressive strength test

Compressive strength is a significant property used for concrete. All properties of concrete always correlate together with the compressive strength and it can be used within some mechanical properties. Also, the compressive strength experiments were performed as per ASTM C39. A test machine with a maximum capacity of 3000 kN was used and the rate of loading was 1.5 KN/s as shown in figure 3.19. The test was executed in the period of 28 and 56 days and test results are compared with control concrete specimens.

The compressive strength was given by the formula;

$\sigma = F/Area$ (3.2)

Where

σ – Compressive strength (MPa)

F - Force applied (N)

Area - cross-sectional area (mm2)

A reduction in compressive strength was found on the following formula:

Reduction (%) = $[1-(d/c)] \times 100$ (3.3)

Where c= Initial compressive strength at the age of 56 days

d = Compressive strength after exposure

Figure 3.19 Sample of compressive strength

3.3.9 Tensile strength test

Splitting tensile strength is known as a measure of the ability of a material to tolerate a force that tends to pull it apart. The tensile strength is one of the substantial characteristics of the concrete. The concrete is not commonly expected to resist the direct tension because of its low tensile and crisp in nature. However, the measurement of tensile strength of concrete is needed to determine the load at which the concrete fails in tension.

The test was subjected at the age of 28, 56 days both for control and geopolymer concrete specimens. Tight packing strips of plywood were placed between the specimen and loading platens of the testing machine, as shown in figure 3.20

The splitting tensile strength was obtained using the following equation:

$$f_s = \frac{2P}{\pi h \Phi} \tag{3.4}$$

Where P, h, and Φ are the maximum load, length and diameter of the cylinder specimen, respectively.

Determination a reduction in split tensile strength was given by the formula:

$$\text{A reduction (\%)} = [1-(e/f)] \times 100 \tag{3.5}$$

Where e = Split tensile strength (in MPa) at the age of 56 days

f = Split tensile strength (in MPa) after exposure

(a) (b)

Figure 3.20 a,b Split tensile strength loading

3.3.10 Fracture toughness test

Studies have proved that GPC has perfect mechanical characteristics and resistance to many strict chemical attacks. However, the hardened GPC is quasi-brittle (i.e., weak against the tensile loads).

The fracture energy Gf of the materials can be defined as the amount of energy that consume to propagate the crack in one unit [73]. Mathematically, it is the area under the load displacement curve or the load-CMOD (Crack Mouth Opening Displacement) that curve obtained by the three-point bending test that proposed by RILEM TC 50 [74] [75] or by the Japan Concrete Institute Standard method [76].

A notch is recognized as a geometric discontinuity which possess a particular path and origin radius [77]–[80]. The redistribution of stress in a shape due to the presence of a crack or a notch can be dissolved by the Linear Elastic Fracture Mechanics mothed. The fracture attitude of concrete is planned by the fracture parameters such a Critical stress density factor (KIC, fracture energy (GF) and Crack Mouth Opening Displacement (CMOD). A three-point bending test can be utilized to determine the fracture parameters.

Fracture toughness (K_{IC}) is an indirect method surface energy determination of cementitious materials[81], [82]. The test was specified according to RILEM 50-FMC

[83]. The displacement was measured together by using a linear changeable displacement transducer (LVDT) at mid-span.

The fracture energy, GF, of one edge notched beam can be determined under three-point bending as measured by the following formula:

$$G_F = \frac{W_{\circ}+mg\delta s\frac{S}{U}}{B(W-a)} \quad (3.6)$$

Where Wo is the area under the load-deflection curve; m is the mass of the beam; g is the acceleration due to gravity; δs is the specified deflection of the beam, while S, U, B, W, and a are span, length, width, depth, and notch depth of the beam, respectively. Moreover, All the prism was loaded at a fixed rate of 0.02 mm/minute [84].

According to previous studies, the net flexural strength,f flex, was obtained by the following formula (Pmax is the ultimate load).

$$f_{flex} = \frac{3\text{PmaxS}}{2B(W-a)^2} \quad (3.7)$$

Where, Pmax, S, B, W and a is the peak load (N), span length (mm), width of beam (mm), depth of beam (mm) and depth of the notch (mm) respectively.

The critical stress intensity factor (K_{IC}) was calculated using Eq. 4. It is also known as fracture toughness and relates to the peak load and the geometric dimensions of the beam.

$$K_{IC} = \frac{3Pmaxl}{2bd^2}\sqrt{a_{\circ}}(1.93-3.07A+14.53A^2-25.11A^3+25A^4) \quad (3.8)$$

Where Pmax is the peak load, l is the span of beam, b is the width of beam, d is the depth of beam, $a_{\circ}$ is the depth of the notch and A = $a_{\circ}$/d [81].

The fracture energy values obtained here were compared with some proposed model equations. The CEB-FIP committee recommended a prediction formula as shown below

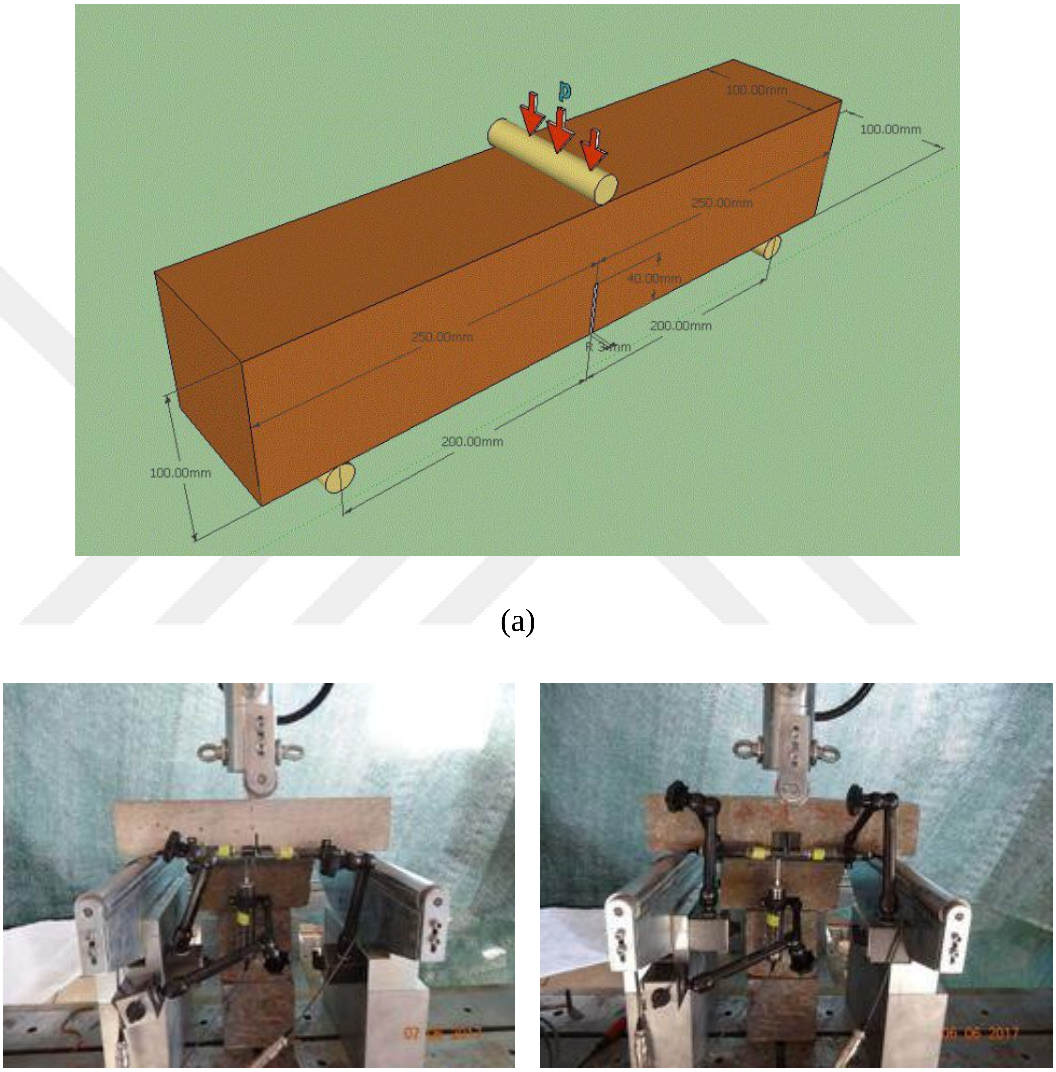
$$G_F = (0.0469s^2-0.5s+26)\left(\frac{f'c}{10}\right)^{0.7} \quad (3.9)$$

Where f'_c is the compressive strength (MPa), s is the maximum aggregate size (mm).

Another equation proposed by Bazant and Becq-Giraduon the prediction results of this equation to test results were 29.9% [82]. This equation takes into account the maximum aggregate size (S), compressive strength (f_C') and water to cement ratio (w/c).

$$G_F = 2.5\ \alpha_0\ \left(\frac{f'c}{0.051}\right)^{0.46}\left(1+\frac{S}{11.27}\right)^{0.22}\left(\frac{W}{C}\right)^{-0.30} \tag{3.10}$$

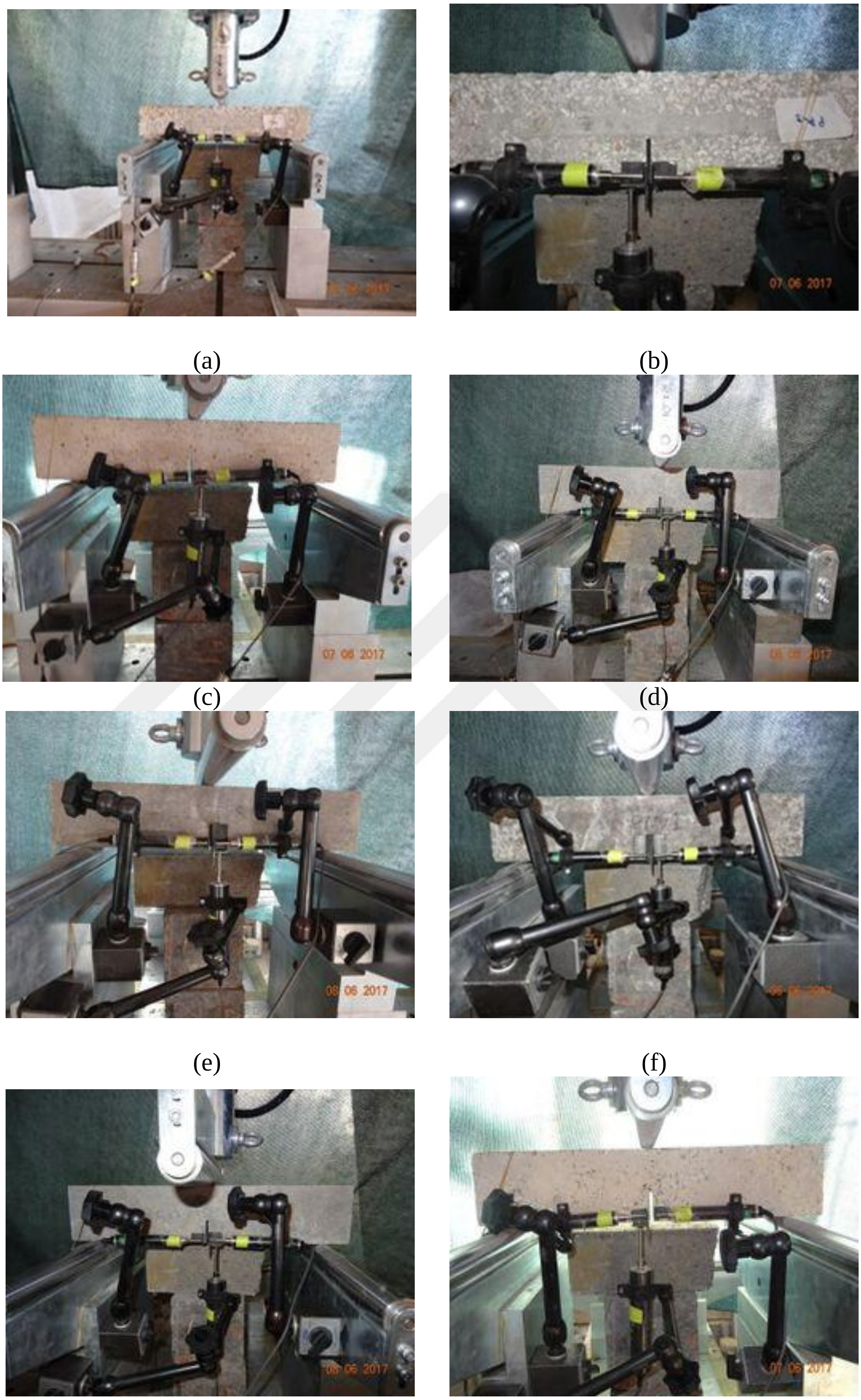
The characteristic length was also calculated by the following equation to describe brittleness of the concretes.



(a)

(b) (c)

Figure 3.21 a,b,c testing setup



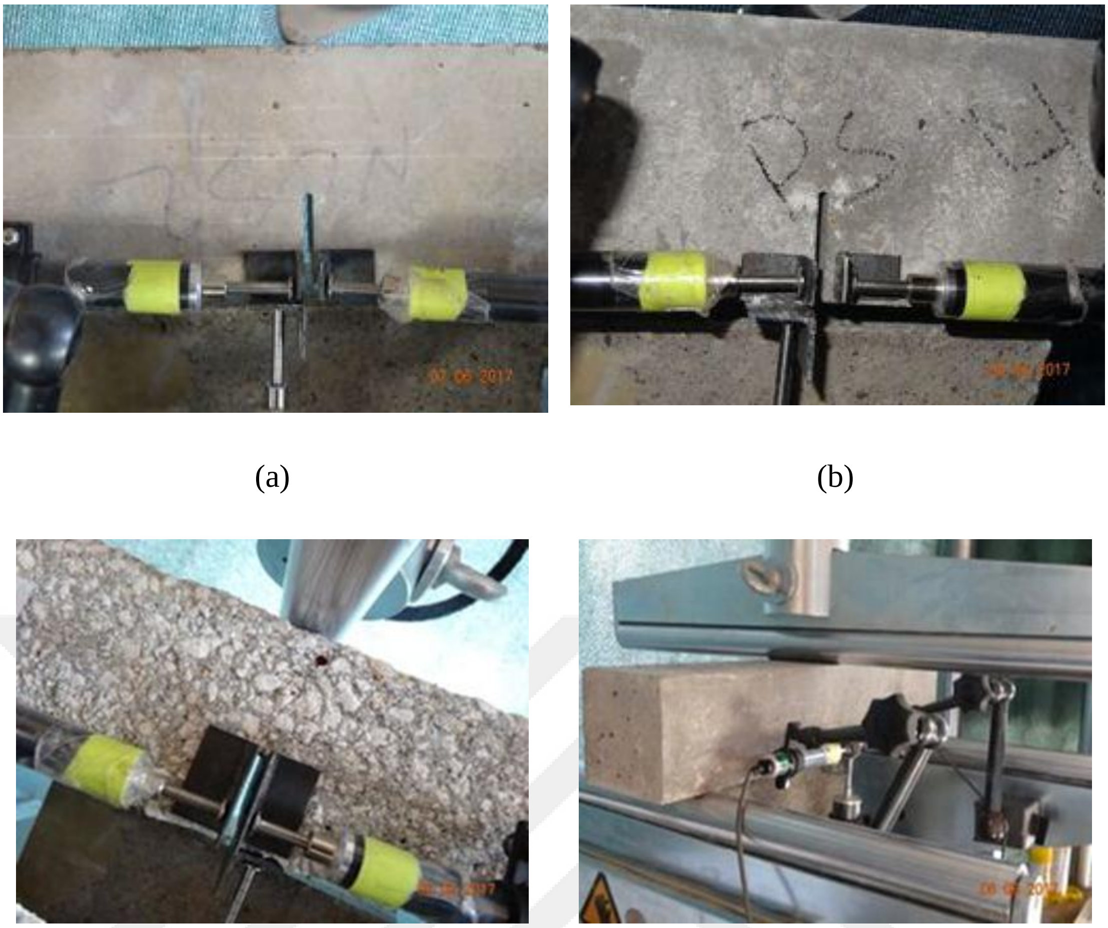
(a) (b)

(c) (d)

(e) (f)

(g) (h)

Figure 3.22 a,b,c,d,e,f,g,h Fracture toughness for different mixtures



(a) (b)

(c) (d)

Figure 3.23 a,b,c,d Notch and LVDT of various specimen

CHAPTER 4

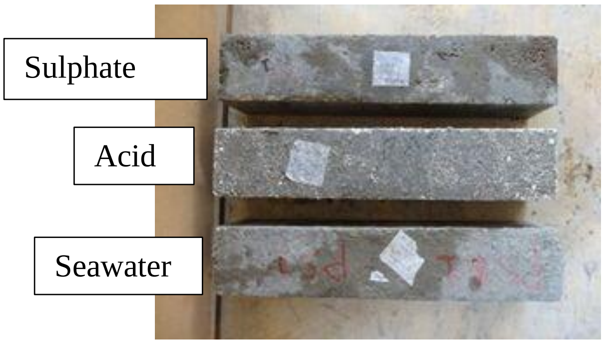
RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, experimental results of OPC and GGBFS-GPC concrete mixtures are discussed. The GGBFS were used with an alkaline solution as a binder for geopolymer mix concrete. Mechanical properties of geopolymer concrete specimens and its resistance to chemical attack were examined. Test results indicate the compressive strength, Split Tensile strength, Fracture toughness, Visual appearance and change weight. Results were compared to those with OPC under same attacks.

4.2 Visual Inspection

Visual inspection for exposed specimens was carried out weekly. Test results represent that GGBFS based geopolymer concrete samples yield less deterioration compared to specimens of OPC. Specimens exposed to 5% sulphuric acid is shown in figures (4.1,4.2). The concentration of the solution affects the severity of the damage and deformation of the samples. It may be observed that the specimens submerged in acid have shown erosion of the surface with a white layer of gypsum crystals created on the specimen surface due to the chemical reactions between calcium monosulfoaluminates and calcium hydroxide, that result in decreasing the mechanical resistance.



(a) GGBFS-GPC prsim

(b) OPC prism

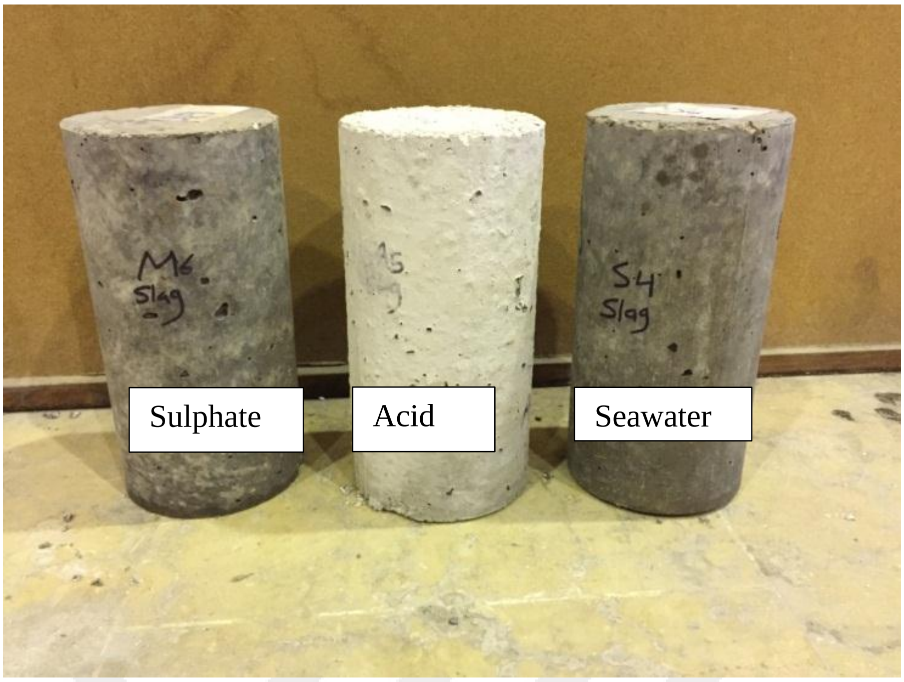
(c) OPC prism

(d) GGBFS-GPC in Acid

(e) GGBFS-GPC in Sulphate

(f) GGBFS-GPC in Sea water

Figure 4.1 a,b,c,d,e,f Visual appearance of concrete specimens when immersed in sulphuric acid 5%, 5% Magnesium sulphate and 3.5% seawater for Prizm of different mix.



(a) GGBFS-GPC cylinder

(b) OPC cylinder

Figure 4.2 a,b Visual appearance of concrete specimens when immersed in sulphuric acid 5%, 5% Magnesium sulphuric and 3.5% seawater for cylinde

Specimens immersed in 5% Magnesium sulphuric and seawater, were observed GGBFS concrete less deterioration, while the OPC concrete experienced significant degradation as shown in figures (4.1,4.2) and appeared some deterioration, like the formation ettringite on the surface. Ettringite formation was the predominant impact in OPC exposed to sulfate attack. it was noticed that ettringite formation was the major technique of damage in OPC, it was noticed that the destruction of C-S-H was a significant result in the case of attack by magnesium sulfate liquid for OPC [85].

4.3 Weight Change

In this study, weight change of specimens exposed to chemical solutions was measured. An initial increase in the weight of GPC specimens after 7 days was noticed because the cavities and pores of the concrete specimens can absorb liquid. Also due to the generation of expansion products like ettringite and gypsum, which made the concrete more compact. After 15 days of exposure, it was observed that the mass of exposure specimens decreased due to the chemical interaction with solutions.

Deterioration of the external surface area of coarse aggregates was exposed to solutions also decomposition of concrete specimens beginning from the exposed surface and transfer to transition zone of specimens immersed in 5% sulphuric acid.

Loss in mass observed after 15 days of exposure to the acid solution, while the amount of loss mass was more in OPC compared to GGBFS-GPC.

As shown in the figures (4.3,4.4,4.5). A similar trend was observed by (Davidovits J., 1994) wentest the GPC immersing in 5% sulfuric acid, which proves that GPC stayed coherent in acidic environments with the loss in weight the range of 5-8%, compared to 30 to 60% loss in weight of calcium-aluminate cement and total destruction of OPC. The time of immersion was not stated in the work [6].

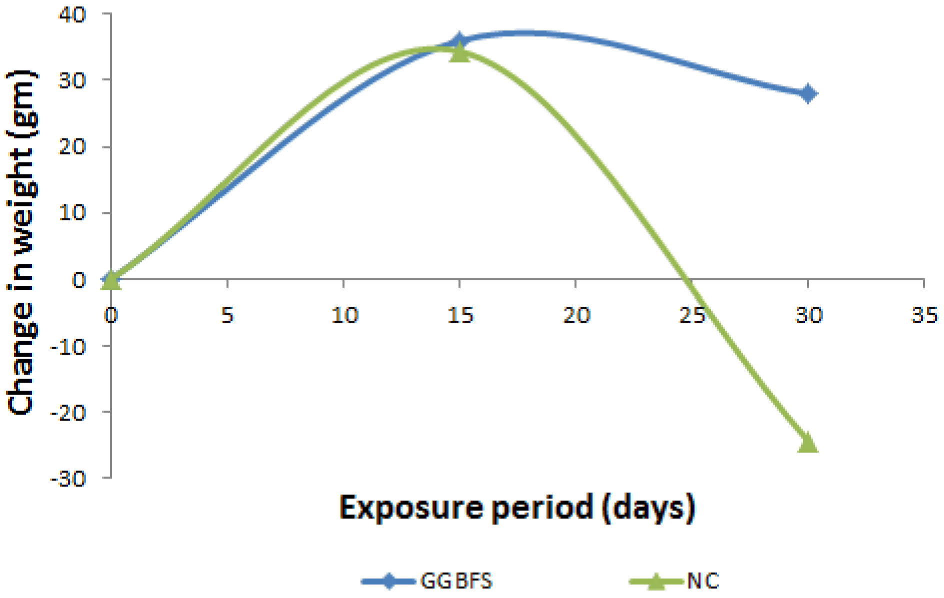


Figure 4.3 Mass Change in 5% sulphuric acid of cube

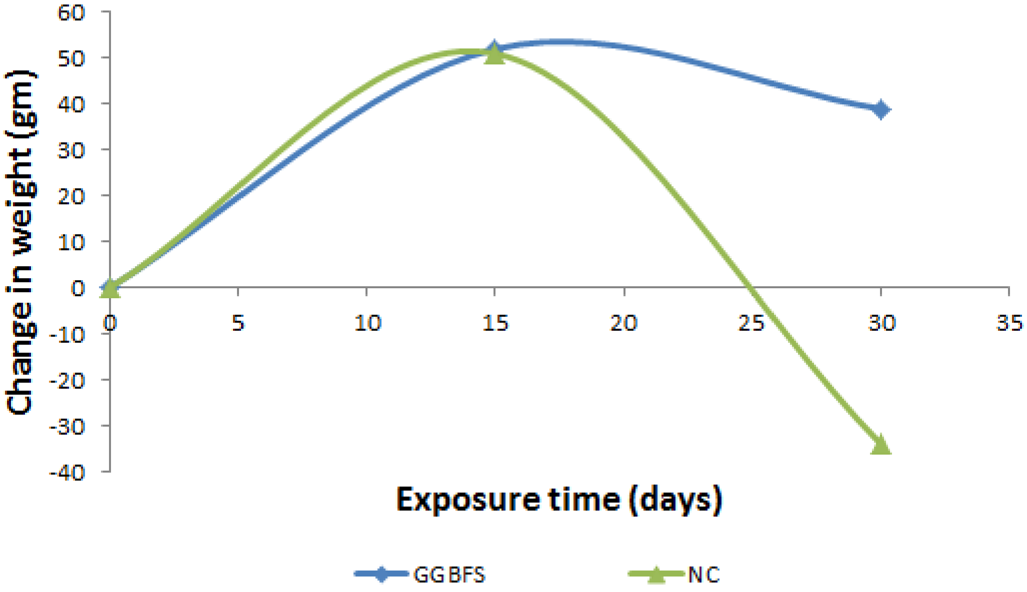


Figure 4.4 Mass Change in 5% sulphuric acid for cylinders specimen

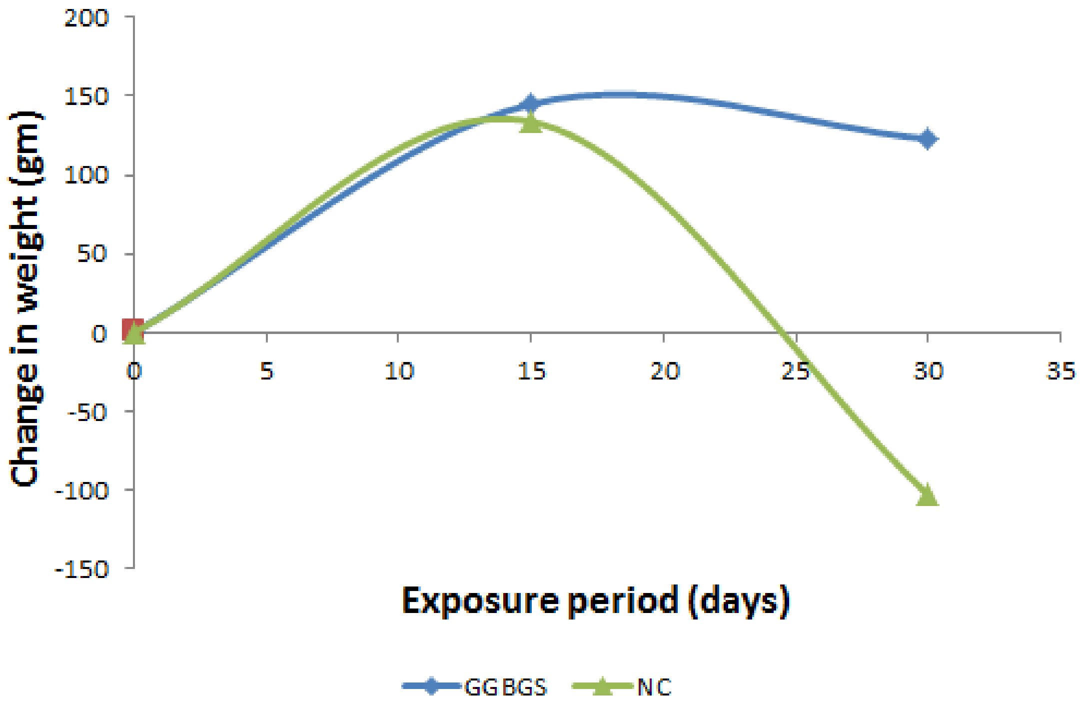


Figure 4.5 Mass Change in 5% sulphuric acid for prism specimen

While specimens were immersed in 5%, 3.5% Magnesium sulfate, and salt water respectively, an increase was noticed in the results of the weight changes because of the chemical interactions with calcium hydroxide and calcium monosulfoaluminates to form gypsum and ettringite.

As shown in the figures (4.6,4.7,4.8,4.9,4.10,4.11,4.12,4.13), the formation of ettringite and gypsum because of sulfate attack, lead to high expansion since these elements could absorb moisture so that their size of the solid stage could increase.

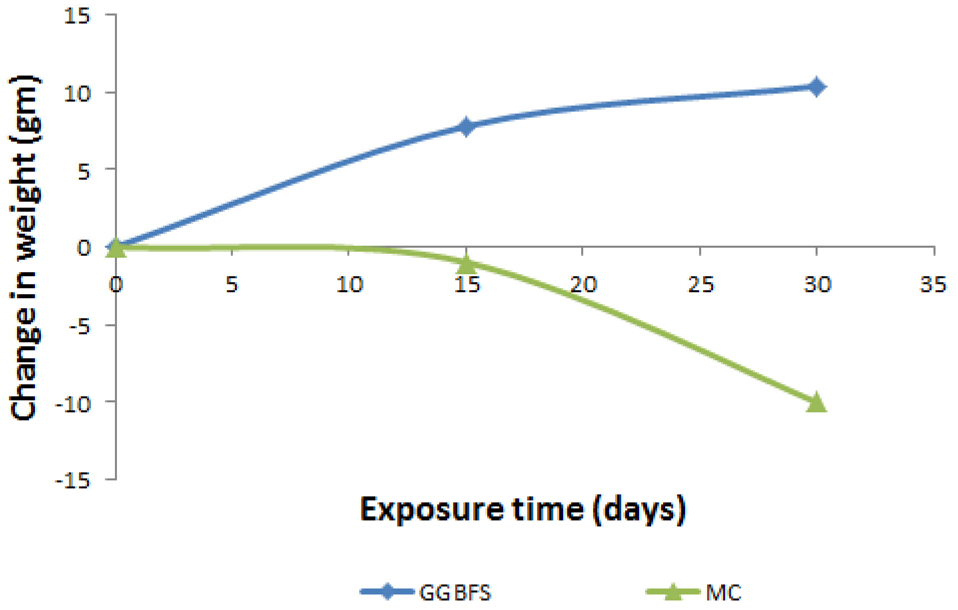


Figure 4.6 Mass Change in 5% Magnesium sulphate of cube specimen

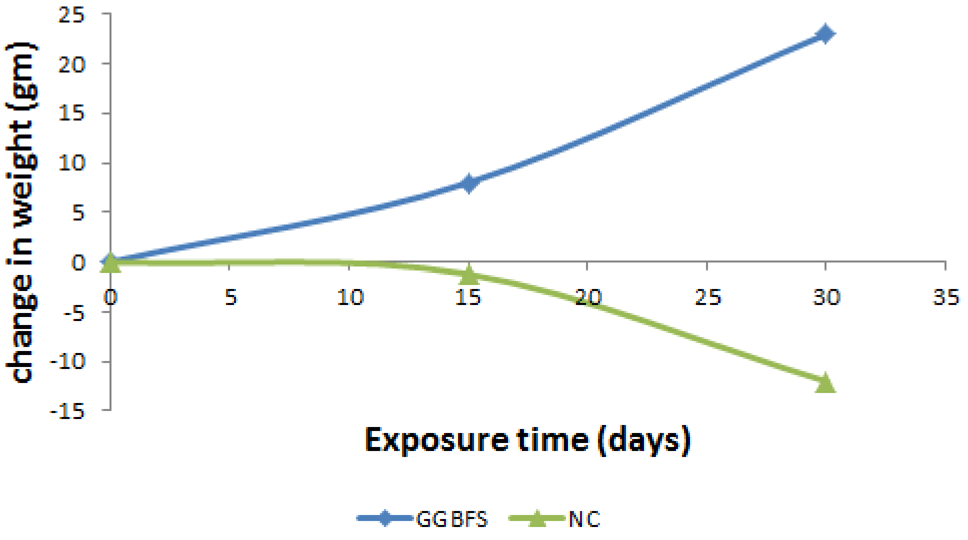


Figure 4.7 Mass Change in 5% Magnesium sulphate of cylinder specimen

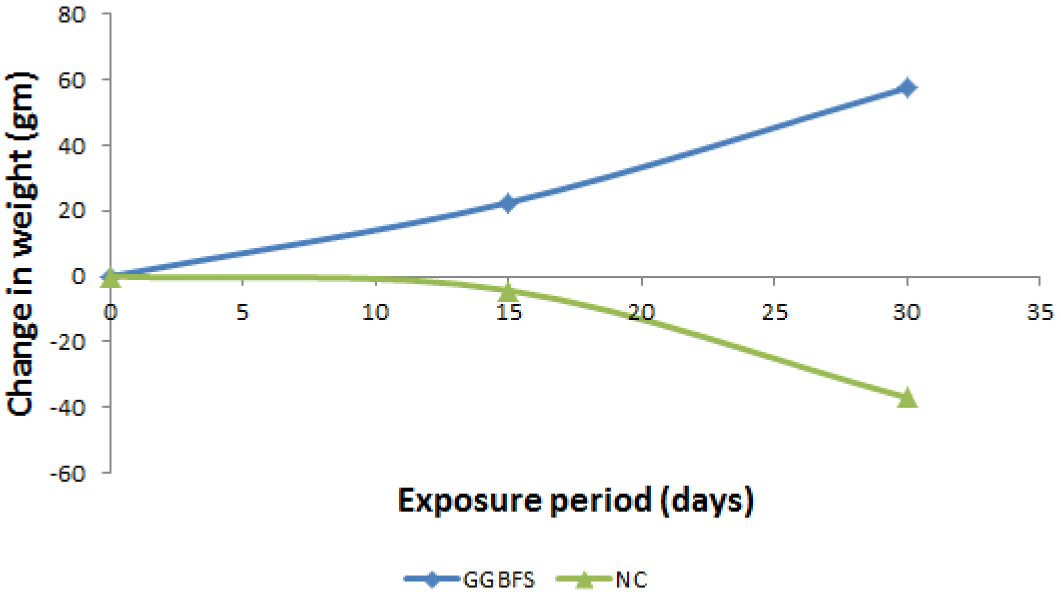


Figure 4.8 Mass Change in 5% Magnesium sulphate of prism specimen

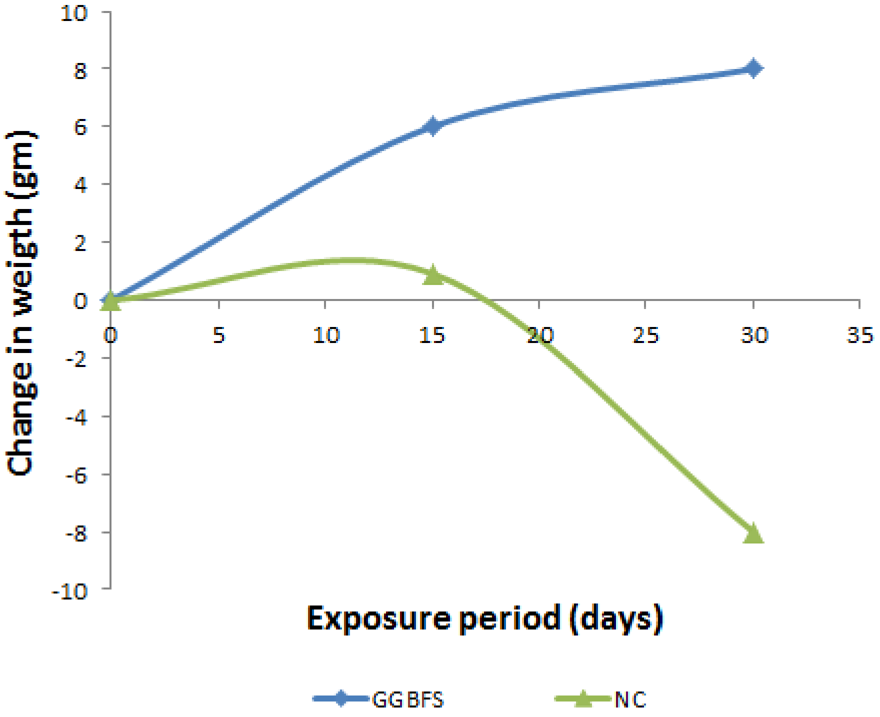


Figure 4.9 Mass Change in 3.5% salt water of cube specimen

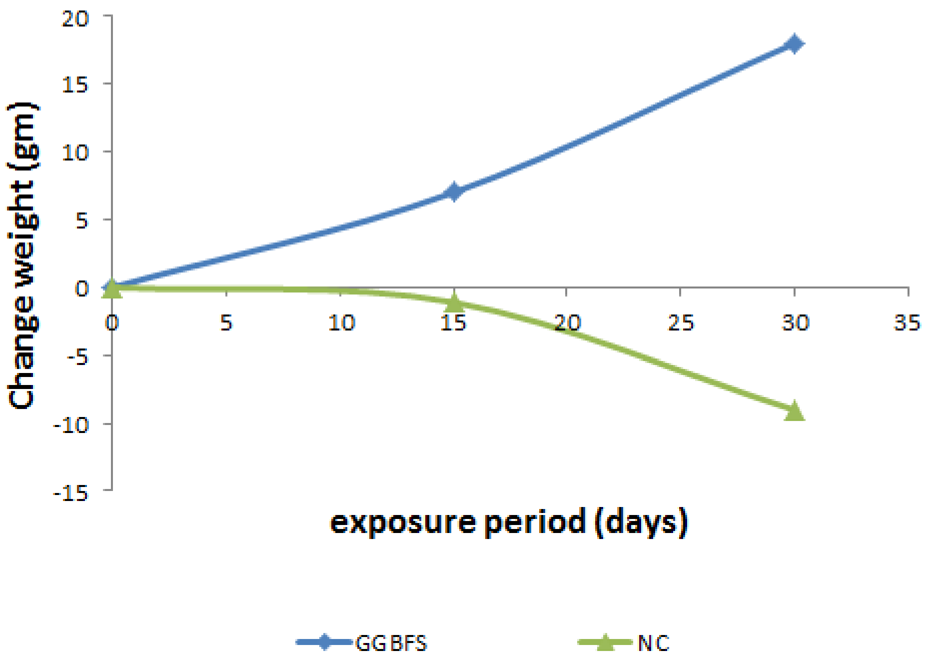


Figure 4.10 Mass Change in 3.5% salt water of cylinder specimen

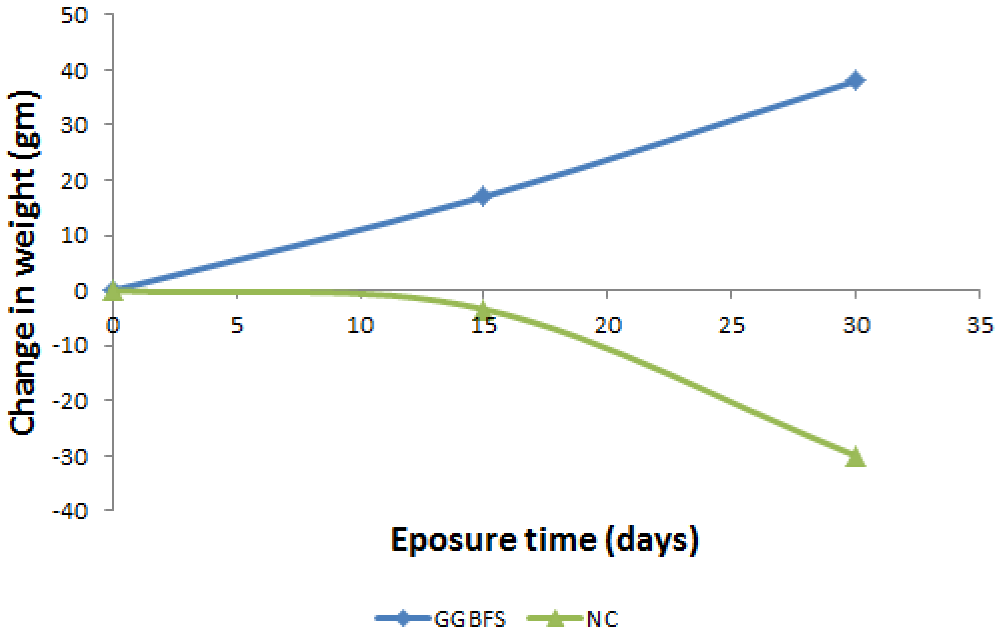


Figure 4.11 Mass Change in 3.5% salt water of Prism specimen

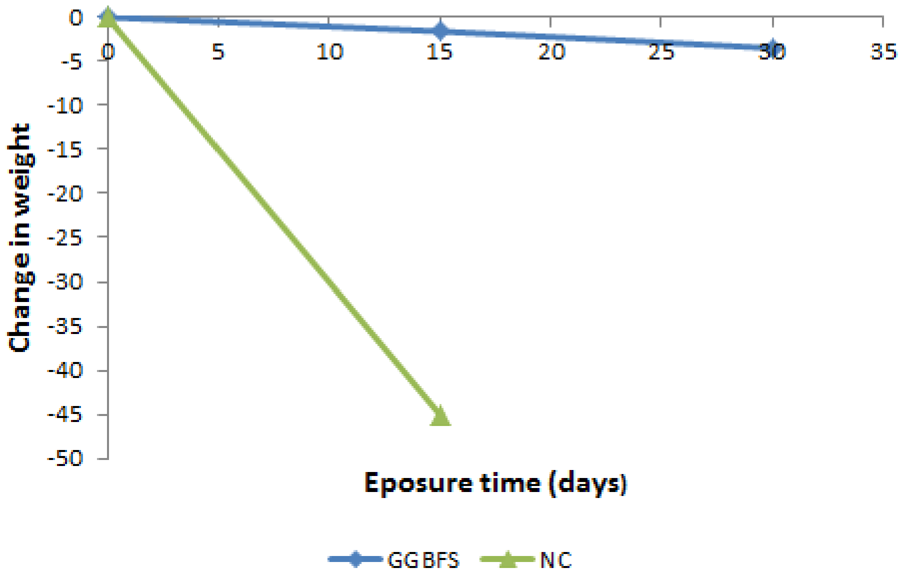


Figure 4.12 Mass Change in control of cube specimen

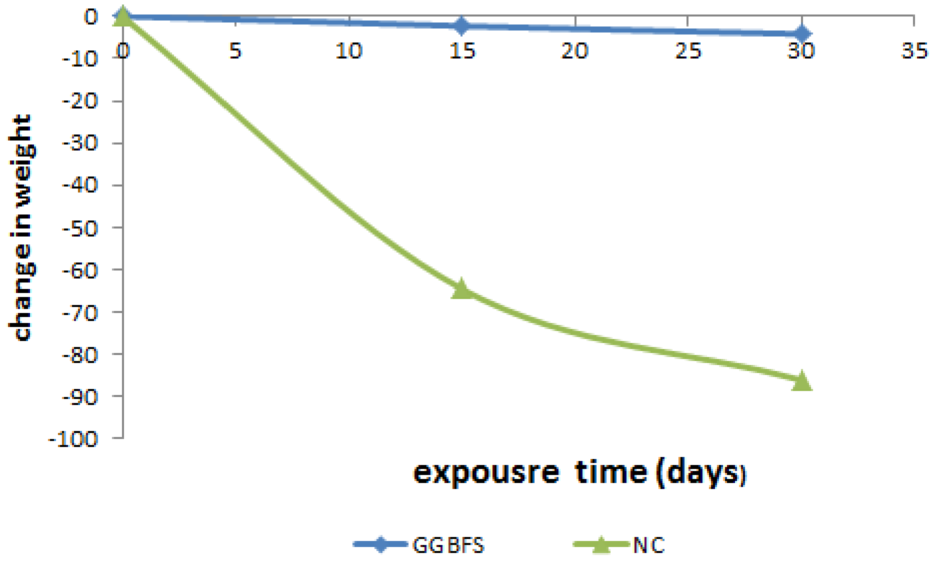


Figure 4.13 Mass Change in control of cylinder specimen

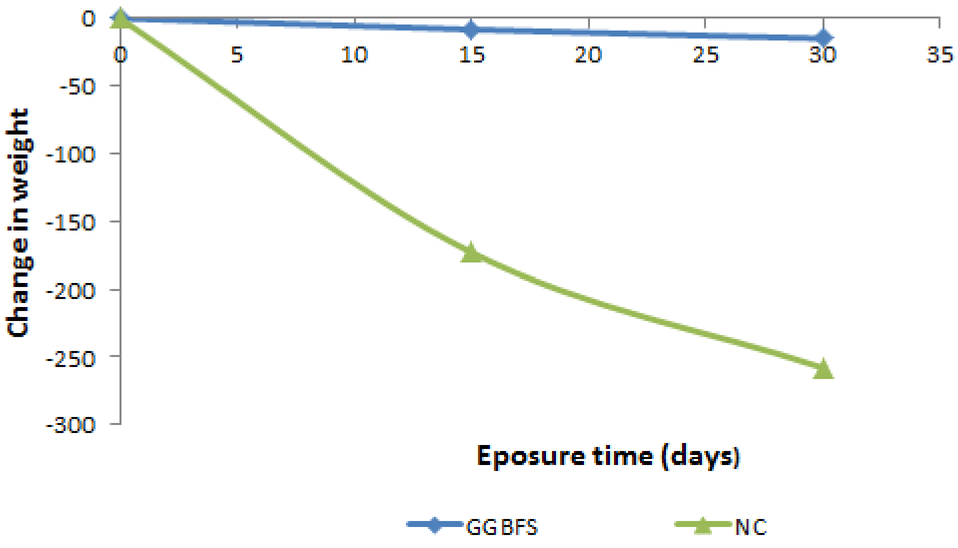


Figure 4.14 Mass Change in control of prism specimen

4.4 Mechanical and durability test of geopolymer concrete

4.4.1 Compressive strength

The reduction in compressive strength after exposure time is one of the important indicators of resistance to chemical attack. The compressive strength of geopolymer specimens exposed to solutions is shown in Table 4.1, and figure (4.15). From the experimental results, it was observed that the reduction in compressive strength is 5.8%, 10.67% and 29% of the specimens of geopolymer concrete made from GGBFS and was immersed in the salt sea water, Magnesium sulphuric and the sulfuric acid solution respectively. Also, the reduction in compressive strength of the OPC samples were 9.23%, 27.46%, and 45.70% when exposed to salt water, Magnesium sulphuric solution, and sulphuric acid solution respectively.

Table 4.1 Mechanical and fracture properties for geopolymer and normal concrete at 56 days.

Series code	Mix code	Comp. Strength (MPa)	Splitting Tensile Strength (MPa)	Peak load (N)	Net flexure strength (MPa)	Final disp.at mid span (mm)	Area under load-disp. curve (Wa) (N mm)	Fracture Energy (N/m)	KIC (Mpa-mm$^{0.5}$)
Control	GGFBS	99.25	5.65	3700	6.17	0.46	549.50	100.05	29.21
	NC	54.9	5.34	3245	5.41	0.65	491.47	93.87	25.62
Salt	GGFBS	93.48	5.34	3345	5.57	0.54	497.53	93.20	26.41
	NC	49.83	4.48	2934	4.89	0.73	396.93	80.10	23.16
Sulfate	GGFBS	88.66	4.96	2958.5	4.93	0.60	453.36	86.90	23.35
	NC	39.82	4.19	2425	4.04	0.84	335.79	72.10	19.14
Acid	GGFBS	70.46	4.44	2688	4.48	0.75	361.98	75.60	21.22
	NC	29.81	3.38	2130	3.55	0.91	152.30	42.30	16.81

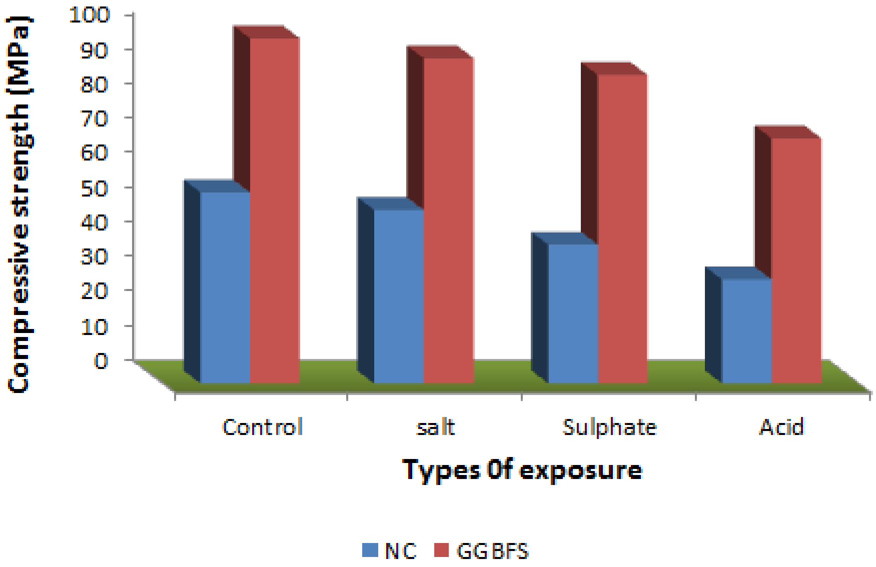


Figure 4.15 Compressive Strength for different mixes

4.4.2 Split Tensile Strength

The Split Tensile Strength for specimens exposed for a period of 30 days is shown in Table 4.1 and figure (4.16).

The results of split tensile strength test showed a reduction in rates were 5.48%, 12.21% and 21.41% of GGBFS-GPC specimens immersed in the salt sea water, Magnesium sulphuric and the sulfuric acid solution, respectively, compared with the OPC samples reduction of 16.10%, 21.53% and 36.70 % that exposed to salt water, Magnesium sulphuric solution and sulphuric acid solution respectively.

Through the results investigated, the best split tensile strength was for geopolymer concrete that made by GGBFS compared with OPC due to the low calcium content of the source material as a major factor of geopolymer concrete.

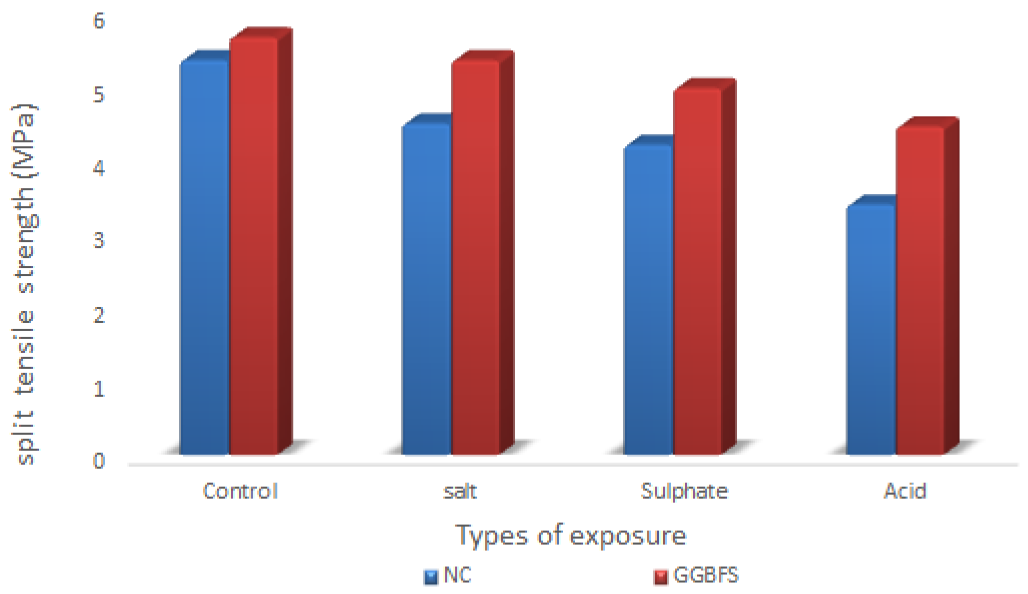


Figure 4.16 Split Tensile Strength for various mixes

4.4.3 Fracture toughness test

After a period of 30 days exposed to solutions, it can be seen from Table 4.1 and figures (4.17,4.18,4.19,4.20) the results of the test as follows

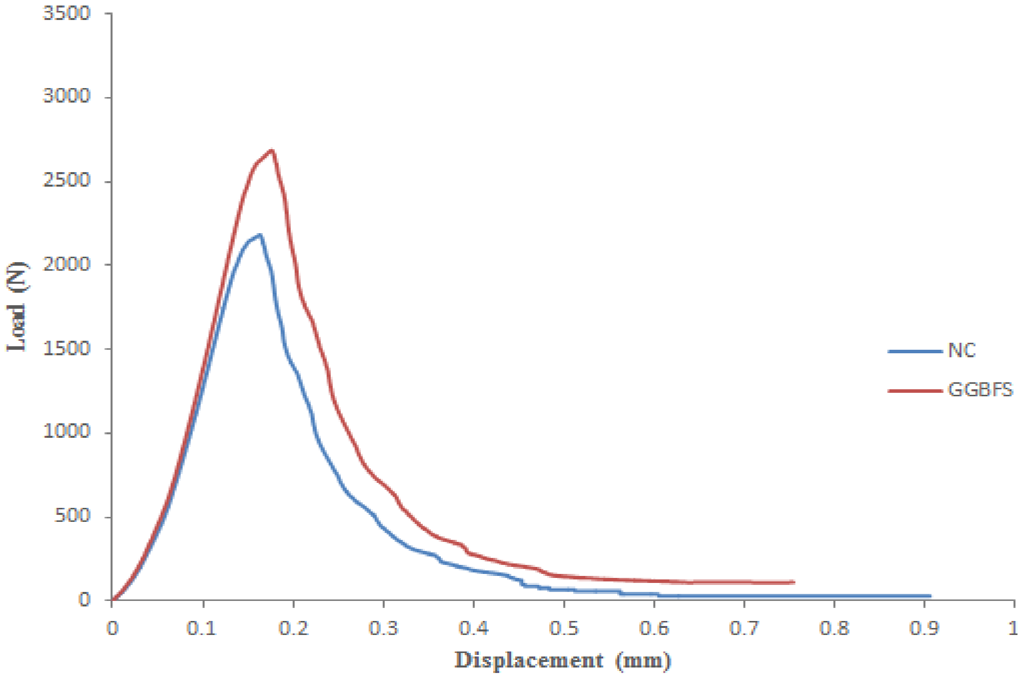


Figure 4.17 Load–deflection diagrams of specimens in 5% sulphuric acid

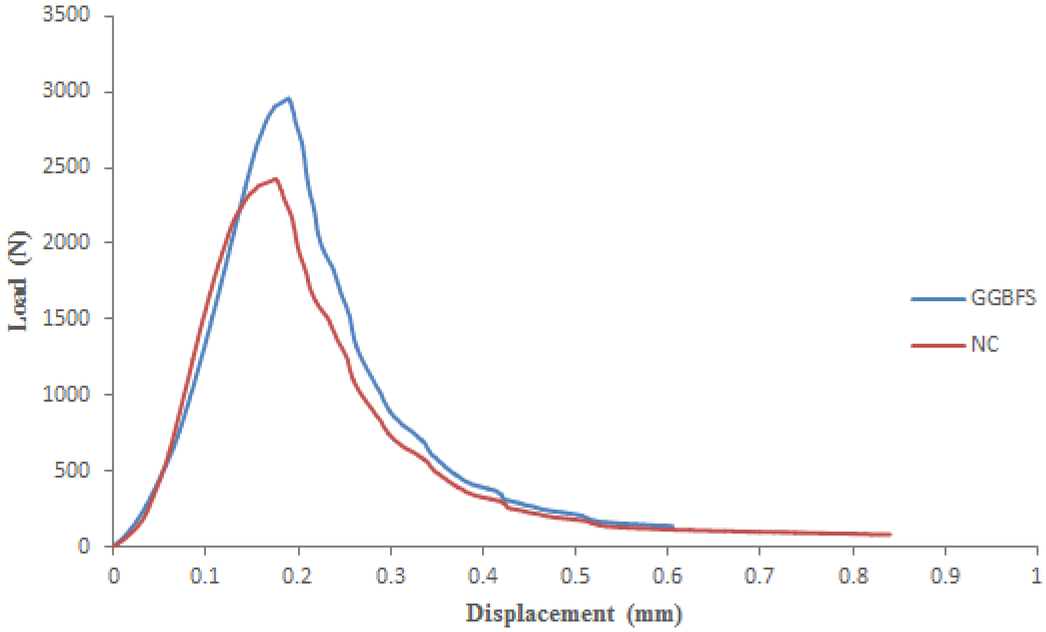


Figure 4.18 Load–deflection diagrams of specimens in 5% Magnesium sulphate

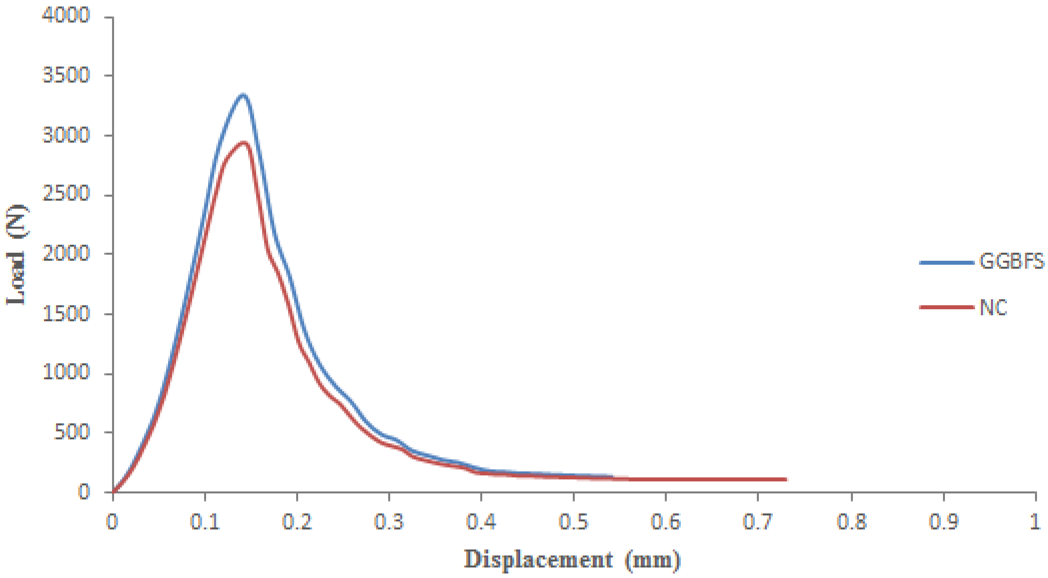


Figure 4.19 Load–deflection diagrams of specimens in 3.5% salt water

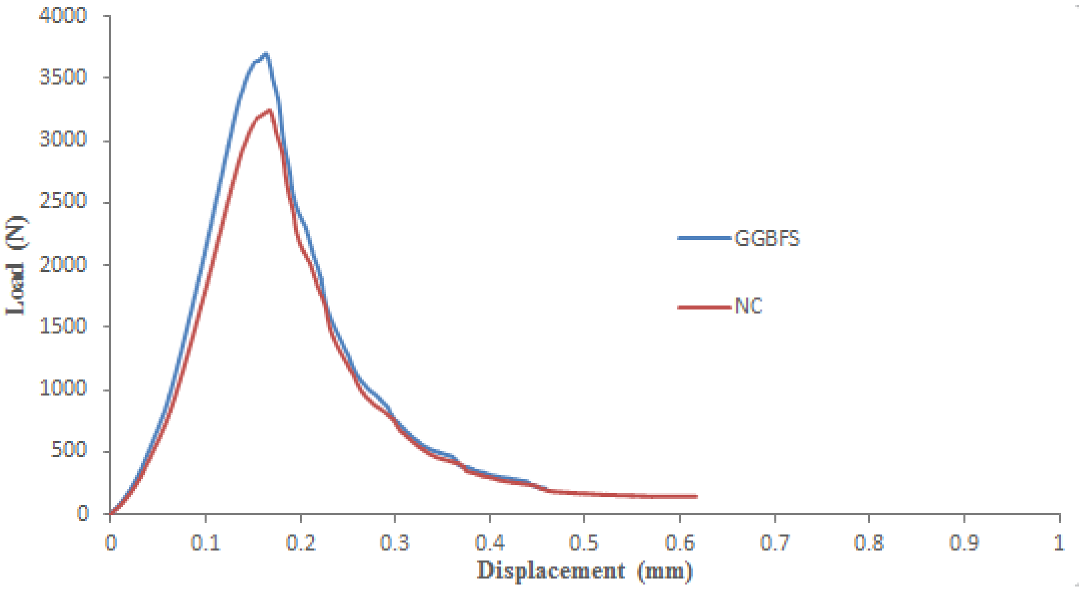


Figure 4.20 Load–deflection diagrams of specimens for control

4.4.3.1 Load–deflection behaviour

During three point bending test, when the load applied on the Prism, the load deflection behavior of specimens displayed a semi-linear behavior and no cracks were observed until its peak value was reached at which point a crack developed at the notch. A crack showed from the end of the notch and began to increase fast in the ligament when the load was at its peak point. It was observed that the crack opened slower in the OPC concrete samples than in the GPC samples. Failure happened in the opening of a single crack in the bond in both kinds of concrete specimens. The load–deflection diagrams of GPC and OPC concrete samples are shown in figures (4.17,4.18,4.19,4.20). Figures show that the peak load for GGBFS-GPC samples were generally higher than that of the OPC concrete samples of the similar compressive strength and split tensile strength. The maximum load for each test specimen is shown in Table 4.1. It was also observed that the lowest peak load in samples exposed to sulphuric acid compared to samples exposed to sea water, Magnesium sulphuric solution and control samples. However, a similar trend in compressive and tensile strength was observed in Fracture toughness, since GGBFS-GPC was more durable to chemical solutions compared to OPC. On the other hand, it is noted from the results that the displacement of the OPC specimens was greater than GGBFS-GPC specimens. This indicates that the GPC is more brittle than OPC as investigated in the literature.

4.4.3.2 Fracture energy

Fracture energy for both GPC and OPC specimens can be calculated by Eq. (3.6), after calculating the area under the curve. These values are shown in Table 1. The values of G_F for the GGBFS-GPC, samples and OPC concrete samples with mix code are shown in figure (4.21). It can be seen that the G_F of batch GGBFS-GPC is higher than that of batch OPC. It was observed from the results that higher G_F was observed in the control specimens followed by the specimens exposed to sea water, then specimens immersed in Magnesium sulphuric and finally specimens immersed in sulphuric acid which has lowest values of G_F. It can be seen that the G_F of GPC is comparable to that of OPC concrete mixtures of similar compressive strength and split tensile strength. The values of G_F for specimens of each batch with compressive strength in figure (4.22) show the relationship between the fracture energy and compressive strength. There is an increase in the value of fracture energy followed by the increase in compressive strength.

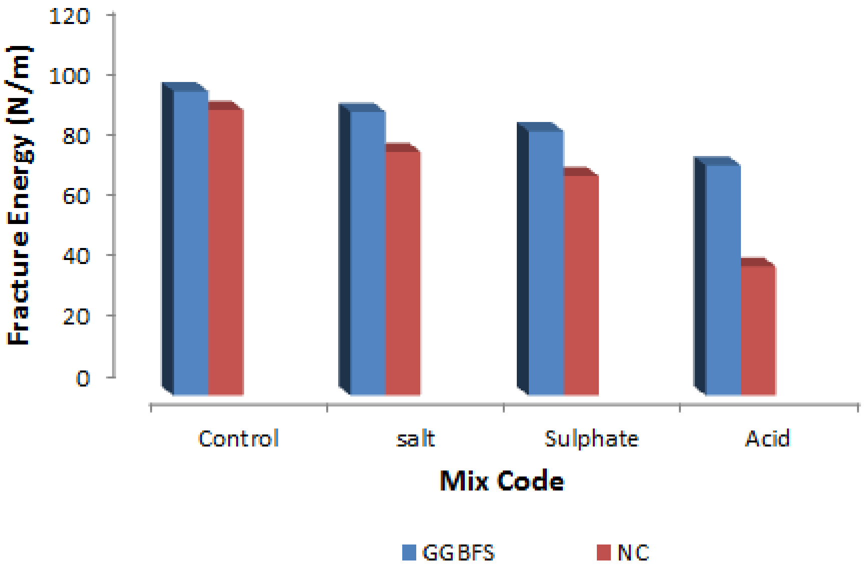


Figure 4.21 G_F of the GPC and OPC concrete

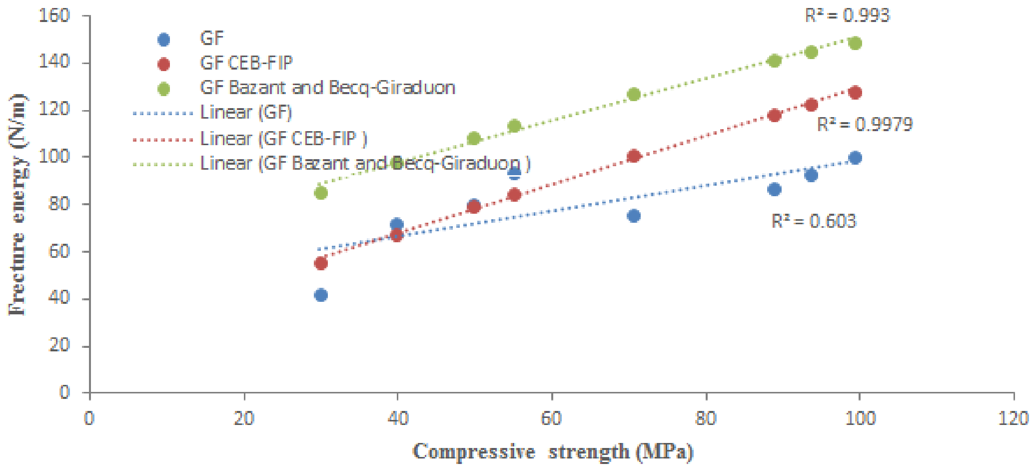


Figure 4.22 Variation of G_F of GPC and OPC concrete vs. compressive Strength

4.4.3.3 Critical stress intensity factor

K_{IC} of the specimens of GPC and OPC concrete were obtained through the Eq.(3.8) K_{IC} value for each test specimen is shown in Table1, and figure (4.23).

K_{IC} of GGBFS-GPC values are higher than OPC values and was in the same path with the compressive strength and split tensile strength.

Also the values of K_{IC} of control specimens are higher than the exposed specimens in seawater, so that the specimens values of K_{IC} exposed in seawater are higher than the specimens that immersed in Magnesium sulphuric and finally specimens immersed in sulphuric acid which has lowest values of critical stress intensity factors. The relationship between the K_{IC} and compressive strength were shown in the figure (4.24), thus increased values of K_{IC} were similar to the increase in compressive strength values for both GPC and OPC concrete.

This displays that the critical stress of the cracking is higher in GPC than OPC concrete, because the brittleness of GPC was higher compared with OPC.

The net flexural strength of the specimens for OPC and GGBFS-CPG concrete was obtained by using Eq. (3.8). The value of net flexural strength for each test specimen is shown in Table 3.1. The values of the net flexural strength of GGBFS-GPC samples and OPC concrete samples with mix code are shown in figure (4.25). The relationship between the net flexural strength and split tensile strength was shown in the figure (4.26). It was observed that the increase in the net flexural strength value was compatibile with the increased value of split tensile strength in both GPC and OPC concrete.

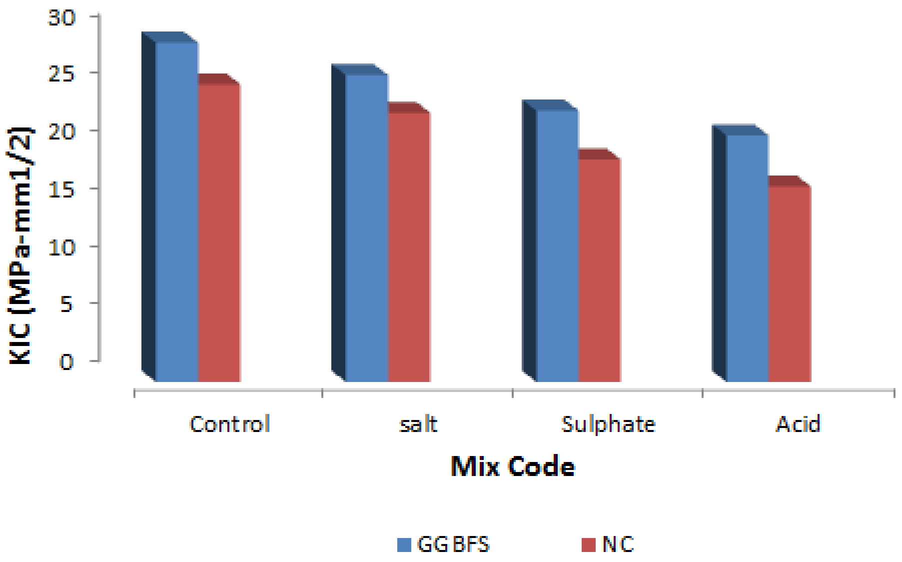


Figure 4.23 Critical stress intensity factors of OPC and GPC concrete

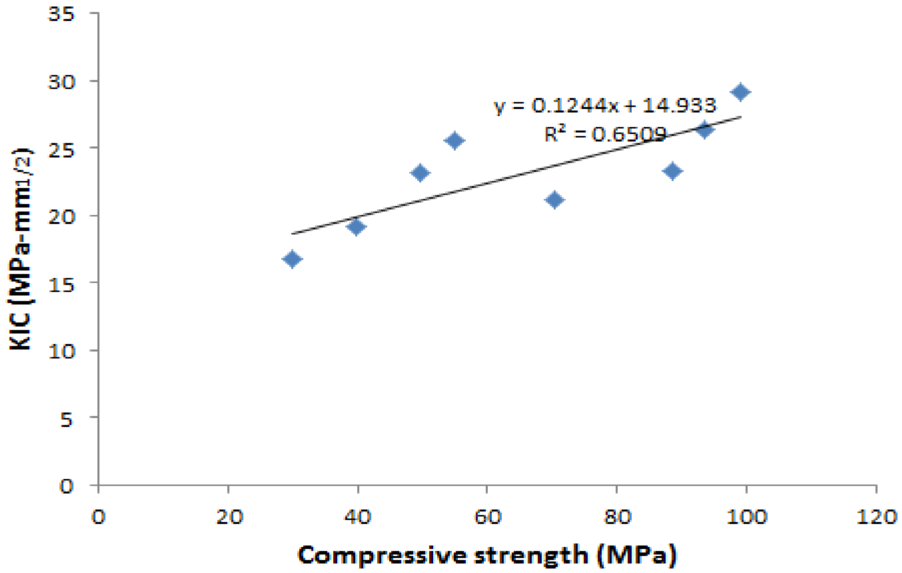


Figure 4.24 Variation of critical stress intensity factors of OPC and GPC vs. compressive strength

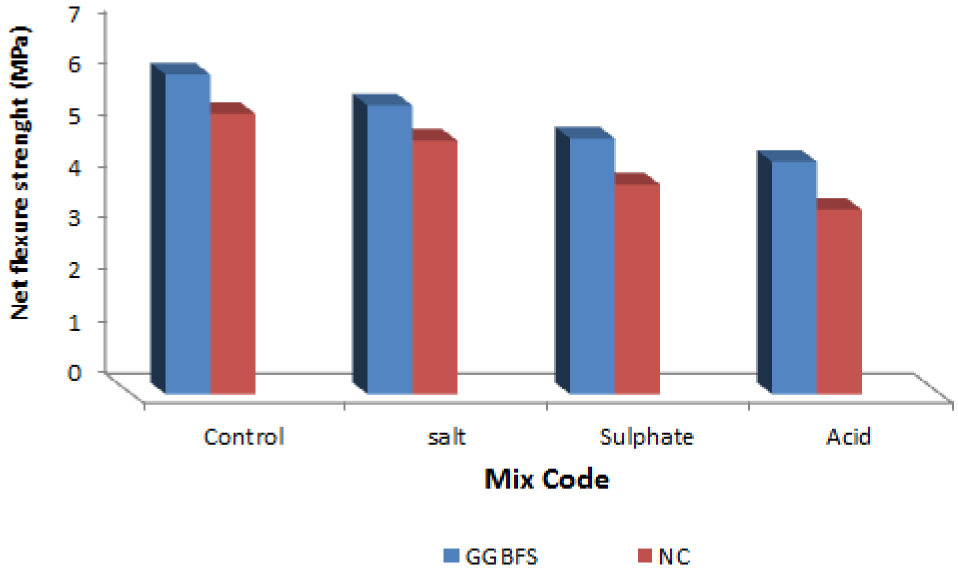


Figure 4.25 The net flexure strength of the OPC and GPC concrete with Mix Code

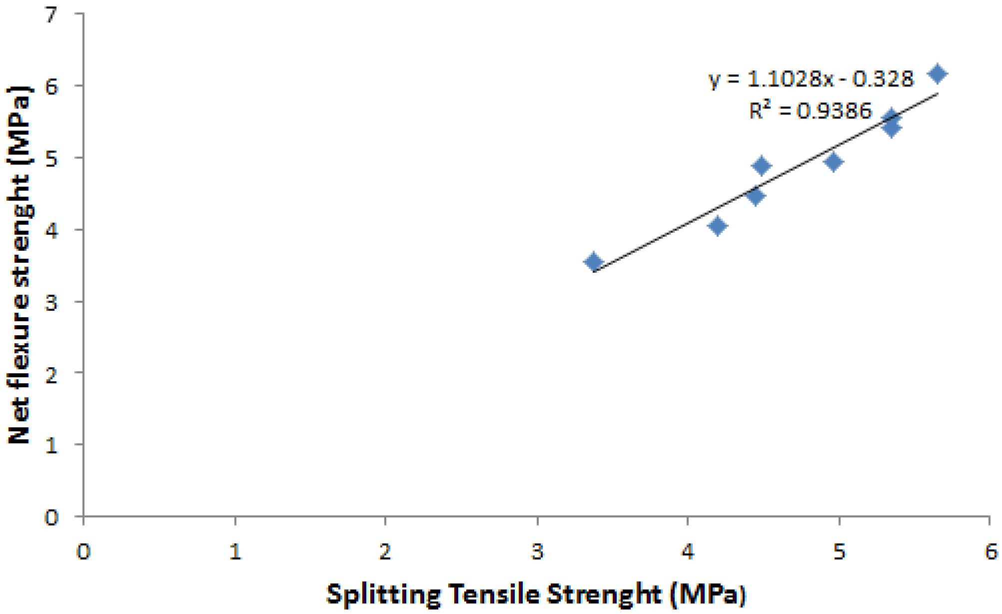


Figure 4.26 The relationship between the net flexural strength and split tensile strength

CHAPTER 5

CONCLUSIONS

This study investigates the durability and mechanical properties of geopolymer concrete based on GGBFS exposed to 5%, 5% and 3.5% sulphuric acid solution, Magnesium sulphuric solution and salt water respectively, compared with OPC at same conditions. Based on the results, the following conclusions can be drawn:

- Through Overall results, it is obtained that GGBFS-GPC has less deterioration to chemical attack compared to OPC.
- It can be investigated that GGBFS-GPC is able to used in the Acid environment (sewage, underground structure, …) due to good resistance to Acid Attack compared to OPC.
- GGBFS-GPG has excellent durability to sulfate attack which indicated from the results of mechanical properties compared to OPC.
- The gain of mass occurred for all GPC specimens during 15 days of exposure to solutions due to an interaction with solution and expansion from ettringite and gypsum generation
- Loss in mass observed after 15 days of exposure to the acid solution, while the amount of loss mass was more in OPC compared to GGBFS-GPC.
- Weight gain increases for GGBFS-GPC samples after 15 days exposure to Magnesium sulfate and seawater.
- Similar trend which was observed in OPC samples lose weight during exposure to magnesium sulphate solution exposed to Magnesium sulfate and seawater.
- Through mechanical tests, it is noted that GGBFS-GPC has better performance than OPC .
- GPC was more brittle than OPC observed from Fracture toughness results for control specimens and exposed specimens.

REFERENCES

[1] Statista. (2014). “United states and world cement production in 2010 and 2013.,” Online. Available: http://www.statista.com/statistics/219343/cement-production-worldwide/ Swanepoel.

[2] Hardjito, D., Wallah, S.E., Sumajouw, D.M.J. & Rangan, B. V. (2004). “on the development of fly ash-based geopolymer concrete.,” ACI Materials Journal, **101**,6.

[3] Motorwala, A., Shah, V., Kammula, R., Nannapaneni, P. & Raijiwala, D. (2008). “ALKALI Activated FLY-ASH Based Geopolymer Concrete,”.

[4] Sakulich, A. (2011). “Reinforced Geopolymer Composites for Enhanced Material Greenness and Durability,” Sustainable Cities and Society. **1**(4).

[5] Alzeer, M. & MacKenzie, K.(2013). “Synthesis and Mechanical Properties of Novel Composites of Inorganic Polymers (Geopolymers) with Unidirectional Natural Flax Fibres (Phormium Tenax),” Applied Clay Science,**76**, 75–76.

[6] Davidovits, J. (1994). “Properties of geopolymer cements on alkaline cements and concretes.,” International conference, 131–149.

[7] Swamy, R. N. (1986).“Cement Replacement Materials,” Glasgow: Surrey University Press, **3**.

[8] Davidovits, J.(2008). “Scientific tools, X-rays, FTIR, NMR. In J. Davidovits(ed) Geopolymer. Chemistry and applications,” Institut Géopolymère, Saint-Quentin, France., 61–76.

[9] Diaz E.I., Allouche E.N and Eklund S.(2010). “Factors affecting the suitability of fly ash as source materials for geopolymers.,” Fuel, **89**, 992–996.

[10] Vijai, K., Kumutha, R. and Vishnuram, B. G. (2010). “Effect of types of curing on strength of geopolymer concrete,” International Journal of the Physical Sciences, **5**, 1419–1423.

[11] Davidovits J, Comrie DC, Paterson JH. (1990). “Geopolymeric concretes for environmental protection,” ACI concrete international, **12**, 30–40.

[12] Davidovits,J. (1998). “Soft mineralogy and Geopolymers,” Geopolymer 88 International conference. Universite and Technologie, Franc, 25–48.

[13] Bakharev, T., Sanjayan, J. G., and Cheng, Y. B. (2002). “Sulfate attack on alkali-activated slag concrete,” Cement and Concrete Research.,**32**, 211–216.

[14] Wallah, S.E. and Rangan, B.V. (2006). “LOW-CALCIUM FLY ASH-BASED GEOPOLYMER CONCRETE : LONG-TERM By Faculty of Engineering Curtin University of Technology,” Research Report GC 2, Faculty of Engineering, Curtin University of Technology, Perth, Australia.

[15] Rajesh, A. M, Joe, M. A. and Mammen, R. (2014). “Study of the Strength Geopolymer Concrete with Alkaline Solution of Varying Molarity,” engineeringcivil.com,**4**,19–24.

[16] Deb, P. S., Nath, P. and Sarker, P. K. (2014). “The effects of ground granulated blast-furnace slag blending with fly ash and activator content on the workability and strength properties of geopolymer concrete cured at ambient temperature” Materials and Design, **62**,32–39.

[17] Wallah, S.E., Hardjito, D., Sumajouw, D.M.J., and Rangan, B.V.(2005). “Performance of Geopolymer Concrete Under Sulfate Exposure,” Paper for Ed Nawy Symposium, American Concrete Institute.

[18] Malhotra, V. M., & Mehta, P. K. (1996). “Pozzolanic and Cementitious Materials, Gordon and breach publishers, advances in concrete” technology, ISSN1024-5038, **1.1**.

[19] (2012).“Slag Cement Association” Slag Cement. http://www.slagcement.org/pdf/no1%20Slag%20Cement.pdf South

[20] Provis, J.L. and J.S.J. van Deventer.(2009). “Geopolymers: Structure, processing, properties and industrial applications” Woodhead Cambridge, UK.

[21] Aïtcin, P.(2008). “Binders for Durable and Sustainable Concrete” ISBN 0-203- 94048-2-Master e book,**10**.

[22] Reeves, C.(1985). “The Use of Ground Granulated Blast-furnace Slag to Produce Durable Concrete.” How to Make Today's Concrete Durable for Tomorrow, Thomas Telford, London, May.

[23] Douglas, E and Zebino, R. (1986). “Characterisation of Granulated and Pelletized Blast- furnace Slag” Cement and Concrete Research, retrieved from http// www.sciencedirect.com, **16**, 662–670.

[24] Frearson, JPH. and Uren, JM. (1986). “ Investigations of Ground Granulated Blast-furnace Slag Containing Merwinitic Crystallisation”Second International Conference on Use of Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Madrid, Spain., **2**.

[25] Cook, DJ. Hinczak, I. and Cao, HT. (1987). “Heat of Hydration, Strength, and Morphological Development in Blast-furnace/Cement Blends” International Workshop on Granulated Blast-Furnace Slag in Concrete, Toronto, Canada.

[26] Krivenko, P. D. (1994). “Alkaline cements” Paper presented at the first international conference on alkaline cements and concrete, Kiev, Ukraine, 11-14 October.

[27] Davidovits, J. (1999). “Chemistry of Geopolymeric Systems, Terminology” International Conference, France.

[28] Temuujin, J. Van Riessen, A. Williams, R. (2009).“Influence of Calcium Compounds on the Mechanical Properties of Fly Ash Geopolymer Pastes” Journal of Hazardous Materials Journal of Hazardous Materials. **167.**

[29] Xu, H. and J.S.J. van Deventer. (2000) “The Geopolymerisation of Alumino-Silicate Minerals” International Journal of Mineral Processing, **59**, 247-266.

[30] Palomo A, Grutzeck, M.W. & Blanco, M.T. (1999). “Alkali-activated fly ashes: A cement for the future” Cement And Concrete Research, **29**, 1323–1329.

[31] Pacheco-Torgal, F., Castro-Gomes, J. & Jalali, S. (2008). "Alkali-Activated Binders: A Review: Part 1. Historical Background, Terminology, Reaction Mechanisms and Hydration Products" Construction and Building Materials, **22**.

[32] Shi, C. and Qian, J. (1999). "'High Performance Cementing Materials from Industrial Slags'" Resources, Conservation and Recycling,195–207.

[33] Ferraris, C.F., Clifton,J.R., Stutzman, P.E., and Garboczi, E.J. (1997). "Mechanisms of degradation of Portland cement-based systems by sulfate attack," In mechanisms of chemical Degradation of cement-based systems, eds.K.L. serivener anf J.F.young, E and FN spon. London.

[34] Taylor, H. F. W. (2003). "Cement Chemistry, Second Edition" Published by Thomas Telford publishing, Thomas Telford services ltd, 1 Heron Quay, London E144JD.

[35] Wallah,S. E. and Rangan, B. V.(2006). "Low-Calcium Fly Ash-Based Geopolymer Concrete: Long-Term Properties" Research Report GC 2 Faculty of Engineering Curtin University of Technology Perth, Australia.

[36] Bakharev, T. (2005). "Resistance of geopolymer materials to acid attack" Cement and Concrete Research, **35**, 658–670.

[37] Glukhovsky VD. (1981). "Slag-alkali concretes produced from fine-grained aggregate" Kiev Vishcha Shkolay.

[38] Jiang W, Silsbee MR, Breval E, Roy MD.(1997). "Alkali-activated cementitious materials in chemically aggressive environments" In: Young JF, editor. Mechanisms of chemically degradation of cement-based systems. E and FN SPON (1997) London, **2**, 89–96.

[39] Davidovits J, Comrie DC, Paterson JH, Ritcey DJ.(1990). "Geopolymeric concretes for environmental protection" Concrete International: Design and Construction, **12**,30–40.

[40] Palomo A, Blanco-Varela MT, Granizo ML, Puertas F, Vasquez T, Grutzeck MW.(1999). "Chemical stability of cementitious materials based on metakaolin" Cement and Concrete Research, **29**, 997–1004.

[41] Shi Caijun, S. J. (2000). “Acid corrosion resistance of different cementing materials” Cement and Concrete Research,**30**, 3–8.

[42] Bakharev T, Sanjayan J.G, Chen B.(2003). “Resistance of alkali-activated slag concrete to acid attack” Cement and Concrete Research, **33**(16),7–11.

[43] Song X.J, Marosszeky M, Brungs M, Munn R.(2005). “Durability of fly ash based geopolymer concrete against sulphuric acid attack.” 10 DBMC International Conference on Durability of Building Materials and Components, Lyon, France, 17- 20 April.

[44] Gourley, J.T. and Johnson, G.B. (2005). “Developments in Geopolymer Precast Concrete,” Paper presented at the International Workshop on Geopolymers and Geopolymer Concrete, Perth, Australia.

[45] Pacheco-Torgal F, Gomes J, J. S.(2010). “Durability and environmental performance of alkali-activated tungsten mine waste mud mortars.,” J Mater Civil Eng, **22**, 897–904.

[46] Mehta, P. (1993). “Pozzolanic and cementitious by-products as mineral admixtures for concrete – a critical review, Proc” 1st Int. Conf. Use fly ash, silica fume, slag other Miner. by- Prod. Concr. ACI SP-79, Am. Concr. Institute, Detroit, 1–48.

[47] Hakkinen, T. (1987). “‘Durability of alkali-activated slag concrete’” Construction and Building Materials journal, **6**, 81–94.

[48] Bassuoni, M. T. and Nehdi, M. L.(2009). “Durability of self-consolidating concrete to sulfate attack under combined cyclic environments and flexural loading” Cement and Concrete Research. **39**, 206–226.

[49] Liu PC. (1991). “Damage to concrete structures in a marine environment” Materials and Structures, **24**, 302–307.

[50] Neville, A. M. (1995). “Properties of Concrete” Essex, England: Pearson Education, Longman Group.

[51] Kong DLY, Sanjayan JG, and Sagoe-Crentsil K. (2007). “Comparative performance of geopolymer made with metakaolin and fly ash after exposure

to elevated temperatures," Cement and Concrete Research**,** **37**,1583–1589.

[52] Fernandez-Jimenez A, García-Lodeiro I, and Palomo. A. (2007)."Durability of alkali-activated fly ash cementitious materials" Journal of Materials Science, **42**,3055–3065.

[53] Adam, A. A. (2009)."Strength and durability properties of alkali activated slag and fly ash-based geopolymer concrete" School of Civil, Environmental and Chemical Engineering RMIT University Melbourne, Australia, 110–127.

[54] Bakharev, T. (2005). "Durability of geopolymer materials in sodium and magnesium sulfate solutions" Cement and Concrete Research, **35**,1233–1246.

[55] Davidovits, J. (1989). "Geopolymers and Geopolymeric Materials," in JournalofThermalAnalysis.

[56] Fernández-Jiménez, a. Palomo, J. Y. Pastor, and a Martin, A. (2008). "New Cementitious Materials Based on Alkali-Activated Fly Ash : Performance at High Temperatures" Department of Materials Science, Polytechnic University of Madrid, E28040 Madrid, Spain, **91**,3308–3314.

[57] Paterson, J. H. Ritchey, D.J, and Comrie, D.C. (1988) "'Geopolymer Technologies in Toxic Waste Management'" Paper presented at the Geopolymer '88, First European Conference on Soft Mineralurgy, Compiegne, France.

[58] Gilbert, R. I. (2002). "Creep and shrinkage models for high strength concrete - proposal for inclusion in AS3600.," Aust. J. Struct. Eng., **4**, 95–106.

[59] Garcia-Loderio, I., Palomo, A., Fernandez-Jimenez, A. (2007). Alkali-Aggregate "Alkali-Aggregate Reaction in Activated Fly Ash Systems.," Cem. Concr. Res., **37**, 175–183.

[60] Hou. X., Struble. L.J. & Kirkpatrick. R. J. (2004). "Formation of ASR gel and the roles of C-S-H and portlandite" Cement and Concrete Research, **34**, 1683–1696.

[61] Zuda, L., Pavlik Z., Rovnanikova, P., Bayer, P., Cerny, R. (2006). "Properties of Alkali Activated Aluminosilicate Material after Thermal Load" International Journal of Thermophysics, **27**,1250–1263.

[62] Crumpton, C. F., Smith, B. J., Jayaprakash, G.P. (1989). "Salt Weathering of Lirnestone Aggregate and concrete Without Freeze-Thaw.," Transportation Research Record.

[63] Abdul-Hamid, Al-Tayyib, J.,Al-Zahrani,M.,M. (1990). "Use of polypropylene fibers to enhance deterioration resistance of concrete surface skin subjected to Cyclic Wet/Dry sea water exposure" ACI Materials Journal, **87,** 363–370.

[64] Olivia, M. and Nikraz, H. (2013)."Properties of Fly Ash Geopolymer Concrete in Seawater" Cement and Concrete Research.

[65] Rangan, B. V.(2008). "FLY ASH-BASED GEOPOLYMER CONCRETE" Curtin University of Technology, Perth, Australia.

[66] C. Barbosa, V. F. F.; MacKenzie, K. J. D.; and Thaumaturgo.(2000). "Synthesis and Characterization of Materials Based on Inorganic Polymers of Alumina and Silica: Sodium Polysialate Polymers" International Journal of Inorganic Materials, **2**, 309–317.

[67] Xie, Z. and Xi, Y. (2001). "Hardening Mechanisms of an Alkaline-Activated Class F Fly Ash" Cement and Concrete Researc, **31**, 1245–1249.

[68] Divya, K., Chaudhary, R. (2007)."Mechanism of Geopolymerization and Factors Influencing Its Development: A Review" Journal Materials Science, **42**, 729–746.

[69] Wang. K, Shah. S, Mishulovich. A. (2004). "Effects of curing temperature and NaOH addition on hydration and strength development of clinker-free CKD-fly ash binders" Cement and Concrete Composites**, 34**, 299–309.

[70] Poon, C., Azhar. S, Anson,M., Wong.Y. (2003). "Performance of metakaolin concrete at elevated temperatures" Cement and Concrete Composites, retrieved from http// www.sciencedirect.com, **25**, 83–89.

[71] Chareerat, T., Lee-Anansaksiri, A., Chindaprasirt, P. (2006). "Synthesis of High Calcium Fly Ash and Calcined Kaoline Geopolymer Mortar." Int. Conf. Pozzolan, Concr. Geopolymer, Khhon Kaen, Thailand, May24-25.

[72] Kong, D.L.Y., Sanjayan, J.G. and Sagoe-Crentsil, K.(2008). “Damage Behavior of Geopolymer Composites Exposed to Elevated Temperatures.” Cement Concrete Composites, **30**, 986–991.

[73] Barros, J. A. O and Cruz, J. S. (2001). “‘Fracture Energy of Steel Fiber-Reinforced Concrete’” Mechanics of Composite Materials and Structures, **8,** 29–45.

[74] F. (Draft R. R. T. 50.(1985). “‘Determination of the Fracture Energy of Mortar and Concrete by Means of Three-Point Bend Tests on Notched Beams,’” Mechanics of Composite Materials and Structures,**18**,285–290.

[75] Hillerborg,A.(1985). “‘The Theoretical Basis of a Method to Determine the Fracture Energy GF of Concrete,’” Mechanics of Composite Materials and Structures, **18**, 291–296.

[76] JCI-S-002-2003.(2003). “‘Method of Test for Load-Displacement Curve of Fiber Reinforced Concrete by Use of Notched Beam’” Japan Concrete Institute Standard.

[77] Kozul R, D. D. (1997). “Effects of aggregate type, size and content on concrete strength and fracture energy” Technical report SM 43. Lawrence, KS: The University of Kansas Research Inc.

[78] Bharatkumar, B.H, Raghuprasad, B.K, Ramachandramurthy, D.S, Narayanan, R, Gopalakrishnan, S.(2005). “Effect of fly ash and slag on the fracture characteristics of high performance concrete.,” Mechanics of Composite Materials and Structures, **38**, 63–72.

[79] Carpinteri A, B. R.(2010). “Fracture behavior of plain and fibre-reinforced concrete with different water content under mixed mode loading.,” Mater Des, 32–42.

[80] Sarker, P. K., Haque, R. and Ramgolam, K. V.(2013). “Fracture behaviour of heat cured fly ash based geopolymer concrete,” Mater. Des.,**44** ,580–586.

[81] PE, P.(1980). “Fracture energy of concrete: method of determination” Cem Concr Res, **10**,79–89.

[82] Bažant, Z. P. and Becq-Giraudon, E. (2002).“Statistical prediction of fracture parameters of concrete and implications for choice of testing standard,” Cem. Concr. Res., **32**,529–556.

[83] Uday, N. P. (2017).“Experimental Determination of Fracture Energy by RILEM Method,” Int. J. Eng. Sci., **6,**106–115.

[84] 50 – FMC, R. T.(1985). “Determination of the fracture energy of mortar and concrete by means of three-point bend tests on notched beams,” Mater Struct, **18**, 85–90.

[85] Gollop, R. S., and Taylor, H. F. W. (1996). “‘Microstructural and microanalytical studies of sulfate attack—IV: Reactions of a slag cement paste with sodium and magnesium sulfate solutions.,’” Cem. Concr. Compos, **26**,1013–1028.