MARCH 2018 M.Sc. in Civil Engineering GHASSAN HUSSEIN HUMUR

REPUBLIC OF TURKEY
UNIVERSITY OF GAZIANTEP
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES

EFFECT OF NANO-SILICA ON THE CHEMICAL DURABILITY AND MECHANICAL PERFORMANCE OF FLY ASH BASED GEOPOLYMER CONCRETE

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GHASSAN HUSSEIN HUMUR

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Effect of Nano-silica on the chemical durability and mechanical performance of fly ash based geopolymer concrete

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Prof. Dr. Abdulkadir ÇEVİK

By

Ghassan Hussein HUMUR

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Ghassan Hussein HUMUR

ABSTRACT

EFFECT OF NANO-SILICA ON THE CHEMICAL DURABILITY AND MECHANICAL PERFORMANCE OF FLY ASH BASED GEOPOLYMER CONCRETE

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This study aims to examine the performance of fly ash/Nano silica-based geopolymer concrete (FANSGPC) to chemical attacks for the first time in literature. For this, an experimental study was carried out to achieve the goals of the study. A specified geopolymer concrete (GPC) with class F fly ash (FA) with and without Nano-Silica (NS) was produced for the investigation. Normal concrete (NC) was also prepared as a control specimen. The chemical attacks were achieved by sulfuric acid solution (H_2SO_4), Magnesium Sulfate ($MgSO_4$), and Salt Water (NaCl) with the amount of (5%, 5%, and 3.5%), respectively. The main factors studied were the evaluation of mass, split tensile strength, compressive strength, and fracture toughness. The study results show that the performance of GPC, when exposed to chemical solutions for 30-days, was superior to NC concrete. This result is attributed to a more stable cross-linked alumina-silicate polymer structure formed in the geopolymer concrete. Furthermore, incorporating Nano-silica increases the durability of geopolymer concrete due to the formation of a high dense microstructure in geopolymer concrete.

Keywords: Geopolymer Concrete (GPC), Fly Ash, Nano Silica, Chemical Attacks, and Fracture Toughness.

ÖZET

NANO-SİLİKA'NIN UÇUKÜL TABANLI GEOPOLİMER BETONUN KİMYASAL DAYANIKLILIĞI VE MEKANİK PERFORMANSI ÜZERİNDEKİ ETKİSİ

HUMUR, Ghassan Hussein
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Mart 2018
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Bu çalışma, literatürde ilk defa uçucu kül/silika katkılı geopolimer betonun (FANSGPC) kimyasal ataklara karşı performansını araştırmayı hedeflemektedir. Çalışmanın hedeflerini başarabilmek için deneysel bir çalışma yürütülmüştür. Araştırma için F sınıfı uçucu kül (FA) içeren nano-silikalı ve nanosilikasız belirli bir geopolimer beton üretilmiştir. Aynı zamanda, normal çimento içeren beton da kontrol numunesi olarak hazırlanmıştır. Kimyasal ataklar sırasıyla 5%, 5% ve 3.5% miktarlarında sülfürik asit çözeltisi (H_2SO_4), magnezyum sülfat ($MgSO_4$) ve tuzlu su (NaCl) ile sağlanmıştır. Çalışılan temel faktörler kütle, yarmada çekme mukavemeti, basınç mukavemeti ve kırılma tokluğudur. Çalışma sonuçları 30 gün boyunca kimyasal çözeltilere maruz kalan geopolimer betonun normal betona kıyasla daha üstün olduğunu göstermiştir. Bu durum geopolimer betonda oluşmuş daha kararlı çapraz bağlanmış alümina-silikat polimer yüzeyinden kaynaklanmaktadır. Ayrıca, nano-silika eklenmesi geopolimer betonda yüksek yoğunluklu bir mikroyapı oluşturduğu için geopolimer betonun dayanıklılık özelliklerini arttırmaktadır.

Anahtar Kelimeler: Geopolimer Beton (GPC), Uçucu Kül, Nano-Silika, Kimyasal Atak, Kırılma Tokluğu.

To My Father, Mother and my country

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LIST OF SYMBOLS

GPC	Geopolymer concrete
FA	Fly ash
FAGPC	Fly ash based geopolymer concrete
NS	Nano silica
NC	Normal concrete
OPC	Ordinary Portland cement
GHG	Greenhouse gases
GGBFS	Ground granulated blast furnace slag
Al	Aluminum
Si	Silicon
C-S-H	Calcium silicate hydrate
ASTM	American society for testing and materials
LOI	Loss of ignition
GPS	Geopolymer paste
HVFA	High volume fly ash
SP	Super-plasticizer
SNF	Sulphonated naphthalene formaldehyde
SSD	Saturated surface dry

f_c'	Compressive strength
f_s	Splitting tensile strength
G_F	Fracture energy
f_{flex}	Net flexural strength
K_{IC}	Critical stress intensity factor
FA+NS	Fly ash blended with Nano silica
LCFA	Low calcium fly ash
CEB-FIP	CEB-FIP committee equation
LVDT	Linear variable displacement transducer
W/C	Water cement ratio

CHAPTER 1

INTRODUCTION

1.1 General

Concrete is traditionally manufactured by utilizing the Ordinary Portland cement (OPC) as the main binder. The manufacture of cement generates an approximately equal quantity of greenhouse gases (GHG) and that cement production is considered responsible for (6%–7%) of all GHG released worldwide. For this, the investigation of alternative materials has increased. Nowadays, different types of waste are used as additives to concrete in order to develop its durability, strength and fracture toughness [1].

GPC is considered as a new form of concrete materials which has recently been grown as a future concrete used by product materials like FA instead of cement. Geopolymer besides to its eco-friendly characteristic, demonstrate several superior properties like a heat resistance, a good resistance to chemical attacks, high early strength, low shrinkage, and low creep. The main elements of GPC are the alkali-activated solution and the source materials. The quantity of silicon and aluminum should be high in alumina-silicate based source materials to create a reaction between the alkali-activated solution and the source material. The selection of source materials to produce GPC depends on many factors like cost, type of application and availability. The mechanism of GPC represented by strong alumina-silicate (Al-SiO_2) polymeric structures involves generation of alumina and silica by sodium or potassium hydroxides (KOH) and sodium silicates (Na_2SiO_3) as alkaline liquid [2]. Moreover, the existence of calcium (Ca) compound in the geopolymer source material like FA, slag, metakaolin, rusk ash and silica fume play an important role, since the calcium ion is able to act as a charge balancing cation in the geopolymer binder.

The alkali-activated solution consists of soluble alkali metals which are mostly Potassium (K) or Sodium (Na) based. The incorporation of (potassium or sodium) Hydroxide with (potassium or sodium) silicate is the most common alkali-activated solution utilized in geopolymerization. Increasing the concentration of NaOH in FAGPC appears to enhance the compressive strength together with a substantial influence on the early strength cured at 60 °C for 48 h [3].

On the other hand, GPC has a good resistance to chemical attack more than NC, and alkaline nature of normal is susceptible to chemicals attack. More recently, alkali-activated binders turn into a promising alternative for highly durable concretes due to their high resistance to aggressive environments, which was already demonstrated for sulfuric acid, acetic acid, and Sulfate. Davidovits et al. mentioned that normal concrete shows mass losses between (78%, and 95%) [4]. For the same conditions, he also states mass losses of (6% and 7%) for GPC exposed to 5% of sulfuric acids and hydrochloric for 28 days. A high resistance to chemicals attack is resulted due to a high alkali concentration and the presence of Ca in the binder which reduces the rate of mass transfer within the pore structures of the alkali binders [5].

Most of the study conducted on FAGPC was about the molar concentration, the change of strength for GPC with a different temperature of curing range between (45°C – 80 °C) for about (2–3) h, and mix proportion [6]. FAGPC usually involves heat activation of different temperatures, which has been considered as an essential limitation for its practical application. Such limitation can be overcome by the addition of a suitable amount of NS in the mixture. GPC with NS increases the dissolution degree of Si and Si–Al phases, which strongly influences the proportion of polymerization. The existence of NS in GPC mixture is the vital factor to improve the polymerization process for its amorphous estate [7]. The strength of FAGPC is increased with the addition of NS up to particular dosage and trends to decrease with the further addition [8].

1.2 The aims of the research

The main objectives of the study are:

- The hardened properties will be experimentally investigated in terms of mechanical properties.
- Investigation of the effect of Chemical attacks on durability and mechanical properties of geopolymer and normal concrete in presence of Nano silica.
- Investigation of the influence of Nano silica on the durability and mechanical properties of geopolymer concrete.

- Estimation of the relationships between split tensile strength, fracture strength, compressive strength, net flexural strength and critical stress intensity factor.

1.3 Organization of thesis

Chapter one: This chapter contains a brief introduction about geopolymer and normal concrete, the purpose of research and the significance of research as well as a brief introduction to chemical attack.

Chapter two: In this chapter was discussion the previous researches related to the geopolymer concrete, alternative material and the effect of the chemical attack on the durability of NC and GPC.

Chapter three: This chapter contains all details related to the experimental program like materials, mixing, curing and test procedure.

Chapters four: In this chapter, the results of the test have been presented and discussed.

Chapter five: This chapter presents the conclusions.

CHAPTER 2

LITERATURE REVIEW

2.1 Geopolymer

Geopolymer concrete can play a vital role in the context of sustainability and environmental issues. The manufacturing of cement responsible for 6% of global CO_2 emissions and the large uses of cement are poses threat to the living organism day by day. The manufacture of one tone of OPC releases approximately one tone of CO_2 to the atmosphere [9].

The using of alternative materials throughout of the world quickly increasing with the growth of the industrial sector, especially in China and India. Last decades, the application of FAGPC becomes an important part of the research. The total worldwide production of FA in 2011-2012 was approximately 780 Mt. Though effective utilization of FA was limited to 53% of total production and usually different from country to another [10].

On the other hand, the production of FA reduces the greenhouse from 80% to 90% less than cement. Therefore a 100% replacement of OPC with FA or GGBFS would significantly reduce the CO_2 emission of concrete production [11].

2.1.1 Terminology and Chemistry

The term "geopolymer" was first presented by Davidovets in 1978 to characterize a family of metal volumes with a chemical composition similar to zeolite but with amorphous microscopy. He noted that the utilize of the term "poly (silate)" for the chemical designation of GPC on the basis of silica aluminate [12] Silate is an abbreviation for silicon Ox-aluminate.

Geopolymerization involves the chemical reaction of alumina-silicate oxides (Si_2O_5, Al_2O_2) should be rich in Si and Al with alkali poly-silicates yielding polymeric Si – O –

Al bonds. Poly-silicates are mostly sodium silicate or potassium silicate supplied by chemical industry or produced from fine silica powder as a by-product of ferrosilicon metallurgy.

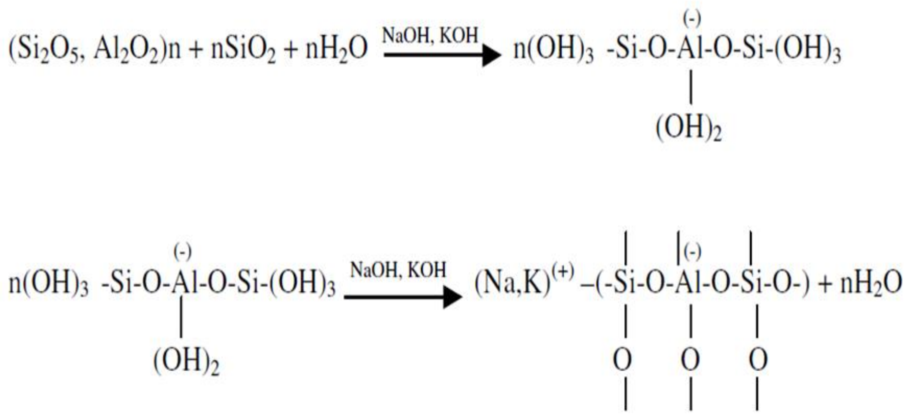


Figure 2.1 Indicates the reaction of poly-condensation by alkali into Poly-silicates [13]

The last term (nH_2O) in equation (2-1) indicates that water is liberated during the chemical reaction occurs between alkali activator and source materials and this reaction generated a formation of strong alumina-silicate polymeric structures.

2.1.2 Geopolymerization process

The geopolymer process mostly depends on many variables such as the concentration of the alkali activator, the water content, curing temperature and the mineralogical and chemical composition of the binder material. The stages of the geopolymerisation process as shown below:

1. The first step is the dissolution of the alumina and silica ions within the amorphous phase of the binder material. The process is motivated by the alkali activator liquid during initial mixing [14]. As shown in figure 2.1.

2. The reaction between the neighboring silica and alumina molecules as known condensation which takes place in the liquid. The alkali activator solution also behaves as a catalyst during this phase. This reaction causes the neighboring hydroxyl ions to create an oxygen bond which links a water molecule and the molecules.

3. The final step is named poly-condense, which leads to form an interlocking network of oxygen bonded tetrahedrally.

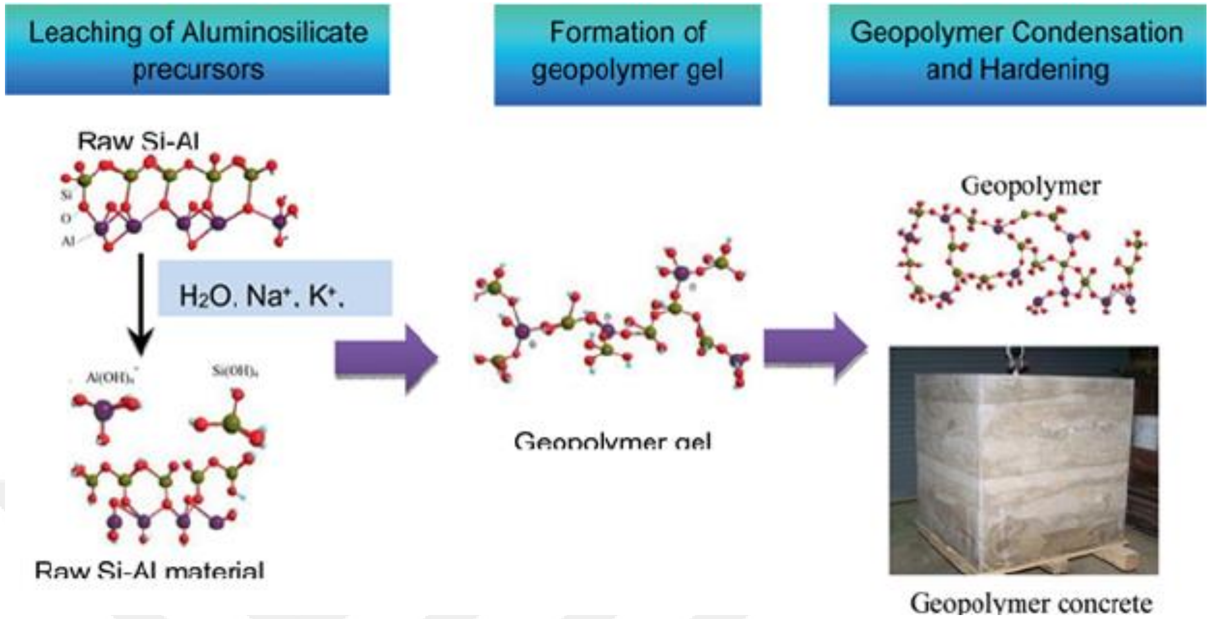


Figure 2.2 Geopolymerization process [15]

2.1.3 Constituents of Geopolymer

2.1.3.1 Source of materials

The source materials for GPC based on alumina-silicate should be rich in Al and Si. The source materials could be natural minerals like clays, mica, kaolinite, andalusite, etc. whose empirical formula contains silicon, aluminum, and oxygen [16]. The choice of the source materials for manufacturing geopolymer depends on many factors like cost, availability, specific demand of the end users and type of application. The most common materials among the waste materials are FA and GGBFS because it's most potential as a source of geopolymer.

Almost all source material based GPC has advantages and disadvantages. For example, Fly ash has high reactivity that comes from its finer particle size than slag. Furthermore, FA considered more desirable than GGBFS for geopolymer feedstock material. Many studies have been stated the use of the source materials. Gurley [17] reported that the Low calcium FAGPC is preferred as a source material than high calcium FAGPC. The existence of calcium in high quantity may interfere with the polymerization process and adjust the microstructure. On the contrary, FA with a higher quantity of CaO formed higher geopolymer compressive strength, resulting in a formation of calcium aluminate hydrate and other calcium compounds, particularly in the early ages [18].

2.1.3.2 Alkali activator

The most common alkaline activator liquid utilized in manufacturing GPC is a mixture of sodium or potassium silicate with sodium or potassium hydroxide [19]. The type of alkali activator plays a central role in the polymerization process. The use of alkaline activator solution depends on many factors like cost of the solution and the reactivity required. The disintegration operation of aluminum and silica, obtainable in FA, is shown in Fig. 2.2. Previous research has been concluded that NaOH blended with Na_2SiO_3, considered to be an effective binder, yielding promising mechanical properties as it develops the reaction between the alkaline activator solution and the binder [20]. Palomo et al. explained that the kind of alkaline activator used for activating FA significantly affects the reaction development. Moreover, they reported 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 [19].

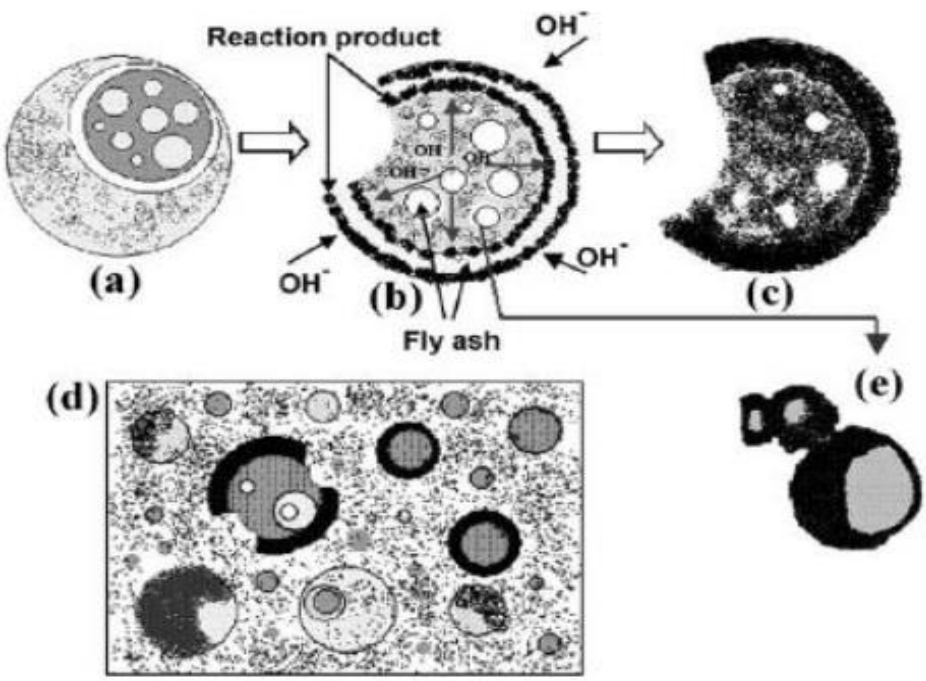


Figure 2.3 Adjective model of the alkali activation of fly ash [21]

2.1.4 Applications of geopolymer

Geopolymer materials have extensive applications in the field of industries like metallurgy, nonferrous foundries, plastic industries, aerospace, civil engineering, and automobile. The kind of application of GPC depending on the chemical structure in terms of the atomic ratio Si: Al in the polysialate [22]. Table 2.1 indicates the application of GP according to Si/Al ratio.

GPC used in many applications like the precast industry to manufacture railway sleepers, sewer pipes, and other pre-stressed building components in additional that this application applied in many countries especially in Australia, GPC used in this field because of the early strength of GPC gains when cured in temperature. Also, the strengthening of concrete structural elements considered the important application of geopolymer concrete.

Table 2.1 The application of geopolymer [13]

Si: Al ratio	Applications
1	Fire protection, Ceramics, Bricks
2	Low carbon dioxide OPC and concrete
	toxic waste, Radioactive, and Encapsulation
3	Fire protection
	foundry equipment, heat resistance composite, 200 °C - 1000 °C
>3	Tooling for aeronautics titanium procedure
	Sealants for industry, 200 °C - 100 °C
20-35	Heat and fire-resistant composites

2.2 Factors affecting on geopolymer concrete

2.2.1 Heat resistance

Heat curing of FAGPC is usually recommended. Heat curing significantly improves the chemical reaction that happens in the GPS. Both time and heat curing effected by the mechanical properties of GPC. Heat curing can be done by either dry or steam curing. The previous research showed that the dry cured GPC increasing the compressive strength approximately 15% higher than that of steam-cured GPC [23]. P. Rovnaník [24] proposed that the increase in temperature up to 90 °C leads to increase the compressive strength of the GPC. J. June *et al* [25] investigated that the increase in curing time enhanced the polymerization process which leads to increase the compressive strength. The noticeable increase in compressive strength was up to 24 hours of curing time Therefore, the curing time (rest period) suggested not exceed than 24 hours in practical applications.

2.2.2 Chemicals attack

2.2.2.1 Acid resistance

Normal concrete can suffer serious losses when submerged in a chemical attack like sulfuric acids, nitric, acetic and hydrochloric. The most important cause of acid motivate damage to infrastructure elements is biogenic acid corrosion, which happens often times in sewer systems [26].

Many authors reported that the GPC has a good resistance to chemical attack. Song et al. X. J. Song [27] reported that alkaline activator FA has high chemical resistance when exposed to 10% acid solution up to 8 weeks, the losses in strength and mass were 35% and 3% respectively (figure 2.3). Also Bernal [28] reported that alkaline activator based GPC has a better sulfuric acid resistance than NC, retaining compressive was 75% of their original strength after 150 days of submerging in acetic acid and that's attributed to the fact that alkaline activated solution has higher stability, low CaO/SiO2 ratio, lower initial permeability and higher alkalinity of the pore solution under acetic acid attack as compared with NC.

The pH level considered another indicator effect on chemical resistance and the small amount of PH considered responsible for the main chemical attack. 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 NC concrete suffered mass losses of 78-95% [4].

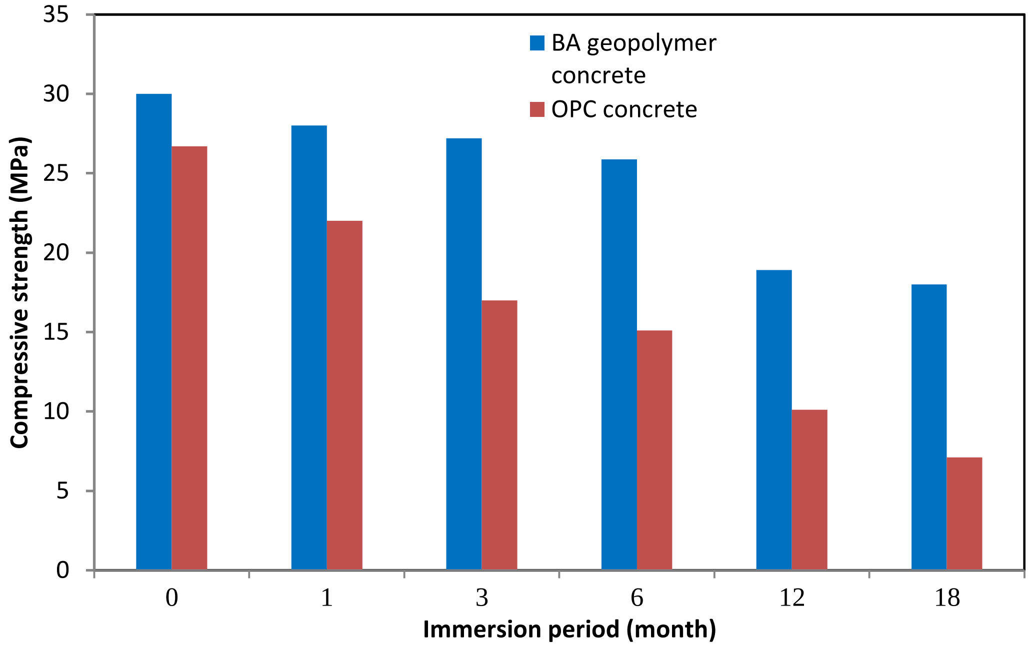


Figure 2.4 The effect of sulfuric acid on compressive strength [29]

2.2.2.2 Sulfate resistance

Sulfate magnesium or sodium attack is one of the major concerns for durability of GPC, it's considered a complex damage phenomenon due to an immersion of concrete products to an immoderate amount of sulfate solution from external or internal sources. The previous studies of sulfate magnesium or sodium attack on NC concrete discovered that NC concrete has a complicated mechanism because of reactions between sulfate solutions and C-S-H.

Otherwise, Wallah and Rangan [30] stated that the low calcium FAGPC heat cured shows high resistance when submerged in a sulfate solution. Specimens submerged in sodium sulfate for 365 days exhibited no cracking or spalling and no examination signs of surface deterioration. The change in length of GPC submerged in sodium sulfate solution for various ages of immersion is less than 0.01% of the initial geometry in addition that the best behavior in different sulfate solutions was noticed in the geopolymer material prepared with NaOH and cured at the elevated heat.

2.2.2.3 Seawater attack

FAGPC has good properties which were comparable or even higher than the NC concrete. The GPC was claimed to be durable in specific aggressive environments like fire and sulfate [31]. This is mostly due to the reaction product or alumina-silicates and low Ca content in the geopolymer. The GPC could resist synthetic NaCl without strength degradation and important mass loss [32]. The porosity of the concrete in the NaCl stayed low after 9 months of exposure [33]. The FAGPC has low Cl ions diffusion factor because of low permeability factor.

M. Olivia and H. Nikraz [34] concluded that the NC concrete was susceptible to degradation in a salt water. The cyclic immersion to NaCl improved the rate of degradation of normal concrete. Whereas the GPC exhibited no important change in degradation and strength. The high resistance of GPC due to high heat after being submerged in wetting-drying cycles was due to earlier crystallization. Moreover, FAGPC presented a marginal mass change after being immersed in continuous exposure. Likewise, chloride crystallization in the ordinary Portland cement pores was clear due to a gradual decrease in mass percentage over time.

2.3 Fly ash

2.3.1 Production of fly ash

The term of FA can be defined according to ASTM [35]. “The finely separated residue that results from the process of combustion of powdered coal or ground and that is transferred by flue gasses”. FA is usually manufactured by the steam generating plants and coal-fired electric. Characteristically, coal is pulverized and blown with air into the boiler's burning chamber where it directly ignites, creating heat and generating a molten mineral remainder. Boiler tubes excerpt heat from the boiler, refrigerating the flue gas and causing the molten mineral remainder to harden and form ash. The lighter fine ash particles named fly ash, and stay suspended in the flue gas. While coarse ash particles named to as bottom ash, fall to the bottom of the combustion chamber. As shown in figure 2.4.

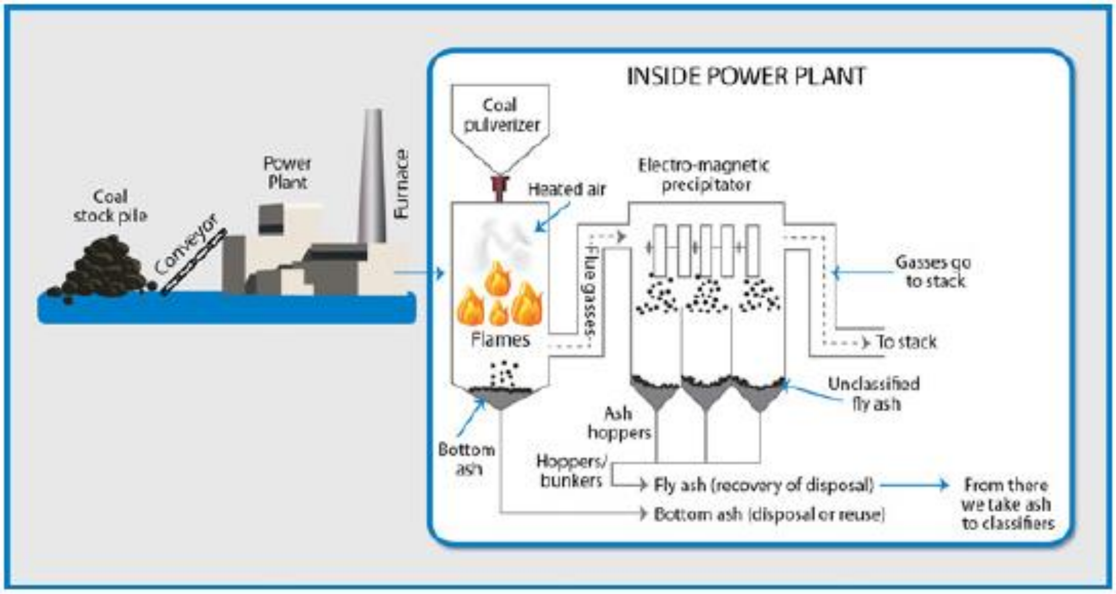


Figure 2.5 The process of manufacturing of fly ash (FA) in a power plant [36]

FA particles are naturally spherical, finer than lime NC, the diameter of particles ranging from less than 1 µm to no more than 150 µm (figure 2.5). ASTM 618-12 [37] specified two major classes of FA depending on chemical composition resulting from the kind of coal burned; The two types of FA named class C and F. Class F is FA usually manufactured from bituminous coal or burning anthracite, and FA class C is generally formed from the burning of sub-bituminous coal and lignite [38].

According to ASTM, the main difference between class F and C is the amount of silica, calcium, alumina, and iron content in the FA. The amount of calcium in class F fly ash is less than 20%. While class C FA has higher calcium content (20-40 mass %) than class F while a lower amount of silica and alumina when compared with class F. The influence of high CaO normally leads to increase the rate of reaction. Moreover, the high amount of calcium in class C FA may product in a rapid reaction and may not be appropriate for applications that need longer setting time or workability. In addition to chemical composition on FA, the other characteristics of FA that usually considered are uniformity, fineness, and loss of ignition (LOI). Loss of ignition is a measurement of unburnt carbon staying in the ash.

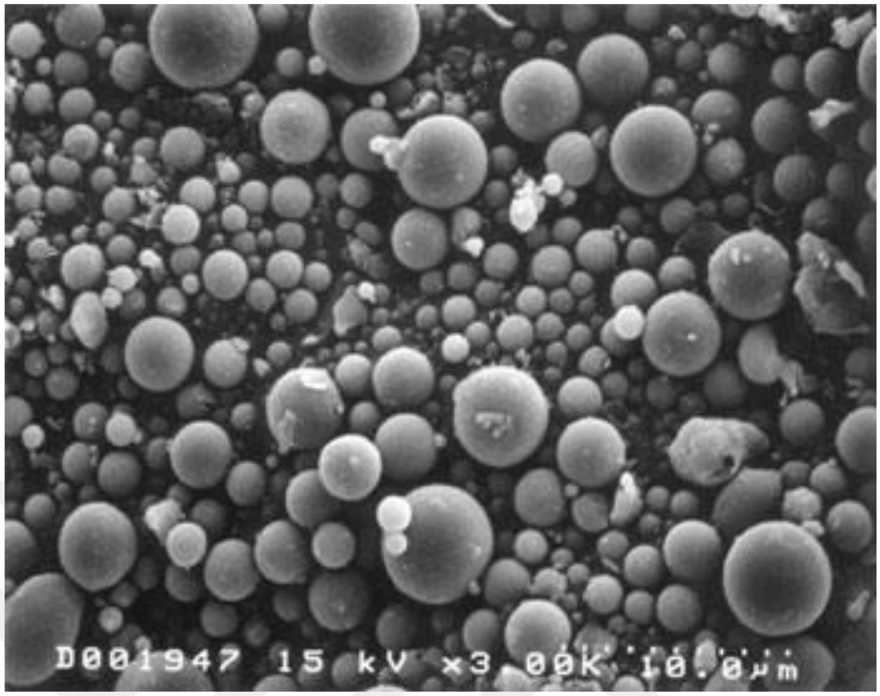


Figure 2.6 Fly ash particles enlargement [39]

2.3.2 Use of fly ash in concrete

The spherical shape of FA often supports to develop the workability of the fresh concrete, whereas the small particles size of FA plays an important role as a filler of voids in the mixture, and make dense and durable concrete. The use of FA can enhance a lot of properties in concrete such as better workability, durability, ultimate strength and cohesiveness. In additional that, the fine particles in fly ash can lead to diminishing bleeding and segregation in concrete which helps to enhance the finishing properties, particularly in lean mixes.

Use of FA in concrete can be useful to decrease permeability to water and aggressive agents. A significant achievement in utilize of FA in NC concrete is the improvement of high volume fly ash (HVFA) that successfully substitutes utilize of NC in concrete up to 60% and yet has outstanding mechanical properties with improved durability performance. High volume FA concrete has been showed to be more resource-efficient and durable than the ordinary Portland cement concrete [40]. The HVFA technology has been placed into practice, for example, the construction of ways in India, which implemented 50% ordinary Portland cement replacement by the HVFA.

2.4 Nano silica

Nano Silica (NS) is a crystalline compound happening abundantly as quartz and sand is utilized to produce different materials particularly glass and concrete. Nano Silica (NS) particles depending on their structure, are divided into two types: S-type (Spherical particles) and P-type (Porous particles) P-type NS surface has a number of Nano-porous with the pore rate of 0.611ml /g; consequently, P-type has a much greater surface area as compared with S-type. The particle size of NS ranges from 15-20 nm [41].

2.4.1 The effect of Nano silica on concrete

There are many properties influenced by NS particles like setting time, workability, bleeding, permeability, durability and strength. Min-Hong Zhang [42] reported the Small doses of Nano silica have shown to decrease setting times. He studied the add 2.5% NS by weight of cement reduced the setting time by 60%. The incorporation of NS with cement or FA helps to reduce the workability and bleeding of the mixture. A.M. Said [43] stated that the addition of NS has revealed to increase the rate of heat evolution and peak temperatures generated during the first 24 hours because pozzolanic reactions are usually slower and depend on the hydration of the cement phases first to access reserves of CH. F. Kontoleontos [44] concluded the addition of NS increase the cohesiveness and viscosity of mixtures with increases in the dose, also Nano silica has a very effective at preventing segregation of aggregates.

L.P. Singh [45] studied the influence of NS on the microstructural, the compressive and flexural strength in the paste, mortar, and concrete, he mentioned the addition of NS increase the compressive strength concrete higher than normal strength concrete without NS. Also, the addition of NS will minimize the cement consumption for a limit grade of concrete Moreover, the decrease in cement utilize will support in keeping the environment to a great extent.

In another hand, the addition of NS on the geopolymer mixture enhance the mechanical properties and durability of geopolymer concrete. Sarker, and S. Barbhuiya proposed the combination of NS in geopolymer mortar developed the early age compressive strength.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Introduction

This chapter shows the details of manufacturing FAGPC. The present study approved a strict trial and error process in order to improve the FAGPC technology. Although GPC can be made using various source materials, the present study utilized low calcium FA (ASTM Class F). Also, NC concrete used as a reference, the aggregates occupy 70-75 % of the total mass of concrete. The aims of the study were to identify the durability and mechanical properties that effect by the mixture properties and the properties of FA-GPC. The results investigated by compressive, splitting tensile strength and fracture toughness.

3.2 Materials

3.2.1 Fly Ash

Low calcium FA (class F) conforming to American Society for Testing Material C 618 was used for producing GPC obtained from thermal power plant called Ceyhan Sugozu, in Iskenderun-Turkey. Table 3.1 indicated to the physical and chemical compositions of FA. It can be seen from Table 3.1 FA contained a very low percentage calcium oxide and loss of ignition as compared with NC, the color of FA was dark as shown in figure 3.1.

3.2.2 Nano Silica

NS is silicon oxide nanoparticles and obtained from a local supplier. NS is a synthetic product of porous and approximately spherical particles as shown in Figure 3.2. Table 3.1 indicated to the chemical properties of. NS consists of pure silica. The average particle size of NS was 15 nm and the Blaine fineness was 640 m^2/kg.

Figure 3.1 FA used in the geopolymer mixes

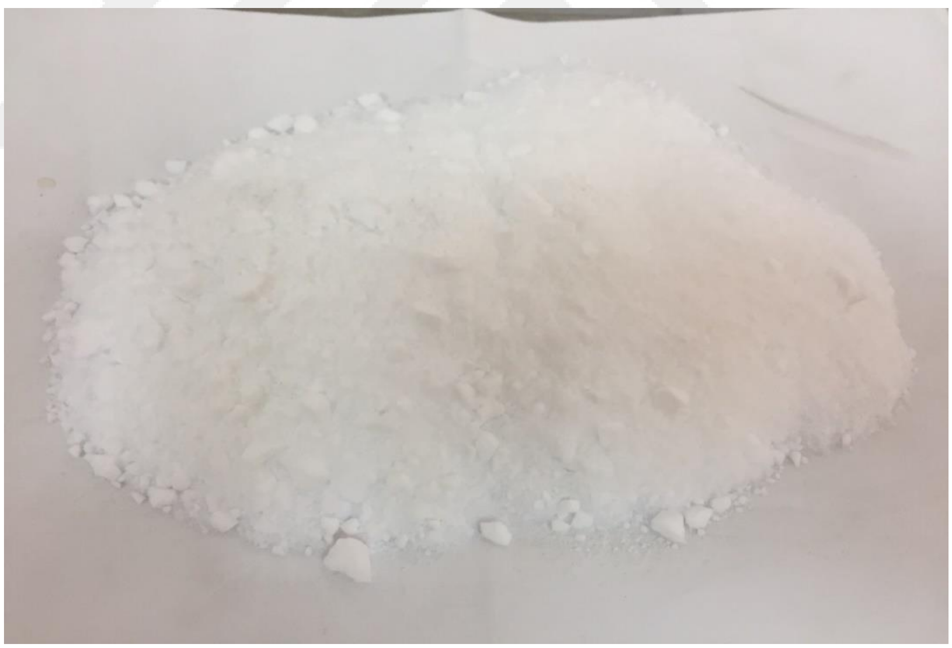


Figure 3.2 Nano silica used in the geopolymer mixes

3.2.3 Portland Cement

Ordinary Portland cement kind CEM I 42.5 R was utilized to producing normal concrete for determination of mechanical properties. OPC having Blaine fineness of 394 m^2/kg and 3.14 specific gravity. Table 3.1. Shows the chemical composition and physical properties of OPC.

3.2.4 Aggregates

Local crush limestone was utilized as coarse aggregate and fine aggregate with a specific gravity of 2.6, the water absorption was 0.8 for coarse aggregate and 1.4 for fine aggregate and the grains size of coarse aggregate were 7 and 10mm as shown in figure 3.3. The volumetric gradients of coarse and fine aggregate are presented in figure 3.4.

3.2.5 Super-Plasticizer (SP)

Sulphonated naphthalene formaldehyde (SNF) based high range water decreasing additive with a specific gravity of 1.19 as shown in figure 3.5. The super-plasticizer was altered at the time of mixing to enhance the workability of the mixture. SP was bought from a local supplier; all details are presented in Table 3.2.

Table 3.1 Chemical composition and physical properties of FA, OPC, and NS.

Chemical analysis	FA	OPC	NS
Cao	1.60	62.12	-
Sio_2	62.53	19.69	99.8
Al_2O_3	21.14	5.16	-
Fe_2o_3	7.85	2.88	-
MgO	2.4	1.17	-
So_3	0.10	2.63	-
K_2o	0.73	0.88	-
Na_2o	2.45	0.17	-
Loss of ignition	2.07	2.99	≤1.0
Specify gravity	2.30	3.15	2.2
Blaine fineness (m^2/kg)	227	394	-

(a) Coarse aggregate (b) Fine aggregate

Figure 3.3 Aggregates used in GPC and NC mixes

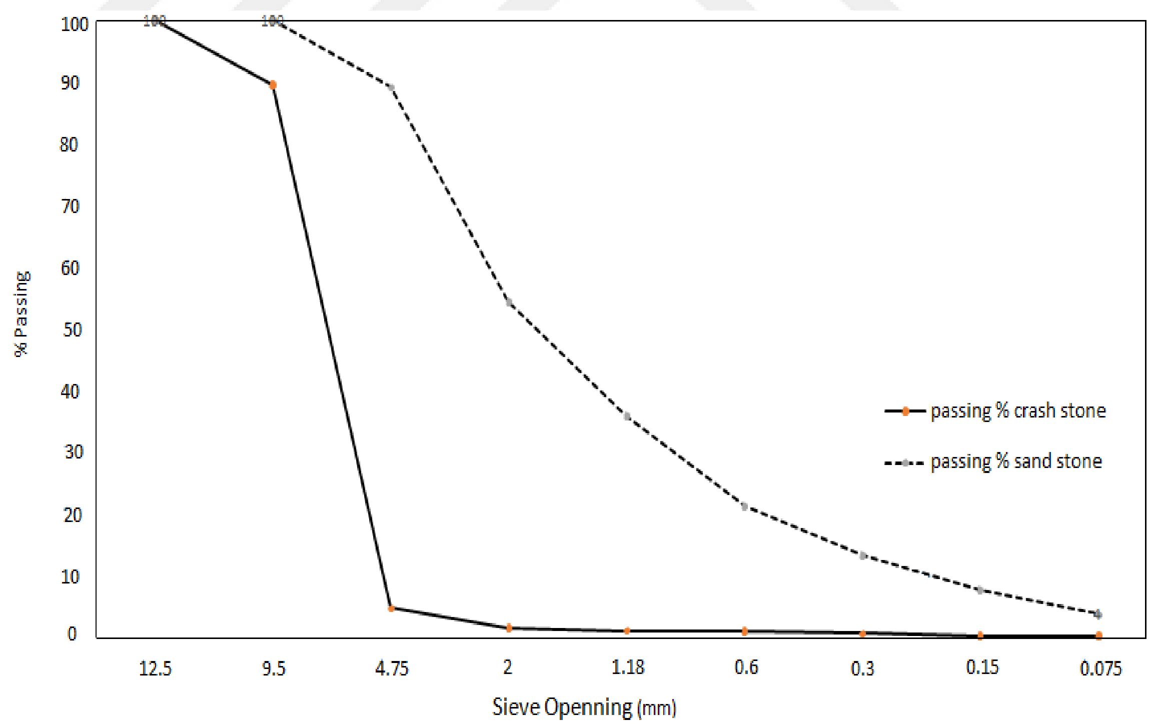


Figure 3.4 Volumetric gradients for coarse and fine crush aggregate

Table 3.2 Properties of Super-Plasticizer

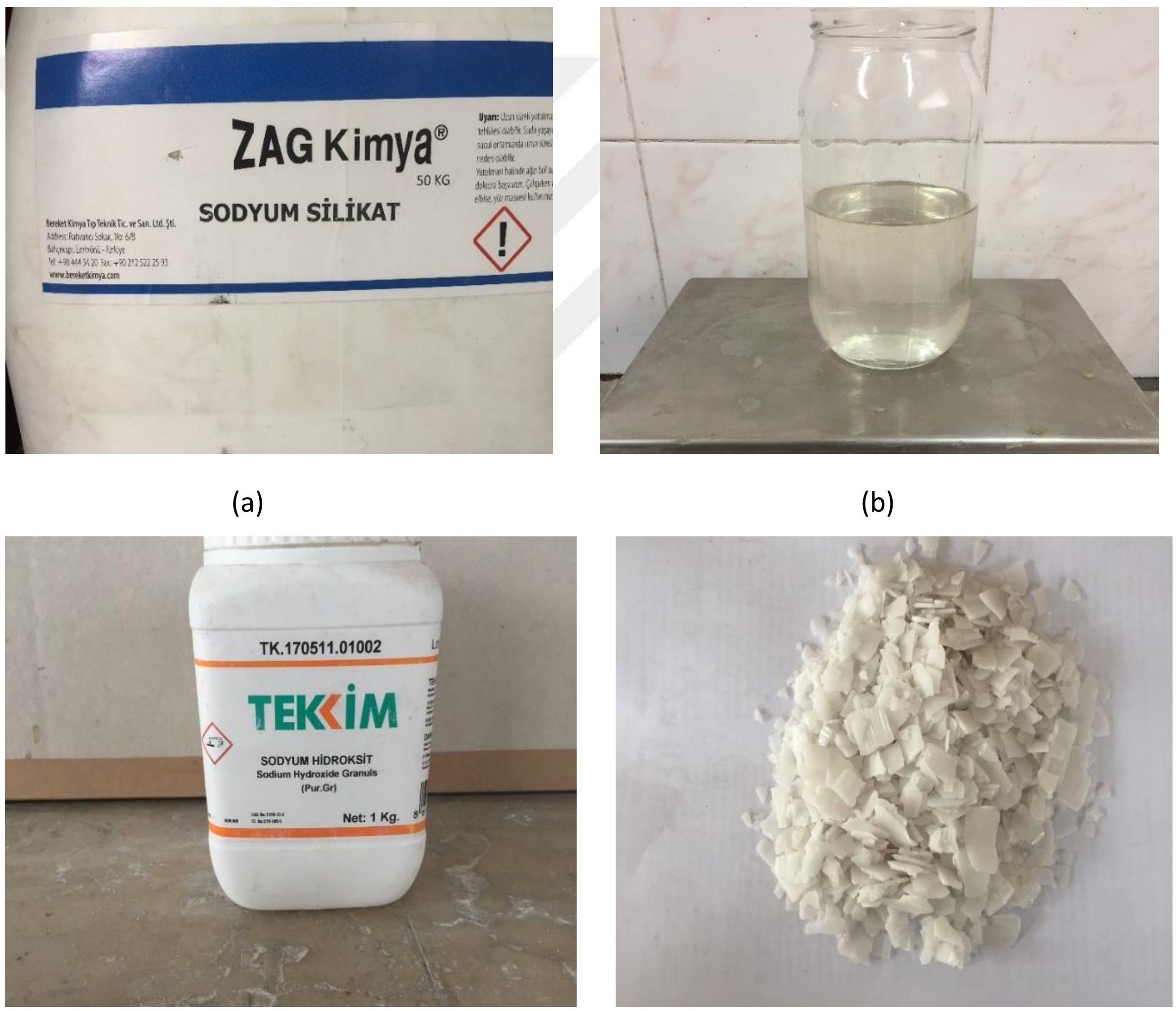
Property	Super-plasticizer
Name	Daracem 200
Color	Dark Brown
State	Liquid
Specific Gravity [kg/lt]	1,19
Chemical	Sulfonated Naphthalene Formaldehyde
Freezing Point	-4

Figure 3.5 Super-plasticizer used in GPC and NC mixes

3.2.6 Alkaline Activators

A combination of sodium hydroxide (NaOH) solution and sodium silicate solution (Na_2SiO_3) was selected as the alkaline liquid solution to react with FAGPC. In the present study, sodium silicate was used because they were cheaper than Potassium silicate. The chemical composition of sodium silicate is presented in Table 3.3. Sodium silicate commercially available, obtained from Gaziantep, Turkey as shown in figure 3.6.

The sodium hydroxide with 14M was prepared by dissolving commercially available NaOH pellets with 97%-98% purity in water as shown in figure 3.6. The 14M was considered the worst concentration in dissolution when exposed to chemical attack. Kumaravel and Girija [46] reported that the maximum reduction in strength after exposure to sulfuric and sulfate solutions was in 14M as compared with other concentrations.



(a) (b)

(c) (d)

Figure 3.6 The details of alkali activator (a) and (b) sodium silicate, (c) and (d) sodium hydroxide

Table 3.3 Chemical composition of sodium silicate

Grade	NA46
% NaOH (w/w)	14.7
% Na_2O (w/w)	13.7
% Si_2O (w/w)	29.4
Wt. ratio SiO_2/Na_2O	2.14
Specific gravity (gm./ml @ 20^oC)	1.458
Appearance	Viscous clear to light yellow liquid
PH	12.8
Solubility (water)	Soluble
% volatiles	> 60% (water)

3.3 Mix Design

The chosen of mix design for GPC needs a balance between economy and requirements for strength, density, durability, and workability. In the present experimental work the numbers of parameters taken into account the molar concentration of NaOH, Na_2SiO_3 to NaOH ratio, alkaline activator to binder ratio, aggregate content and curing methods. The parameters were chosen according to the previous research. An alkali activator to fly ash ratio was 0.45, this ratio is chosen to give good strength and microstructure of the GPC [46], [47] and Na_2SiO_3 to NaOH ratio was 2.5 in additional that there was no extra water added to GPC mixture. Figure 3.7 shows all details to prepare the GPC. The mix design of GPC and NC concrete were per m^3 as indicated in Table 3.4.

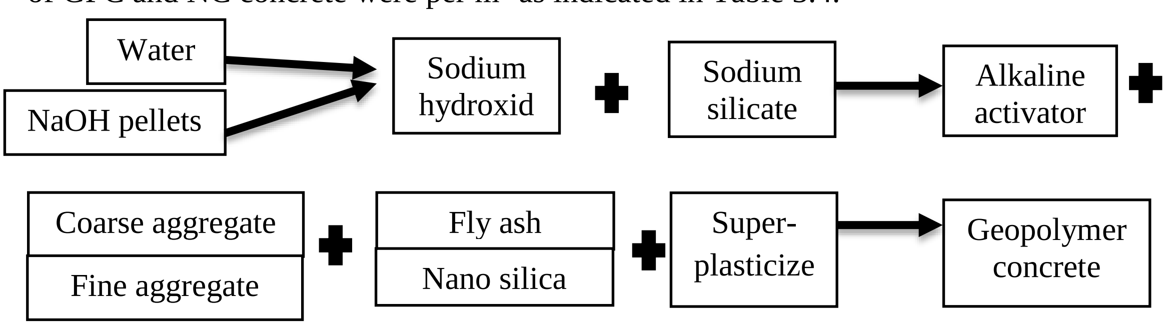


Figure 3.7 Process of preparing Geopolymer Concrete

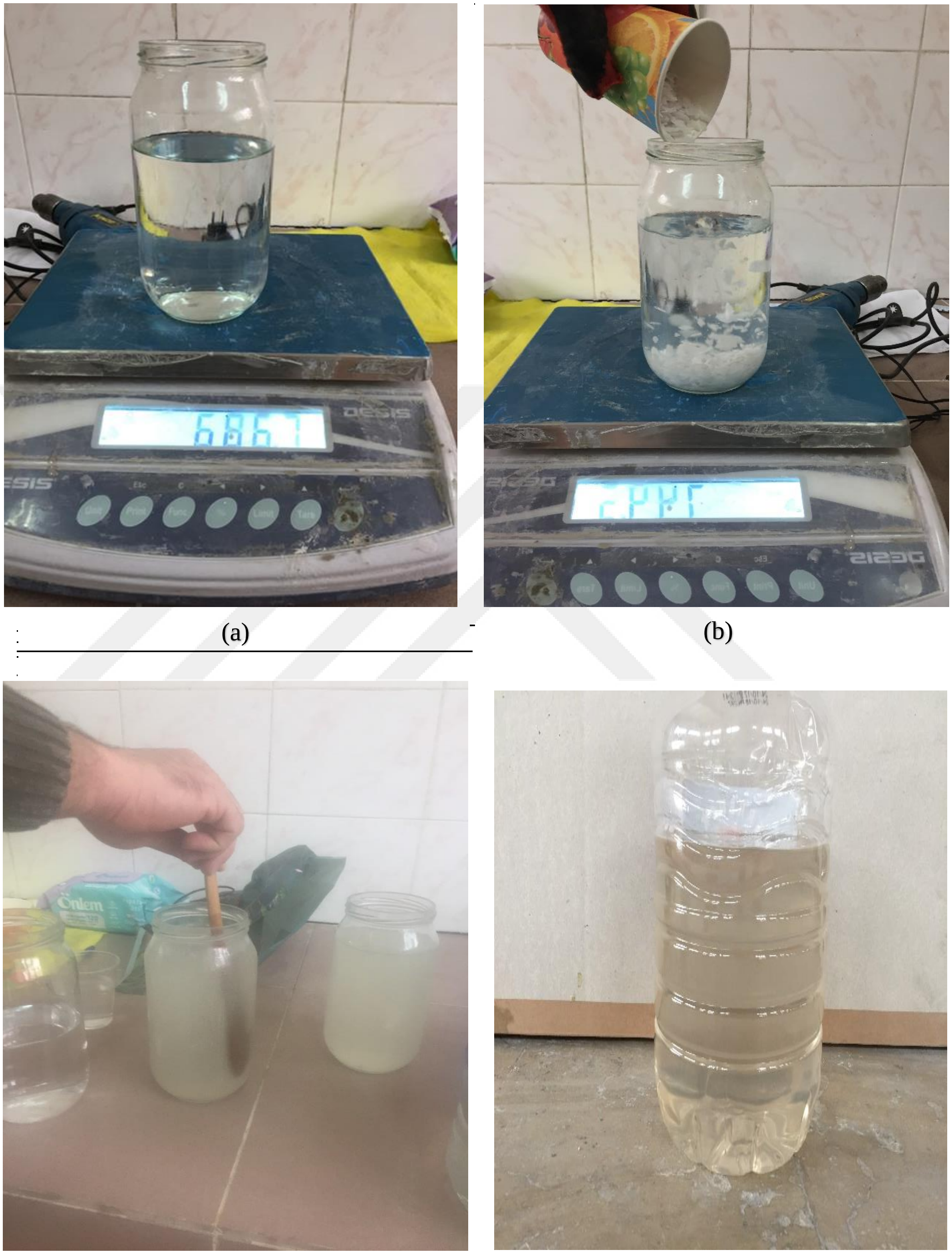
Table 3.4 Geopolymer concretes mix design

Description	Quantity
Fly Ash	500 kg/m^3
Na_2SiO_3+NaOH	225 kg/m^3
Fine Aggregate	575 kg/m^3
Coarse Aggregate	1150 kg/m^3
Nano silica	15 kg/m^3
Super plasticizer (SP)	6.04 kg/m^3
Na_2SiO_3/NaOH	2.5
(Na_2SiO_3+NaOH)/Fly Ash	0.45
48 hr Oven curing	70 °C

3.4 Manufacture of GPC

3.4.1 Preparation of Alkaline Activator Solution

The sodium hydroxide pellets solid was dissolved in water to create the solution as shown in figure 3.8b and c. The weight of NaOH solids in a solution varied based on the molar concentration of the NaOH. In the present study, the NaOH with 14 molarity was used. Sodium hydroxide with 14M consisted of 404 grams of solid and water with 596 grams per liter. The NaOH and Na_2SiO_3 solution were mixed together (figure 3.8d) at least 24 hr prior to preparing the alkali activator solution.



(a) (b) (c) (d)

Figure 3.8 Preparing of alkali activator (a) water, (b) and (c) mixing water with NaOH and (d) mixing sodium hydroxide with sodium silicate

3.4.2 Mixing and Casting

Limestone crushed aggregates were utilized as saturated surface dry (SSD) condition. Firstly, dry materials (fine and coarse aggregates, FA and NS) were added to pan mixer and blended for 2.5 min. After that, alkali activator solution including NaOH and Na_2SiO_3 was added with superplasticizer slowly and mixed for 3.5 min. Two GPC mixtures were produced as well NC mixture as a reference. Test specimens were 100×100×100 mm^3 cube specimens and prismatic 100×100×500 mm^3 were cast and compacted in two layers. While cylinder specimens with the size of 100 mm and 200 mm diameter and height respectively, were cast and compacted in three layers. All specimens were compacted by vibrator for the 30s to eliminate the air voids. The GPC specimens were covered by a plastic bag for 24hr to reduce the water evaporation during curing and specimens stored in ambient room temperature as rest period to prevent the evaporation of alkali activator solution. All details are shown in figure 3.9.

3.4.3 Curing

After casting, the GPC specimens were covered by a plastic bag for 24hr as rest period to prevent the evaporation of alkali activator solution. The GPC specimens were oven cured at 70 °C for 48hr however in the first 24hr (figure 3.10a). Molds removed and specimens covered in plastic bags after then returned to the oven as shown in figure 3.10b. After oven cured specimens stored 28 days at ambient temperature 23°C before exposed to solutions. The specimens of normal concrete were cured in water for 28 days.

(a) (b)

Figure 3.9 The details for mixing and casting GPC

(a)

(b)

Figure 3.10 Curing GPC specimens in oven (a) before curing with molds and (b) after removing molds

3.5 Specimens Preparation

Firstly, test specimens were immersed in water for 24hr to reach the saturation. Initial mass for all specimens was taken. Then specimens were immersed in 5% sulfuric acid, 5% magnesium Sulfate and 3.5% seawater up to 30 days (figure 3.11). To indicate the effect of chemical solutions, the comparison was done between specimens exposed to solutions with unexposed specimens for the same mixture at ambient temperature until testing time.

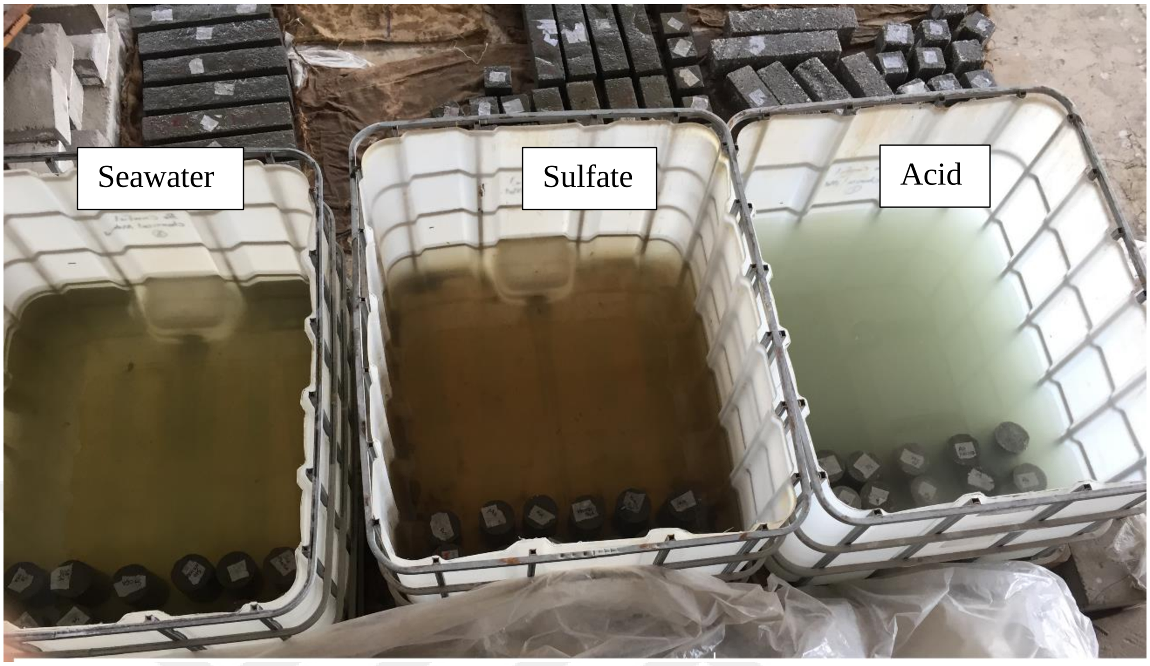


Figure 3.11 GPC and NC concrete specimens submerged in chemical attack

3.6 Test procedure

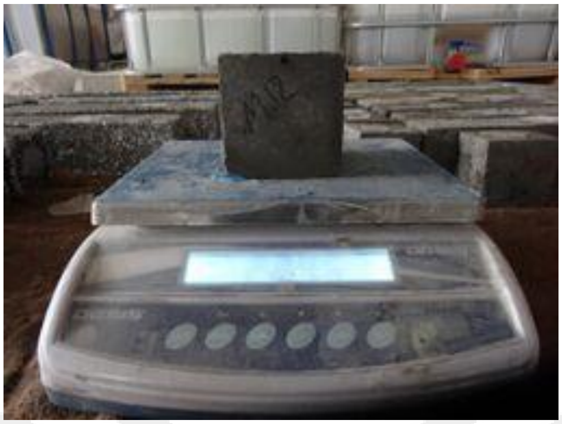
3.6.1 Change in mass

Firstly, the specimens of GPC and NC were put in water for 24hr before submerged in chemicals attack. The weight of specimens was measured in a saturated surface dry situation as initial weight. After then the specimens of GPC and NC were immersed in 5% sulfuric acid, 5% magnesium Sulfate and 3.5% seawater for 30 days. The weights are taken regularly and continuously every 15 days. Weights were measured using a digital balance as shown in figures (3.12). The change of the weight was calculated by the following formula.

$$\text{Change in weight (\%)} = \frac{B-A}{A}\times 100 \quad (3.1)$$

Where A= Initial weight (gm)

B= final weight (gm)



(a)

(b)

(c)

Figure 3.12 Use digital balance to measure the weight of specimens

3.6.2 Strength Test

Cube and cylinder specimens aged 56 days were subjected to compressive and splitting tensile strength respectively using the compression testing machine with 3000 KN capacity as (figure 3.13a). Compressive strength tested by the rate of loading 1.5 KN/s, while 1 KN/s rate of loading was used in indirect split tensile strength. The compressive strength was calculated according to this equation.

$$f'_c = \frac{P}{A} \qquad (3.2)$$

Where f'_c, is a compressive strength (MPa), P is the maximum applied load (KN) and A is cross-sectional area (mm^2).

While Eq (3.3) to calculate splitting tensile strength.

$$f_s = \frac{2p}{\pi h \phi} \tag{3.3}$$

Where f_s, P, h and Φ are splitting tensile strength, the maximum load (KN), the height of the cylinder (mm) and the diameter (mm).

(a) (b)

Figure 3.13 Strength test (a) compression test and (b) splitting tensile test

3.6.3 Fracture Parameters

A closed-loop testing machine with a capacity of 250 KN was utilized to measure the fracture energy (G_F) of prismatic specimens based on the recommendation of RILEM 50-FMC/198 Committee [48]. To evaluate the displacement at mid-span of prismatic specimens, a linear variable displacement transducer (LVDT) was utilized. The ratio of the notch to depth (a/w) for prismatic specimens was 0.4 and the notch opened for prismatic test specimens by cutting in order to reduce the effective cross-section to 60 ×100 mm^2 and the distance between supports was 400mm. All prismatic beams were tested under the rate of loading 0.02mm/minute. Fracture energy of prismatic beam specimens was obtained under three-point loading to according RILEM [48] as follow:

$$G_f = \frac{(w_o + mg\delta_s)}{A_{lig}} \tag{3.4}$$

Where $W_{\circ}$, m, g, δs, and A_{lig} are the area under the load-displacement curve (N-m), the mass of the beam (Kg), the acceleration due to gravity (9.81m/s^2), specific displacement (m) and A_{lig} are the area of the ligament (m^2) respectively.

The experimental results of G_F were compared with some theoretical equations proposed by the CEB-FIP committee [49] as shown below:

$$G_f = (0.0469D_{\max}^2 - 0.5D_{\max} + 26)\times\left(\frac{f_c}{10}\right)^{0.7} \tag{3.5}$$

Where f_c is the compressive strength (MPa) and D_{max} is the maximum aggregate size (mm).

Another equation investigated by Bazant and Becq-Giraduon and the prediction results of this equation to test results were 29.9% [49].

$$G_f = 2.5\alpha_0\left(\frac{f_c}{0.051}\right)^{0.46}\left(1+\frac{D_{\max}}{11.27}\right)^{0.22}\left(\frac{w}{c}\right)^{-0.30} \tag{3.6}$$

Where, f_c , $D_{\max}$, (w/c) and α_0 are the compressive strength (MPa), the maximum aggregate size (mm), water to cement ratio and the aggregate shape factor (1.44 for crushed or angular aggregates and 1 for around aggregates).

The net flexural strength, (f_{flex}), was obtained according to the following equation [50]:

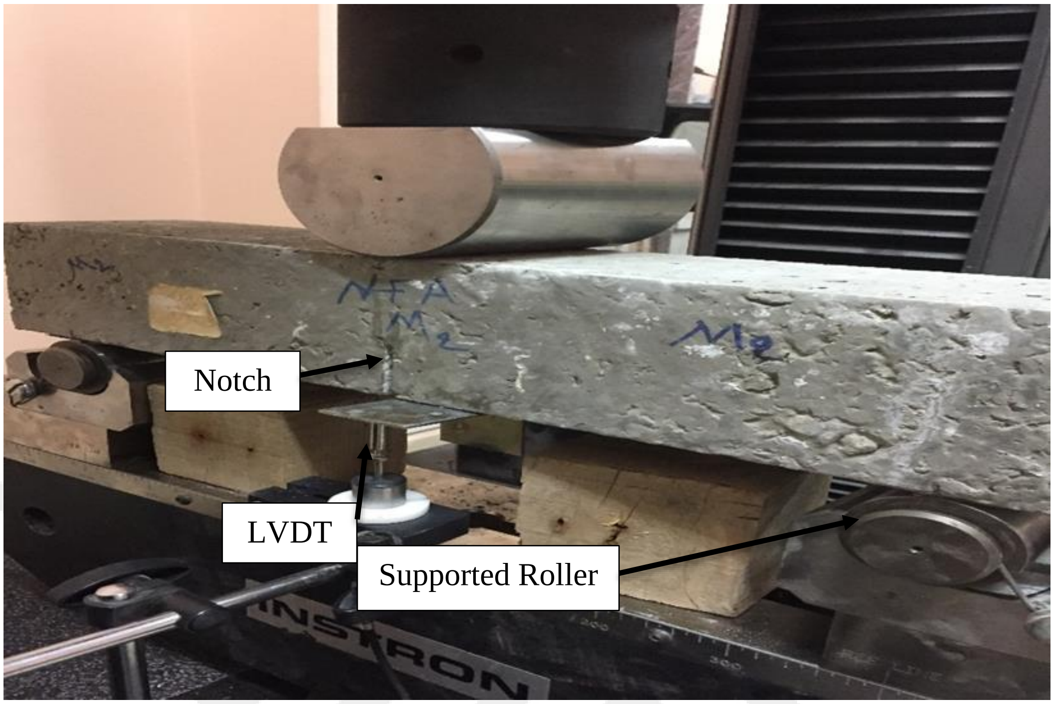
$$f_{flex} = \frac{3P_{\max}S}{2B(W-a)^2} \tag{3.7}$$

where $3P_{\max}$, S, B, W and a are the peak load (N), span length (mm), the width of the beam (mm), depth of beam (mm) and depth of the notch (mm) respectively.

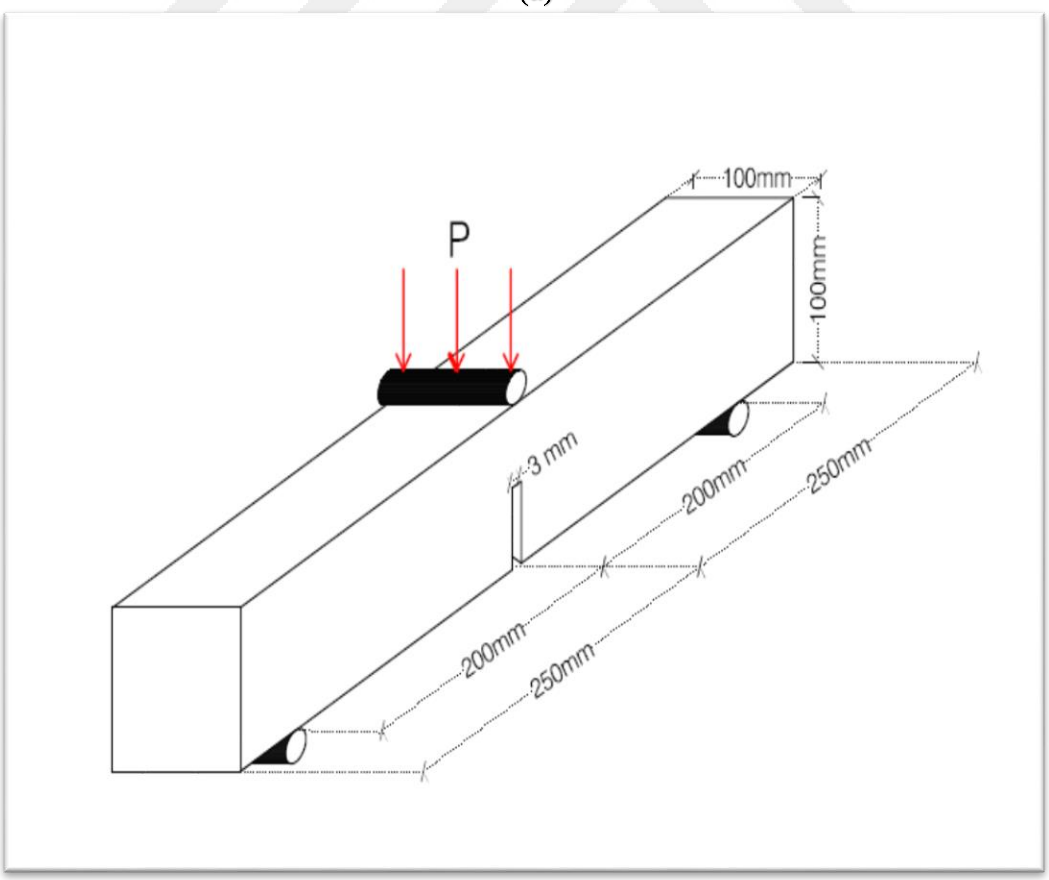
The critical stress intensity factor (K_{IC}) was utilized to specify the magnitude of stress concentration in cracks. The K_{IC} values were obtained according to equation (7) [51].

$$K_{IC} = \frac{3P_{\max}l}{2bd^2}\sqrt{a_0}\left(1.93-3.07A+14.53A^2-25.11A^3+25A^4\right) \tag{3.8}$$

Where, P_{max} , l, b, d, and $a_{\circ}$ are the peak load, the span of the beam, the width of the beam, the depth of beam and the depth of the notch ($A = a_{\circ}/d$).


Notch
LVDT
Supported Roller

(a)


P
100mm
100mm
3 mm
200mm
250mm
200mm
250mm

(b)

(c) (d)

(e) (f)

Figure 3.14 the details for flexural strength and fracture test (a) LVDT details, (b) the geometry of specimens and c, d, e, and f are control, acid, sulfate and seawater specimens under flexural test respectively

CHAPTER 4

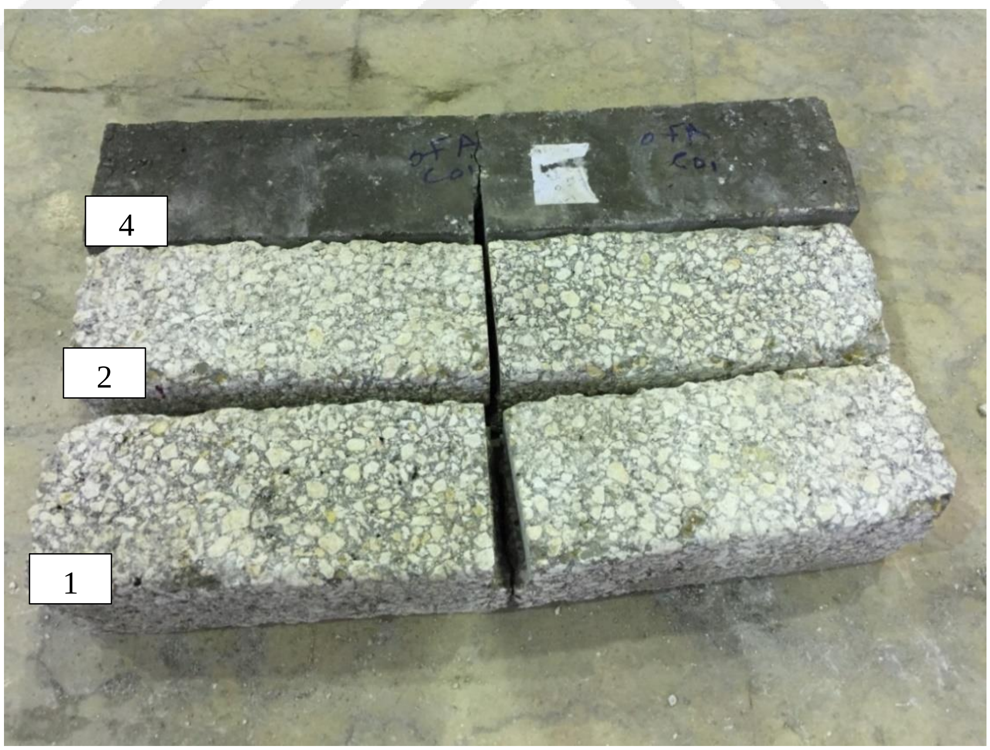
RESULTS AND DISCUSSION

4.1 Visual inspection

The visual inspection GPC and NC specimens submerged in sulfuric acid solution at 30 days as seen in the figure. 4.1a, b, and c. The GPC specimens immersed in sulfuric acid (H_2SO_4) showed erosion in surface started within few days after exposure which increased with an increase in exposure time, while the NC specimens showed severe deterioration more than GPC due to the high amount of CaO as shown in the figure. The superior performance of FAGPC with and without NS in sulfuric acid environments is resulted due to the lower amount of Ca. Compared to unexposed specimens, exposed specimens after 30 days of exposure period found to be softer in touch.

(a)

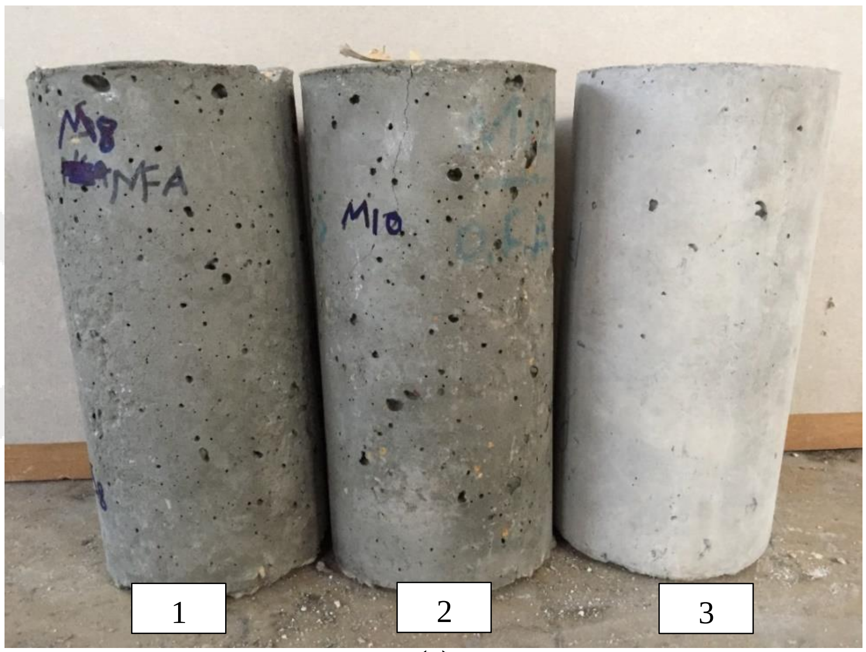
(b)



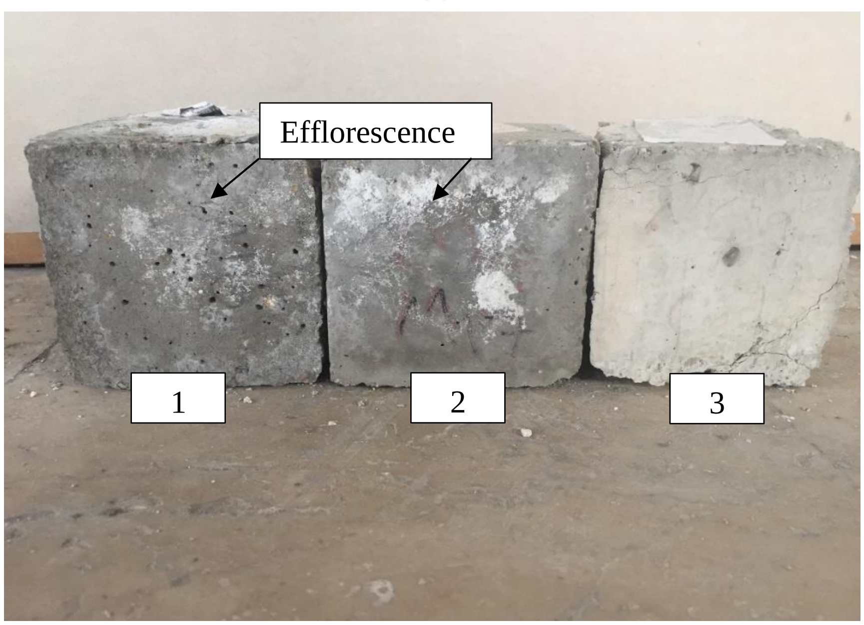
(c)

Figure 4.1 Visual appearance of GPC and NC submerged in sulfuric acid (a) cylinder, (b) cube and (c) prism, the numbers 1, 2, 3 and 4 are FA+NS, FA, NC and before immersion respectively

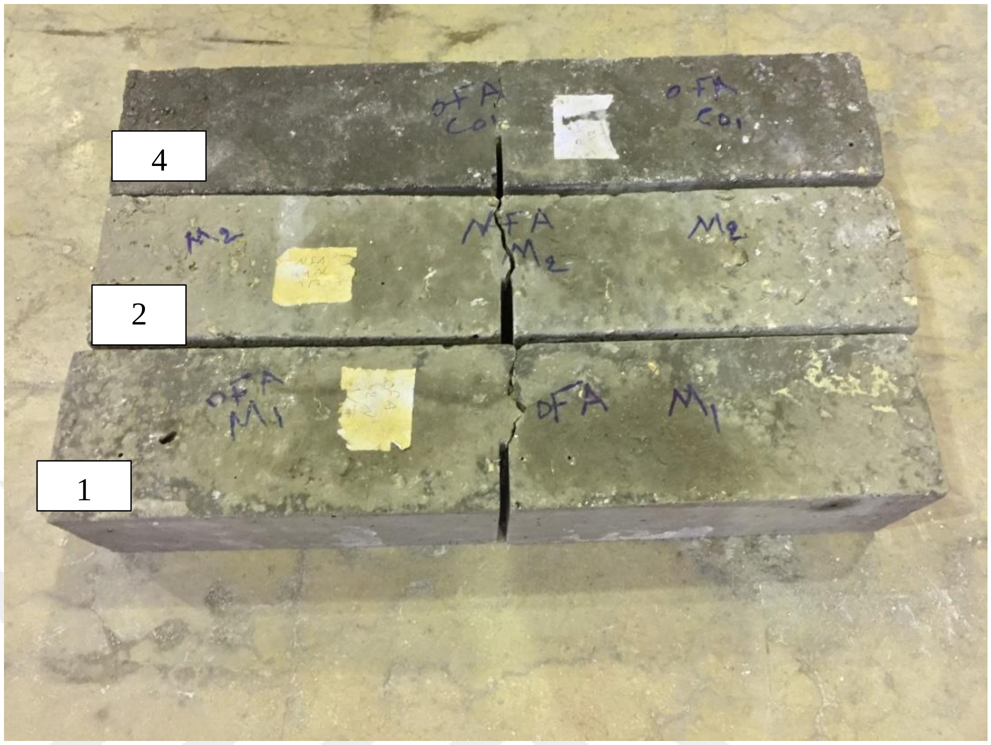
The visual appearance of GPC and NC specimens exposed to $MgSO_4$ and NaCl showed no marked change in visual appearance, spalling or cracking on the specimens except revealed a very small layer of efflorescence on the outer surface of samples as compared to control (figures 4.2 and 4.3). It's stated that GPC with and without NS has excellent resistance to sulfate magnesium. The similar investigation reported by Visitanupong [52] on the specimens exposed to sulfate attacks indicated that there was no marked visual examination of deterioration on the exposure GPC and NC specimens.



(a)

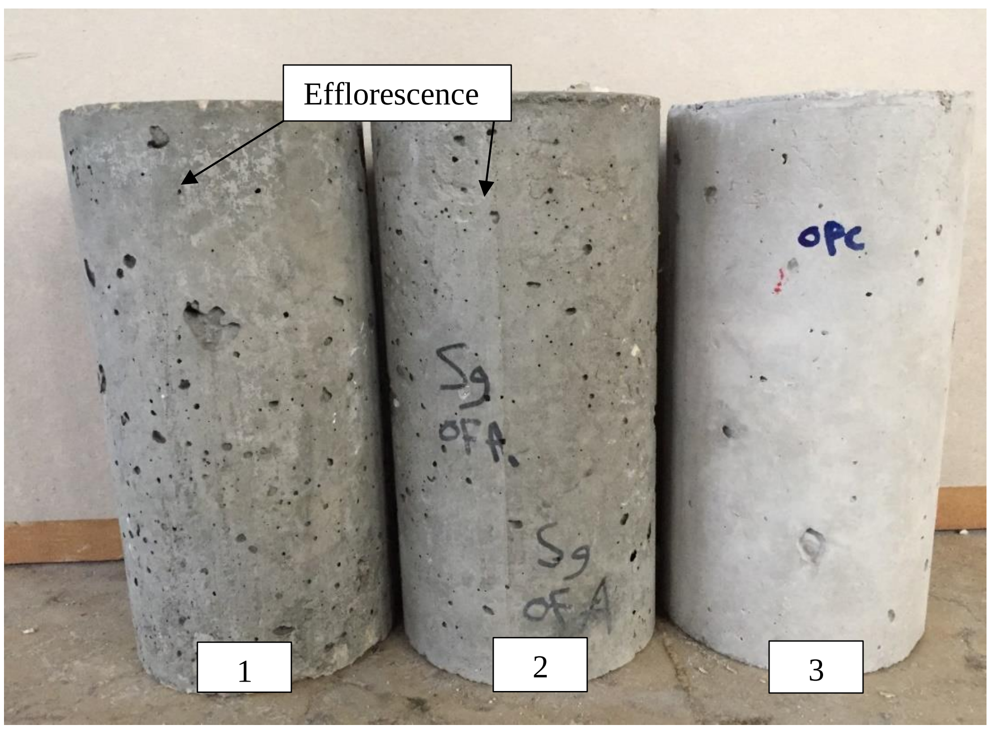


(b)

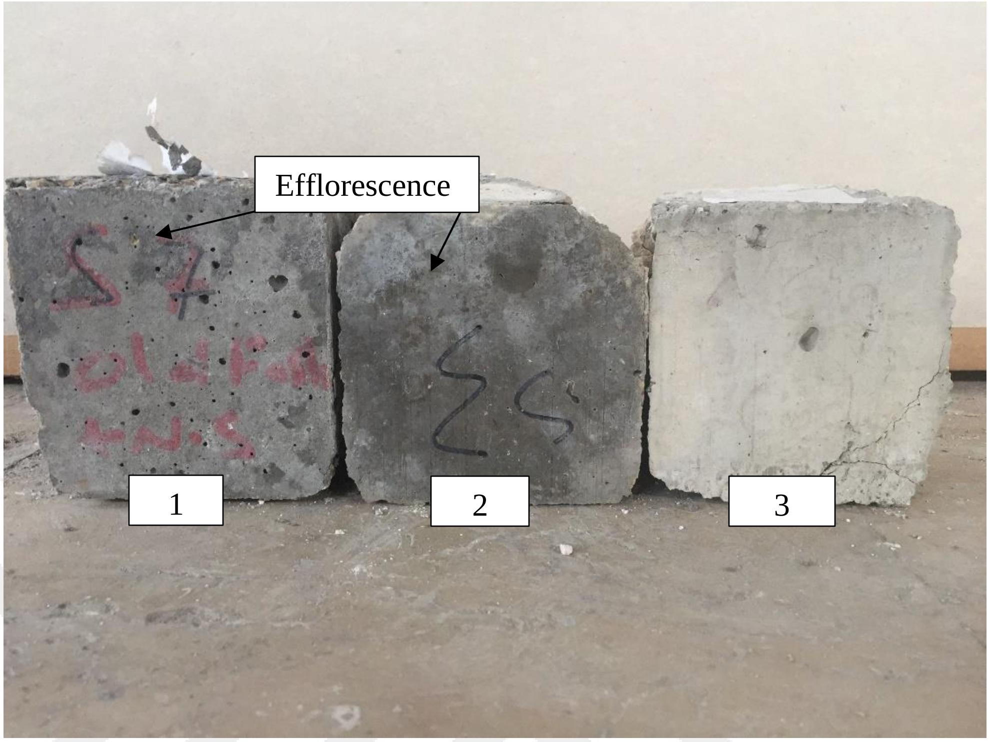


(c)

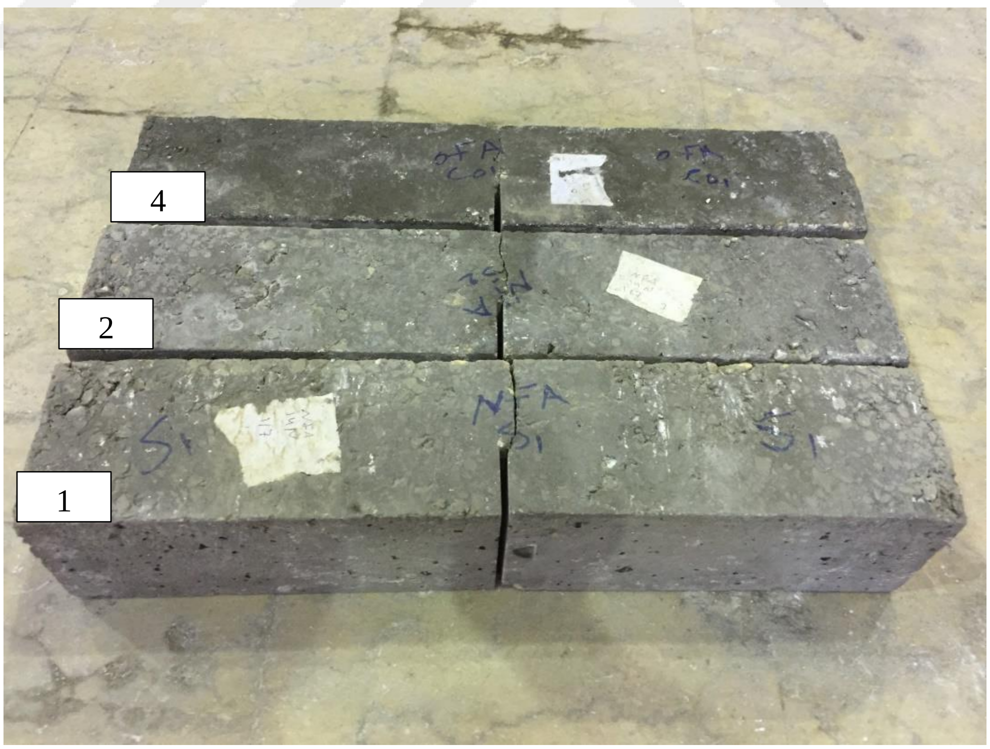
Figure 4.2 Visual appearance of GPC and NC submerged in magnesium sulfate (a) cylinder, (b) cube and (c) prism, the numbers 1, 2, 3 and 4 are FA+NS, FA, NC and before immersion respectively



(a)



(b)



(c)

Figure 4.3 Visual appearance of GPC and NC submerged in sea water (a) cylinder, (b) and (c) prism, the numbers 1, 2, 3 and 4 are FA+NS, FA, NC and before immersion respectively

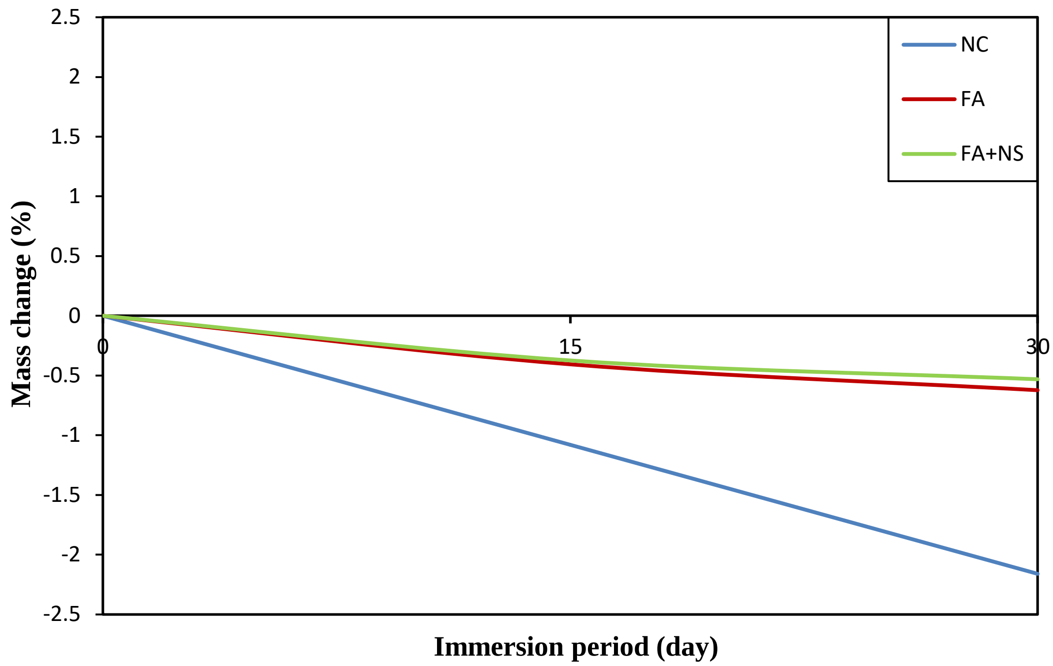
4.2 Mass Change

Figures 4.4 and 4.5 represent the mass change of exposed and unexposed geopolymer and normal concrete specimens. The mass change before and after exposure to sulfuric acid listed in Table 4.1. A control specimen for NC was more compared to GPC concretes due to continuing hydration reaction which was less in GPC [53]. This may be attributed to the oven cured GPC, which most of the hydration reaction took place at early ages after casting of GPC and oven cured. Specimens immersed in sulfuric acid had gained mass in the first two weeks of exposure. The mass gained of cylinder specimens were 1.34, 1.98 and 1.43 for NC, FA, and FA+NS respectively as shown in figure 4.5b. As indicated the mass gain of GPC were more than NC this performed that the GPC specimens were more permeable than NC due to oven curing which caused the extra pores in the GPC matrix. These pores absorbed the solution when GPC exposed to solutions and therefore, the resultant weight at the first few days was increased. A similar investigation was also indicated in the earlier research [54].

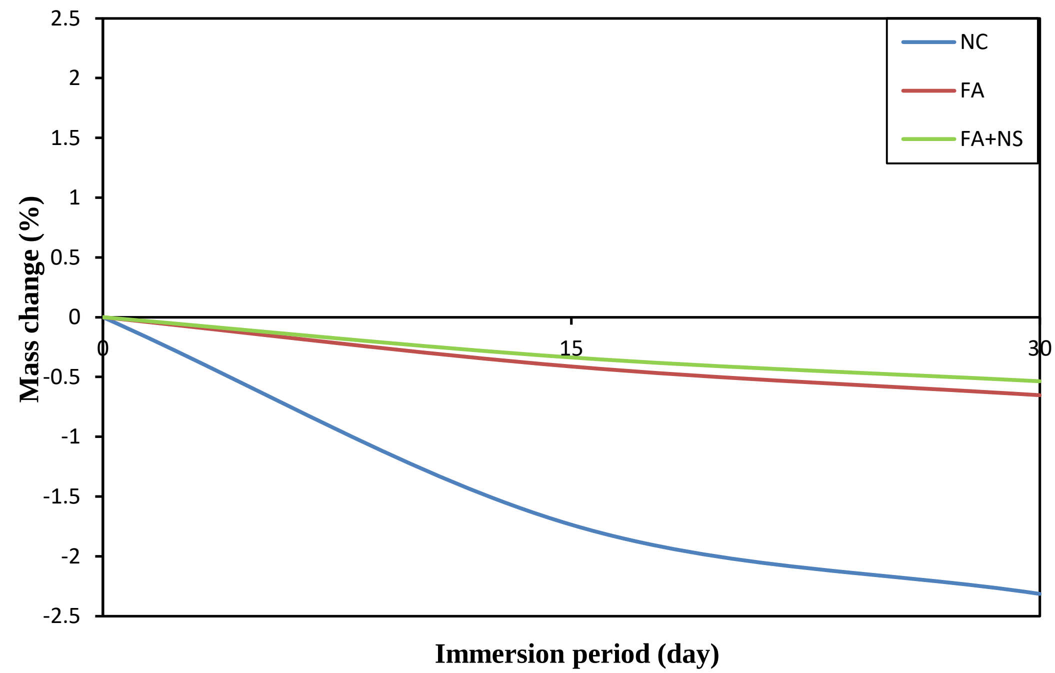
After 15days of the exposure period, reduction in mass was observed compared to the mass measured at first 15days of exposure. The reduction was continuing up to the end of exposure time, while the final mass measured in all GPC was remain more than the initial mass. However, NC specimens show a reduction in mass at the end of exposure time compared to initial mass. The final mass changes values evaluated were -0.89, 0.42 and 0.7 for NC, FA, and FA+NS respectively. As shown the mass change in FAGPC specimens was less than measured by NC specimens under the same exposure condition. This may result mainly from the reaction between CaO presented in the NC matrix and the harmful ions from acid solution [29]. However, the mass change detected in FA+NS was less than observed in the mixes of GPC without NS, this approved that added NS decreased the pores in GPC concrete matrix and increase the density which makes the GPC mixes with NS denser and more durable than GPC mixes without NS [55].

On the other hand, a similar trend was shown in the GPC specimens immersed in magnesium sulfate and seawater showed a mass gain, since a slight loss in mass for NC as indicated in figures 4.6 and 4.7. The maximum increase in mass was observed in FA mix specimens while the slight gain in mass occurred in FA+NS due to the prescience of Nano silica which leads to decrease the pores and makes mixture denser than FA without

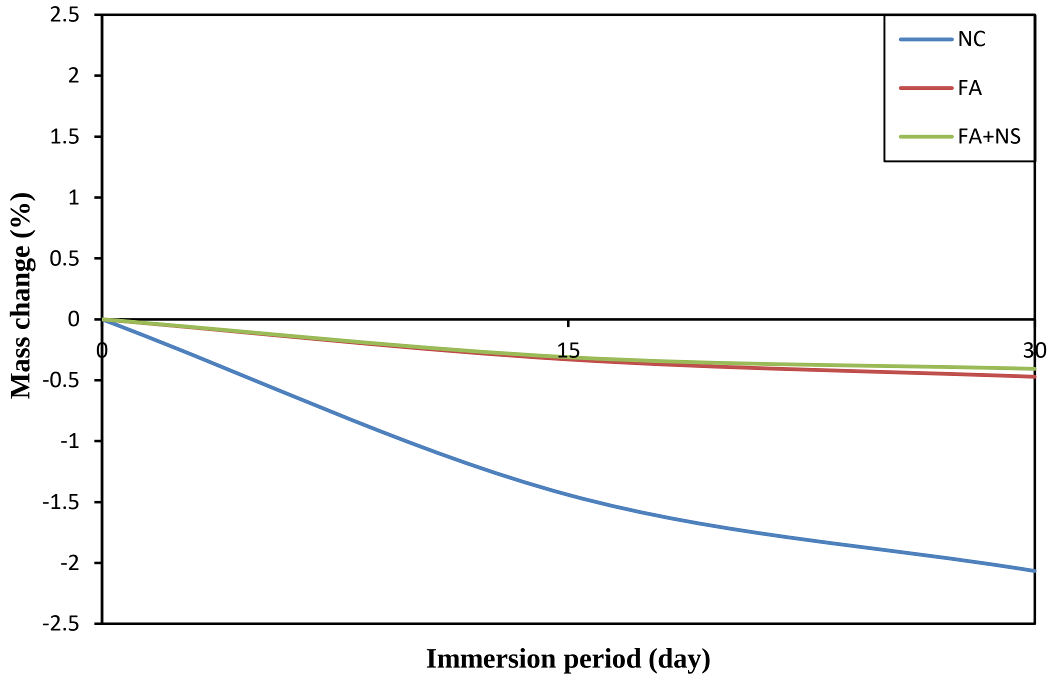
NS. A slight mass gain in specimens exposed to sulfate attack was investigated by Wallah and Rangan [56].



(a)

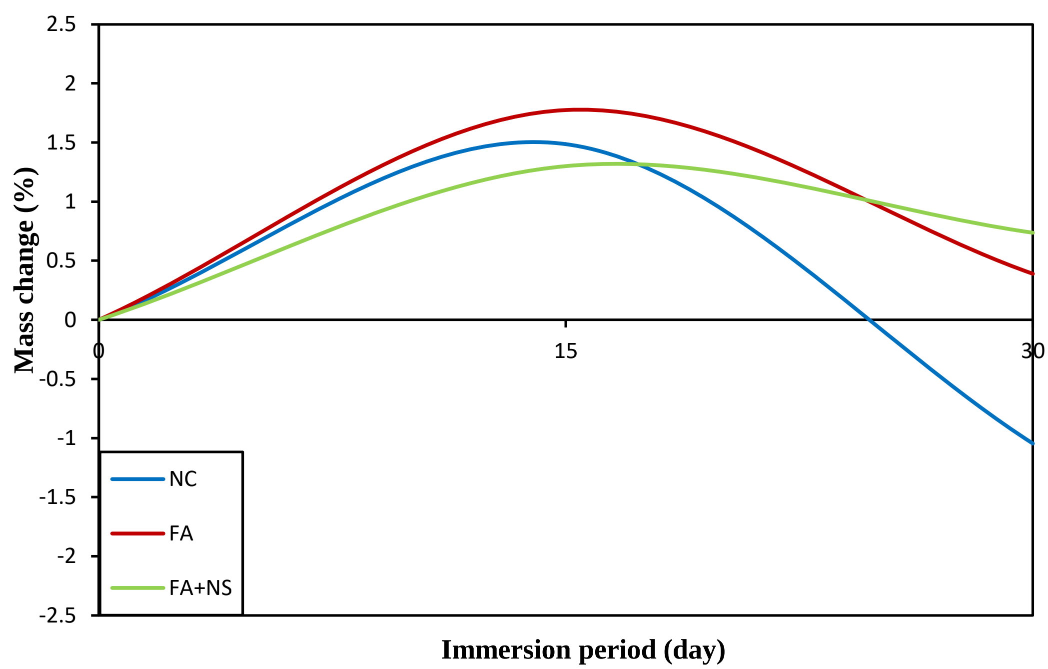


(b)

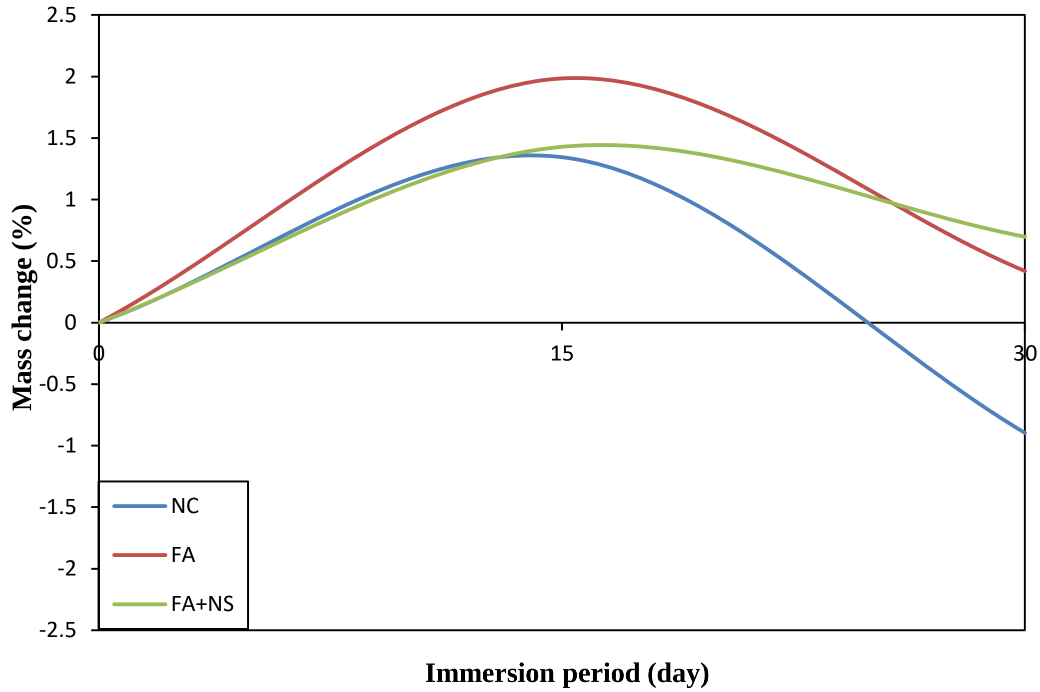


(c)

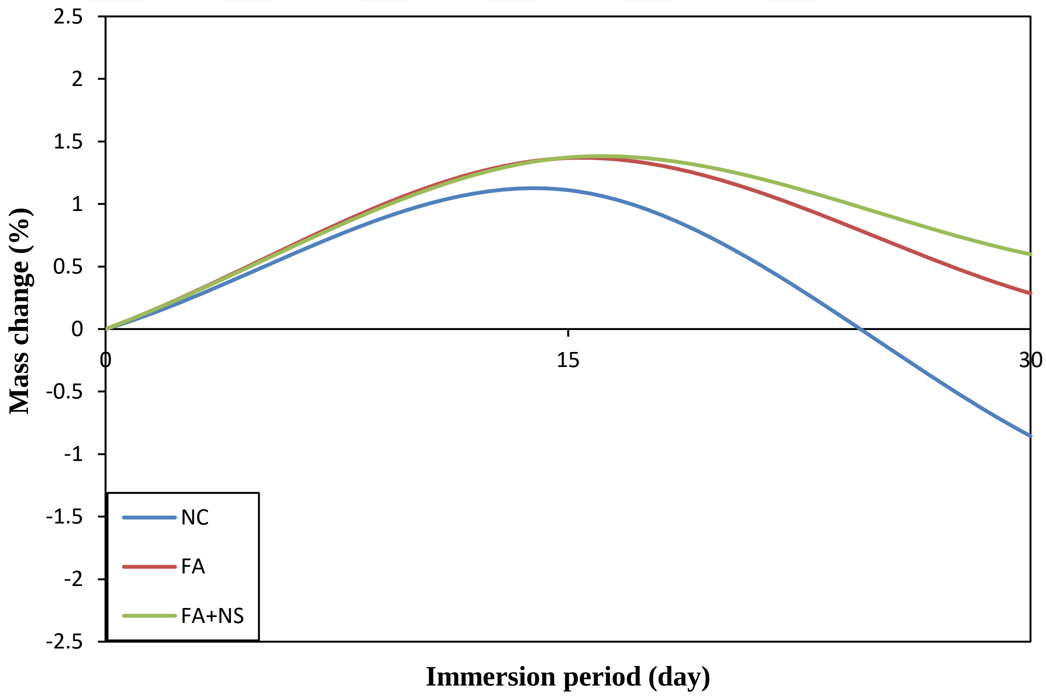
Figure 4.4 Mass change of GPC and NC specimens before submerged in chemical attack (a) cube, (b) cylinder and (c) prism



(a)



(b)

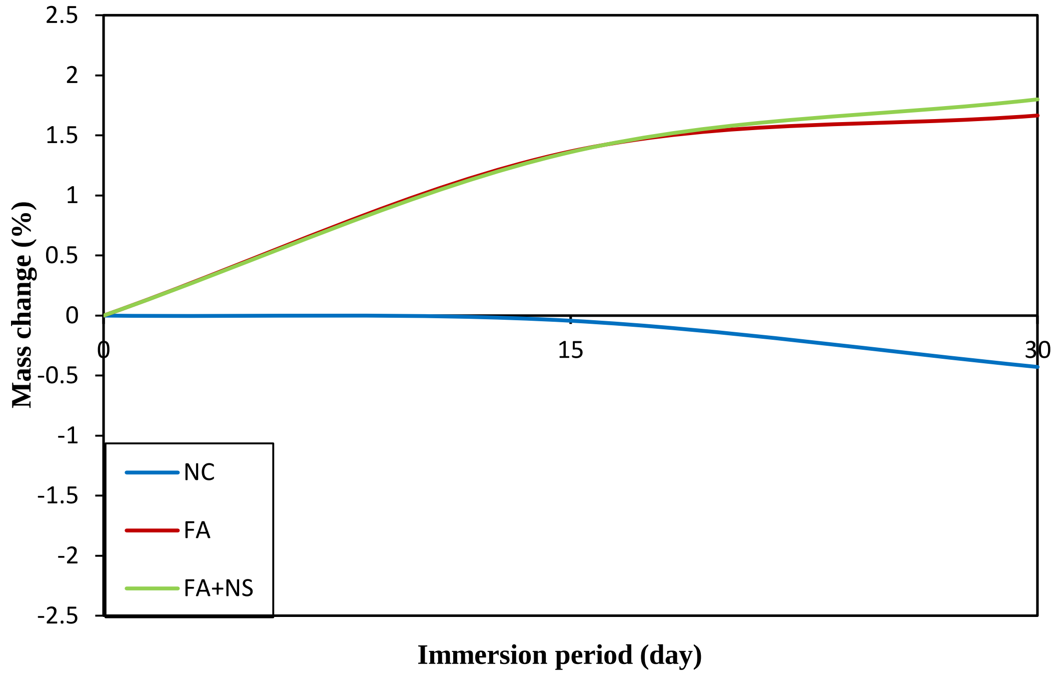


(c)

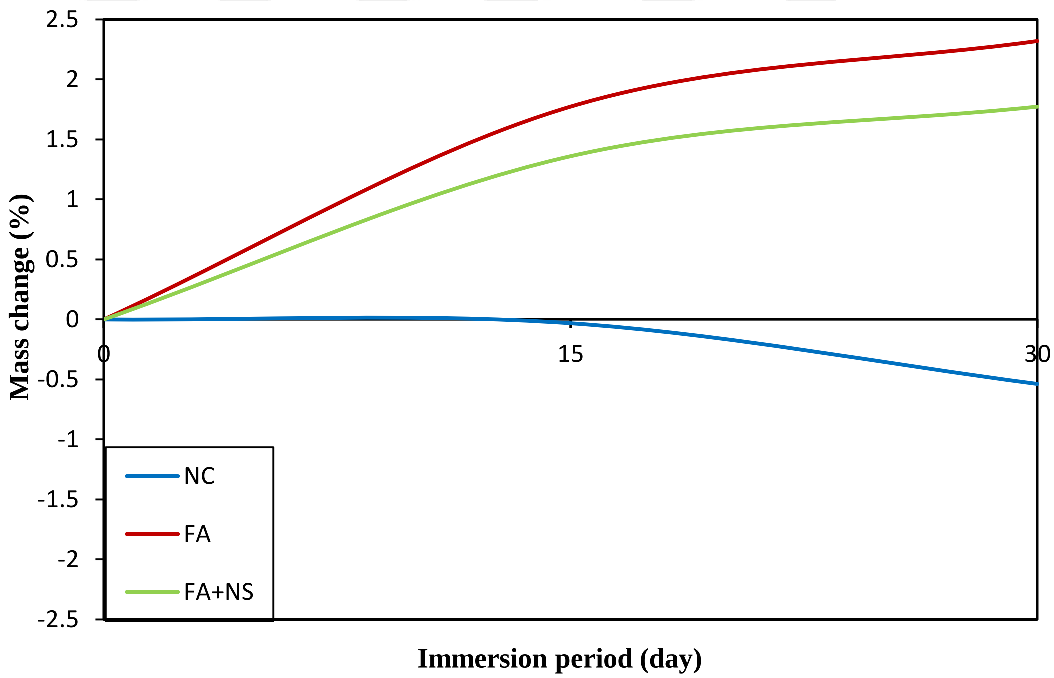
Figure 4.5 Mass change of GPC and NC specimens submerged in sulfuric acid solution (a) cube, (b) cylinder and (c) prism

Table 4.1 Mass change for GPC and NC exposed to 30 days in chemical attack

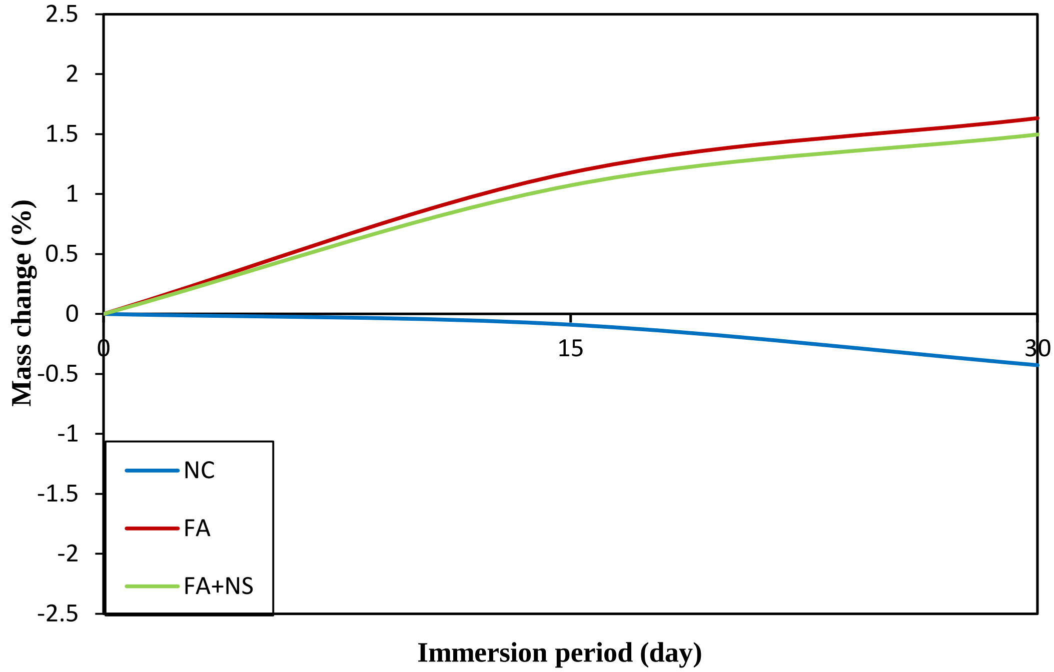
Series code	Mix code	Cube		Cylinder		Prism	
		Before exposure (gm)	After exposure (gm)	Before exposure (gm)	After exposure (gm)	Before exposure (gm)	After exposure (gm)
Control	NC	2314	2264	3715.8	3629.8	12003.8	11755.8
	FA	2215.1	2201.3	3539.7	3516.6	11575.9	11521.3
	FA+NS	2352.3	2339.8	3564	3544.9	11592.1	11545
Seawater	NC	2314	2306	3771.5	3759.4	12216.8	12187
	FA	2275.8	2311.8	3624.2	3662	11836.3	12000
	FA+NS	2352.3	2367.3	3675.3	3707	11731.3	11884
Sulfate	NC	2338.4	2328.4	3815.5	3795	12053.8	12002.3
	FA	2341	2380	3585.8	3669	11887.9	12082
	FA+NS	2277.2	2318.2	3631.6	3696	11789.6	11966
Acid	NC	2321.5	2297.2	3792.4	3758.4	12062.2	11959
	FA	2310.3	2319.3	3576.8	3591.8	11923.8	11957.8
	FA+NS	2307.4	2324.4	3582.8	3607.8	11880.8	11951.8


2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
0
15
30
Mass change (%)
Immersion period (day)
NC
FA
FA+NS

(a)

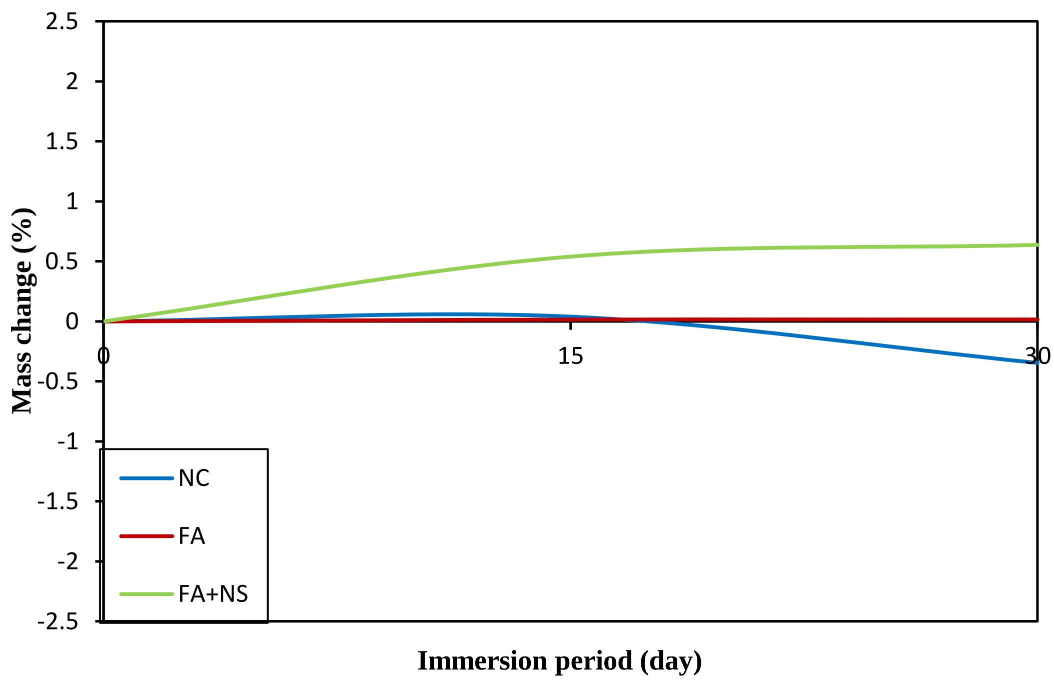

2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
0
15
30
Mass change (%)
Immersion period (day)
NC
FA
FA+NS

(b)

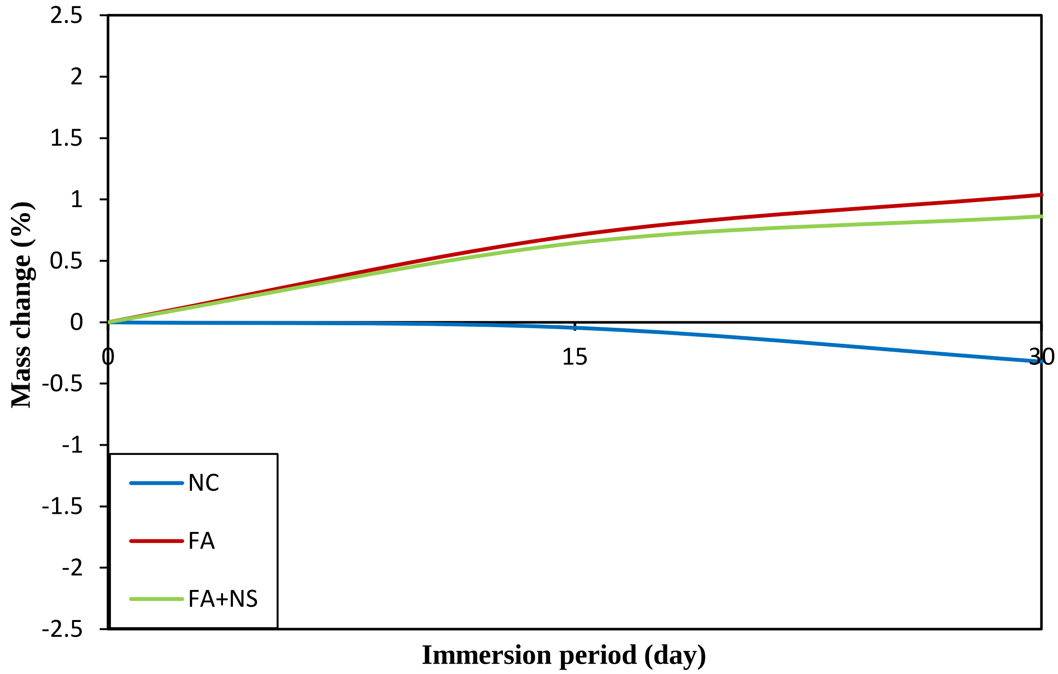


(c)

Figure 4.6 Mass change of GPC and NC specimens submerged in magnesium sulfate solution (a) cube, (b) cylinder and (c) prism



(a)



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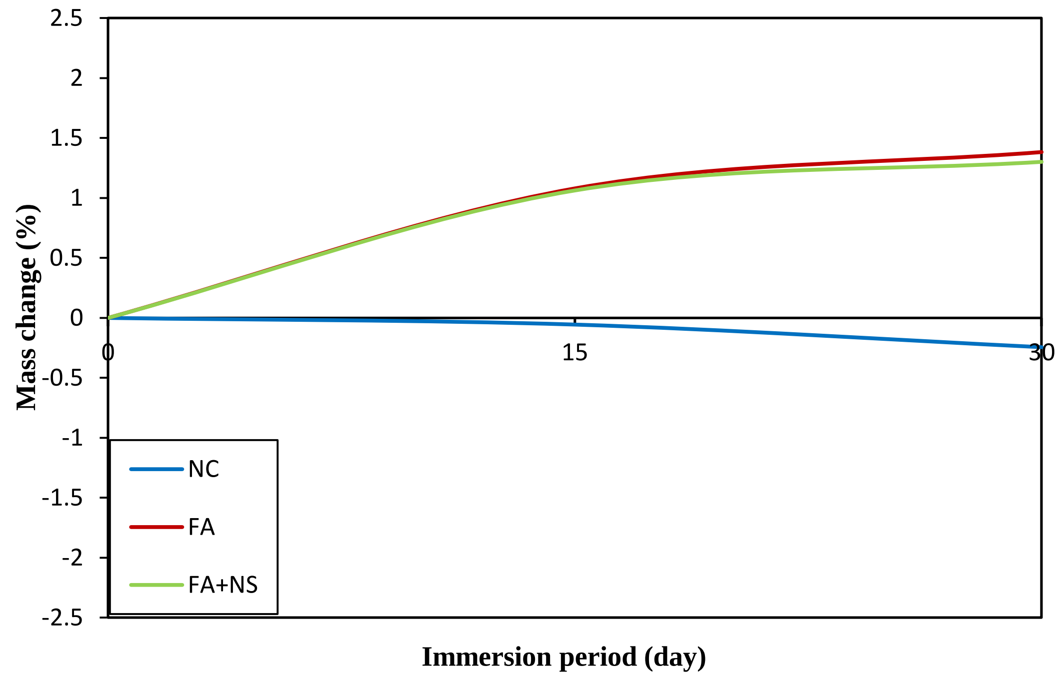


(c)

Figure 4.7 Mass change of GPC and NC specimens submerged in seawater solution (a) cube, (b) cylinder and (c) prism

4.3 Compressive strength

Table 4.2 and figure 4.8 represent the results of compressive strength for exposed and unexposed GPC, and NC specimens. Three identical samples were used to take an average for each value of the results. The compressive strength of NC specimens was higher than GPC specimens due to use LCFA in GPC mixes [57] as seen in Table 4.2. As indicated in figure 4.8 the reduction in strength takes place in all the mixes submerged in sulfuric acid, this reduction is increased with the increase of immersion time in solution. It is noticeable from figure 4.8 that the FA specimen's exhibit higher strength loss compared to FA+NS specimens. The compressive strength losses for specimens without NS were 28.2%, whereas the strength losses for FAGPC specimens with NS were 17%.

The reduction in strength attributed to destroy the oxy-aluminum bridge (-Al-Si-O) of geopolymeric gel when exposed to acidic attack which is the main factor in concrete matrix responsible for strengthening the gel and increasing the bond between matrix compositions [58]. Reduction of permeability occurred by incorporating of NS reduces the entrance of a sulfuric acid solution into GPC matrix which enhances the resistance of GPC to acid. As indicated in figure 4.8 the combination of 3% NS with FAGPC can essentially decrease the rate of a sulfuric acid solution expressed in terms of strength reduction. On the other hand, incorporating of 3% NS decreases the strength attributed to the unreacted NS which leads to producing an excessive self-dehydration in the matrix and cracking that eventually reduces the compressive strength for exposure specimens [59]. Therefore, the strength of specimens without NS is bigger than the compressive strength of specimens with 3% NS as a result of the presence of unreacted particles of NS working as defect particles. However, NC exposed to sulfuric acid shows high deterioration as shown in figure 4.8 due to form an expansive gypsum and ettringite as a result of entrance harmful ions from acid solution to concrete matrix. These ions can make an expansion, cracking and spalling in the matrix of concrete that eventually reduces the strength [60].

Specimens submerged in magnesium sulfate exhibited less reduction in compressive strength as compared with sulfuric acid as shown in figure 4.8. Specimens with NS showed excellent durability to sulfate attack compared to the GPC without NS and NC specimens. The minimum decrease in compressive strength was achieved in FA+NS specimens with 8.9%, while the maximum reduction was observed in NC specimens with 16.2%. Furthermore, it can be investigated from the results that both FAGPC without NS show good resistance to $MgSO_4$ attacks due to a more stable matrix caused by cross-linked alumina silicate (-Al-Si-O) inside polymer-structure. Fernan- Dez et al. [61] mentioned that low calcium content in alkaline activator solution is a significant property in the durability of GPC.

The specimens submerged in seawater showed superior performance when compared with sulfuric acid and sulfate magnesium as shown in figure 4.8. It is noteworthy from the results that the exposure of GPC with or without NS specimen is very little loss in the compressive strength. The losses were 4.23, 6.85 and 7.72% for FA+NS, FA and NC respectively the GPC showed more resistance than normal concrete, moreover, the fly ash with Nano silica exhibited superior resistance to salt water than mixes without NS which led to decrease the pores and increase the density.

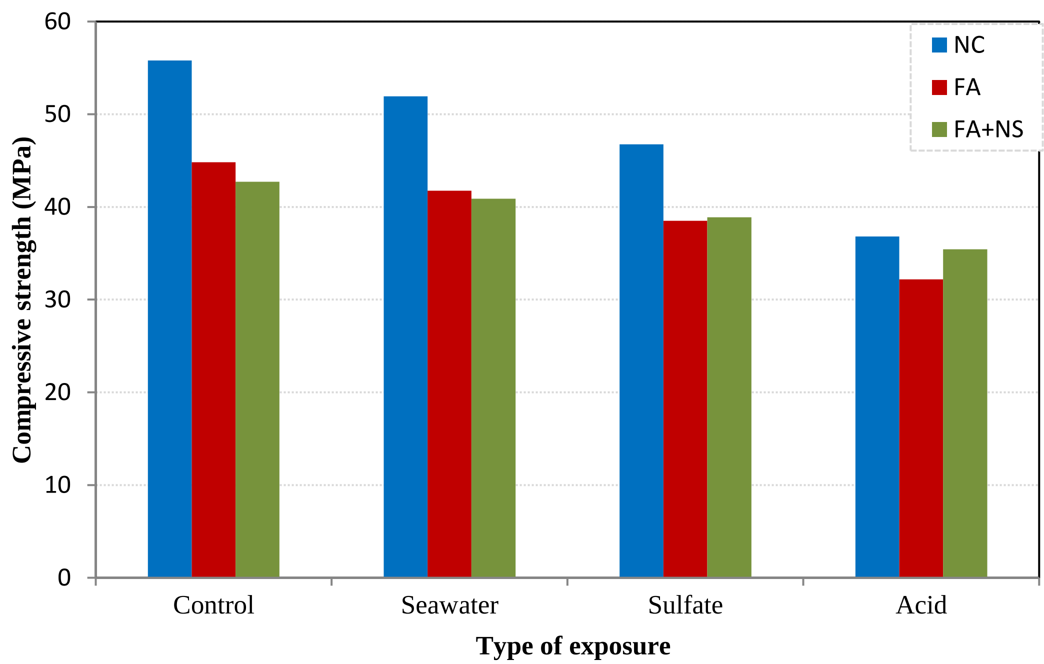


Figure 4.8 Compressive strength of GPC and NC specimens submerged in chemical attack

Table 4.2 Mechanical and fracture properties for GPC and NC 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 curve (N-mm)	Fracture Energy (N/m)	G_F Eq.(5) (N/m)	G_F Eq.(4) (N/m)	KIC (Mpa-mm$^{0.5}$)
Control	NC	55.8	5.22	3215	5.36	0.65	647.99	120	114.38	85.59	25.38
	FA	44.82	4.02	2246	3.74	0.456	541.32	98.89	103.42	73.42	17.73
	FA+NS	42.71	3.85	2132	3.55	0.51	472.10	88.44	101.15	70.98	16.83
Seawater	NC	51.49	4.86	2989	4.98	0.735	564.77	108	109.68	80.29	23.59
	FA	41.74	3.79	2180	3.63	0.516	486.91	91.41	100.08	69.85	17.2
	FA+NS	40.90	3.74	2097	3.49	0.586	431.05	83.71	99.15	68.86	16.55
Sulfate	NC	46.76	4.47	2736	4.56	0.845	479.53	95.7	99.46	69.19	21.60
	FA	38.5	3.52	1950	3.25	0.65	419.41	82.5	96.43	66.01	15.39
	FA+NS	38.71	3.53	1968	3.28	0.72	381.27	77.66	96.67	66.26	15.53
Acid	NC	36.82	3.61	2163	3.6	0.99	377.30	80.9	87.81	57.24	17.07
	FA	32.18	2.99	1637	2.72	0.708	371.55	74.844	86.59	56.04	12.92
	FA+NS	33.74	3.26	1785	2.97	0.766	344.82	71.61	90.75	60.18	14.09

4.4 Splitting Tensile Strength

The splitting tensile strength of cylinder specimens is indicated in figure 4.9 and listed in Table 4.2. The reduction in strength occurred in all specimens exposed to sulfuric acid, magnesium sulfate, and seawater respectively. The maximum decrease in splitting tensile strength detected in normal concrete (NC) was exposed to an acid solution with 30.72% compared to other mixes exposure specimens, while the lower reduction was achieved in FA+NS with 15.2%. The decrease in strength was attributed to the presence of harmful ions from exposure solution which led to forming gypsum and the breakage of alumina-silicate-bonds (-Al-Si-O) than losses in strength, mass and physical damage at the surface of specimens as shown in figure 4.1.

The addition of 3% NS minimizes the loss from 25.6% to 15.3% that attributed to the presence of NS in GPC mix led to increase the density of specimens and make the mixture less permeable which resulted in increasing the resistance to acid attack. Moreover, the existence of NS in mixture helped to increase the magnitude of soluble silica which produced a denser layer and decreased the extent of damage caused by sulfuric acid in the alumina silicate structure [62]. However, the incorporation of 3% NS led to reducing the splitting tensile strength due to the unreacted NS which was responsible for producing an extreme self-desiccation in the matrix which decreased the splitting tensile strength of specimens immersed in acid [59].

The specimens exposed to magnesium sulfate showed a reduction in splitting tensile strength for 14.2, 13.2 and 8.1% for NC, FA and FA+NS respectively. A good resistance to sulfate solution was achieved in FAGPC as compared to NC because GPC had a low Ca content, low water demand and dense microstructure matrix in FAGPC specimens. The FAGPC consist of NS exhibited superior resistance to sulfate solution as compared with NC and FAGPC without NS, because NS avoids the entrance of harmful ions into the deeper layers of microstructure gel by the pore refinement process [59].

As shown in figure 4.9 the resistance of GPC to chloride attack was excellent as compared with normal concrete (NC). The maximum reduction was achieved in NC specimens with 6.81% while the minimum loss was in FA+NS with 2.6% due to low calcium content in alkali activator FAGPC mixes which was considered as the main factor influenced in the durability of the GPC.

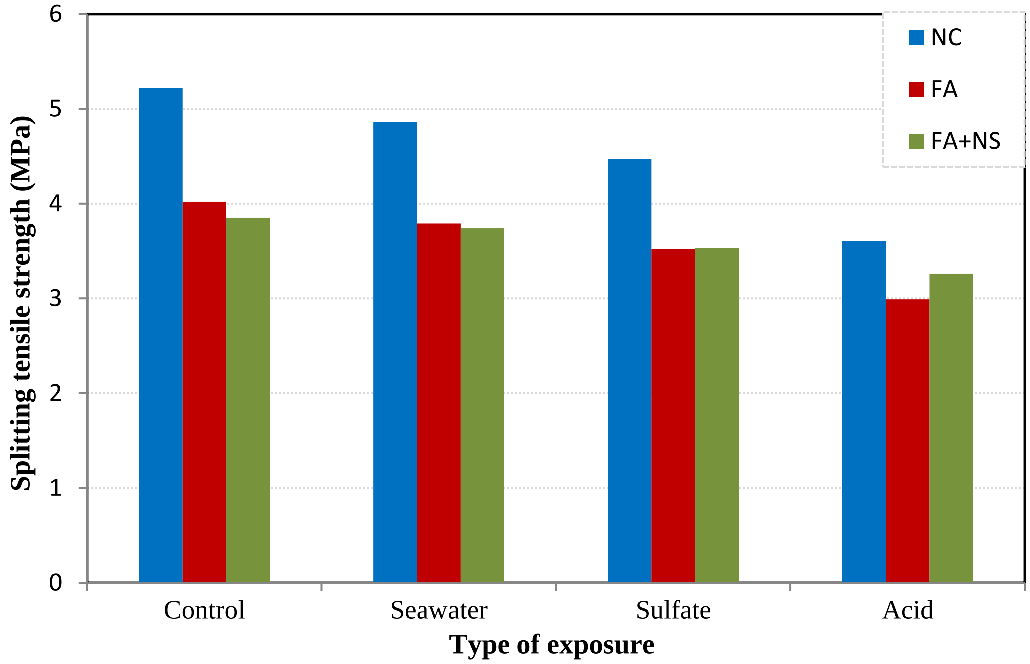
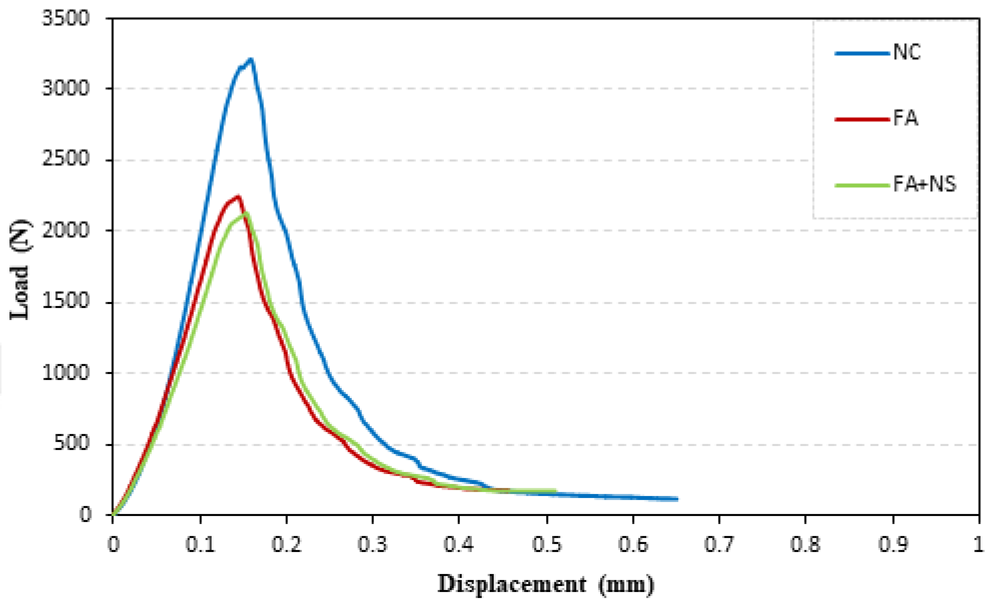


Figure 4.9 Splitting tensile strength of GPC and NC specimens submerged in chemical attack

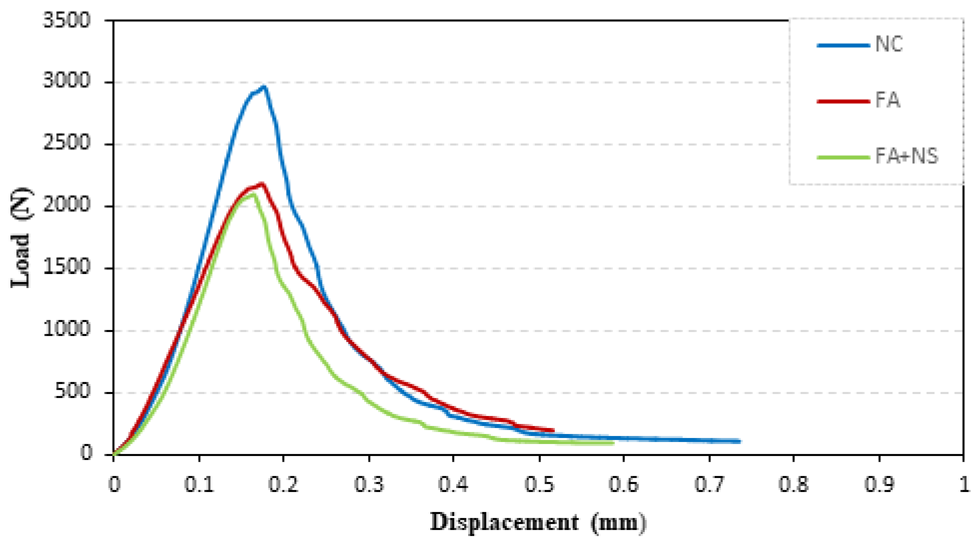
4.5 Fracture Properties

4.5.1 Load-Displacement

The load-displacement patterns of geopolymer and normal concrete exposed to sulfuric acid, sulfate magnesium, and seawater up to 30 days were tested at 56 days presented in figure 4.10a,b,c and d and the results were summarized in Table 4.2, twenty-four beams were tested at three-point load. As usual, all GPC and NC curves exhibited a linear upward slope till load at first cracking of specimens. After the load during the test reach the peak load, the cracks appeared which resulted in a descending curve after peak load. However, the slope of descending part of the curve after peak represented the property of the crack propagation inside the specimen until failure. It is observed from figure 4.10a, b, c, and d that the load-displacement of geopolymer specimens shows slightly smaller than NC specimens because of the brittleness of GPC more than normal concrete. The specimens of FA+NS exhibited more deflection than specimens of FA because the addition of NS led to decrease the pores and increase the density. The displacement values increased when exposed to sulfuric acid, magnesium sulfate, and seawater that was attributed to the low strength of specimens when compared with that specimens before exposure. The maximum increase was achieved in specimens that exposed to sulfuric acid attack while the minimum decrease indicated in specimens that immersed in seawater as presented in figure 4.10b.



(a)



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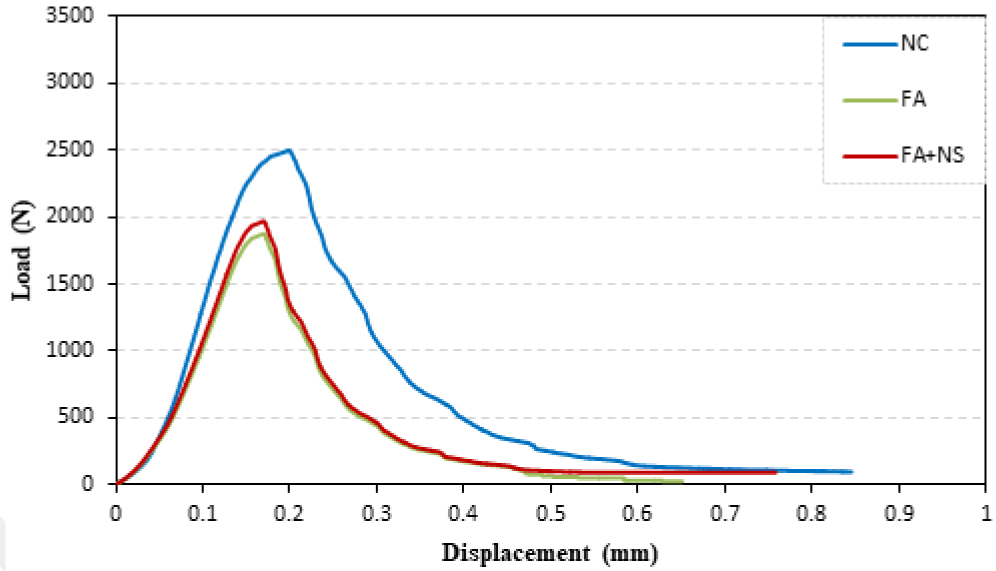
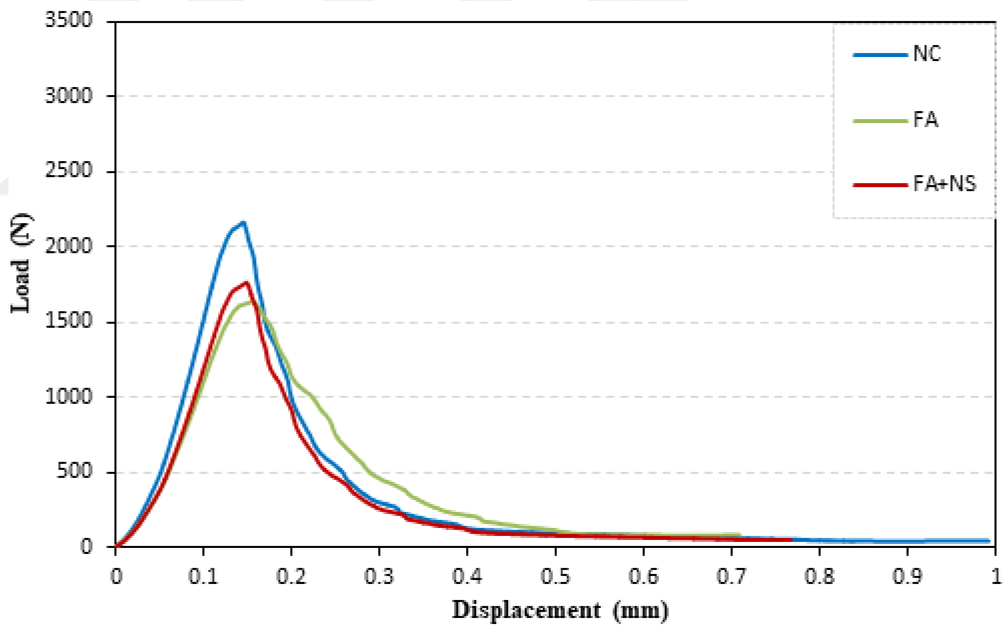


(c)



(d)

Figure 4.10 Typical load versus displacement curves of GPC and NC specimens (a) control, (b) seawater, (c) sulfate magnesium and (d) sulfuric acid

4.5.2 Fracture energy

The area under the load-displacement curve for each prismatic sample was estimated and utilized in Eq. (3.4) at section 3.6.3 to achieve the fracture energy (G_F) of each beam and the results are given in Table 4.2. The fracture energy (G_F) for all mixes are represented in figure 4.11. It was detected that the G_F of GPC and NC specimens which exposed to chemicals attack had decreased as compared with control specimens. The FAGPC with 3% NS showed less reduction in fracture energy as compared with FAGPC without NS and NC. Generally, the G_F of GPC inclined to increase with an increase in compressive strength as shown in figure 4.12. Sarker et al. [63] investigated that the fracture energy improved with the improve of compressive strength for heat cured FAGPC. The value of G_f is also increased with an increase in split tensile strength of concrete as seen in figure 4.13.

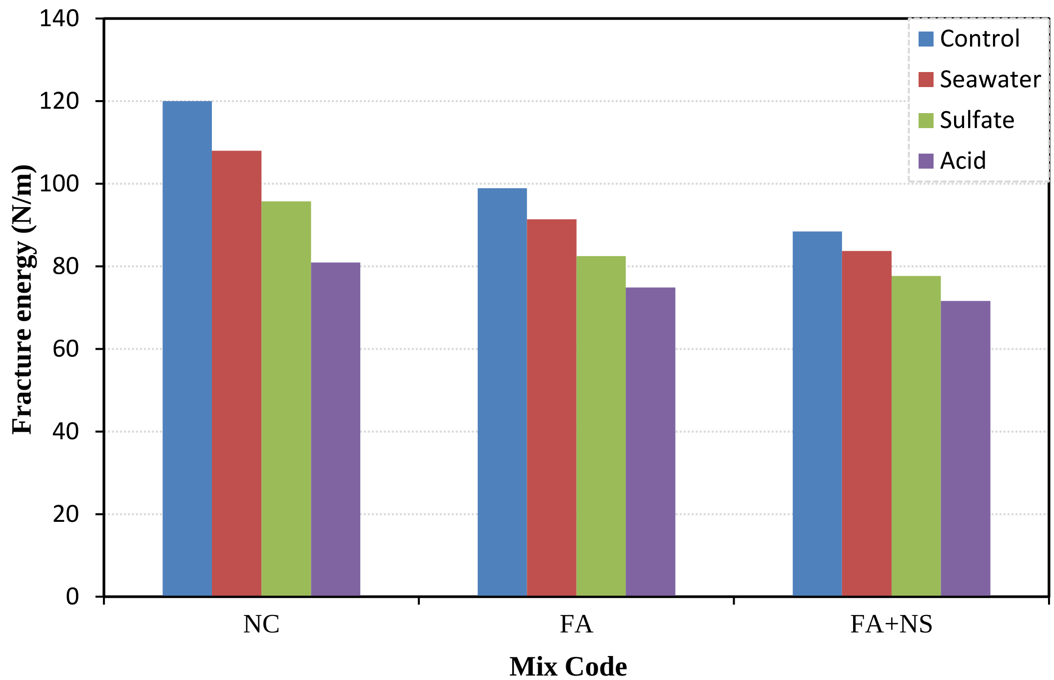


Figure 4.11 The fracture energy for geopolymer and normal concrete

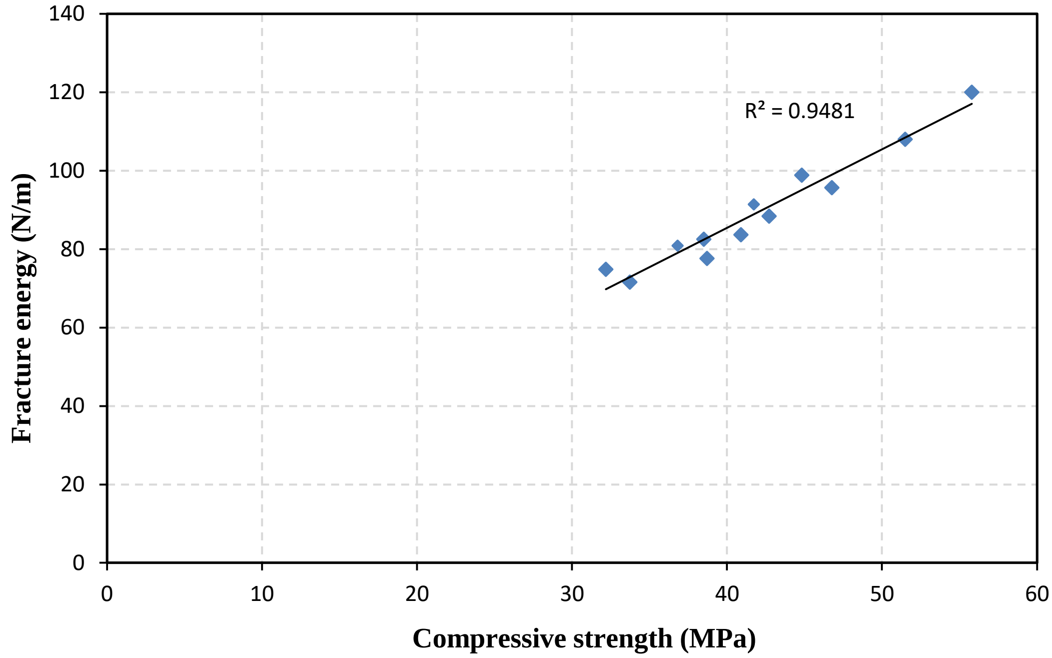


Figure 4.12 The relationship of fracture energy with compressive strength

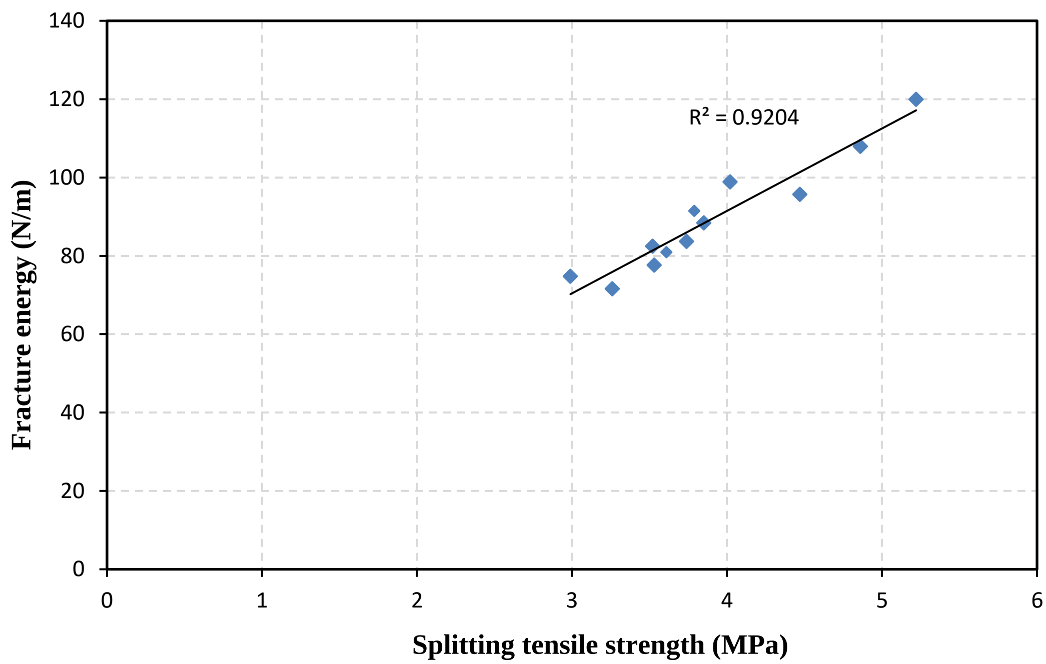


Figure 4.13 The relationship of fracture energy with splitting tensile strength

Figure 4.14 represents the comparison between the experimental fracture energy and the prediction equations offered by CEB-FIP Eq. (3.5) and Bazant and Becq-Giraduon Eq. (3.6) [49] which presented in section 3.6.3. Bazant and Becq-Giraduon offered his equation established on a statistical analysis of (238) test data on G_F achieved an experimental test of varying size specimens. GPC had a term of alkali activator solution to FA ratio instead of water to cement ratio term in normal concrete and this term was used as an equivalent term of (w/c) ratio in theoretical G_F calculation process. The experimental G_F amounts of both GPC and NC were found to be relatively close to the experimental values proposed by Bazant and Becq- Giraduon equation, while compared to the equation proposed by CEB-FIP, the experimental G_F amounts of both GPC and NC were significantly higher than theoretical values. These prediction equations were originally investigated from the values of NC concretes. When applied these equations to GPC the values were calculated lower than NC specimens due to the brittleness of GPC compared to NC.

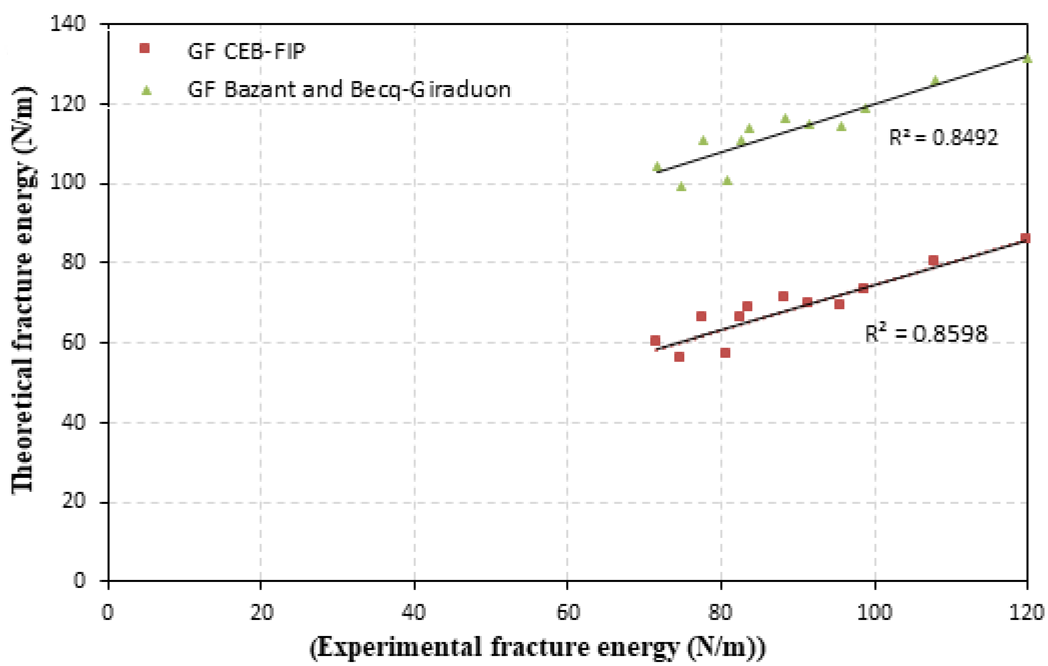


Figure 4.14 The relationship between theoretical and experimental fracture energy

4.5.3 Net Flexural Strength and Critical Stress Intensity

The net flexural strength and critical stress intensity factor (K_{IC}) of NC and GPC at 56 days are indicated in figure 4.15 and 4.16 respectively and summarized in Table 4.2. The net flexural strength was calculated using Eq. (3.7) which presented in section 3.6.3. As seen in Table 4.2 the net flexural strength of GPC and NC samples was increased with an increase of load applied on those specimens, however, the net flexural strength decreased with the increase of exposure time as shown in figure 4.15. The stress intensity factor was calculated using Eq. (3.8) presented in section 3.6.3 which refers to the amount of the stress concentration near the crack tip when the crack starts to propagate. K_{IC} decrease with the increase of exposure time as shown in figure 4.16. Figures 4.17 and 4.18 shows the relationship between K_{IC} with compressive strength and K_{IC} with split tensile strength respectively. Similar to G_f exhibits, the value of K_{IC} improves with an improvement in compressive and splitting tensile strength values. Furthermore, an excellent relationship detected between theoretical net flexural and practical values of both compressive and splitting tensile strength as seen in Figs. 4.19 and 4.20. The value of (R^2) obtained from the relation between experimental compressive strength and splitting tensile strength with the theoretical values of stress intensity factor (KIC) and net flexural obtained from different equations was the same. Therefore, it can be concluded that both equations are closed to each other, in addition to the experimental results.

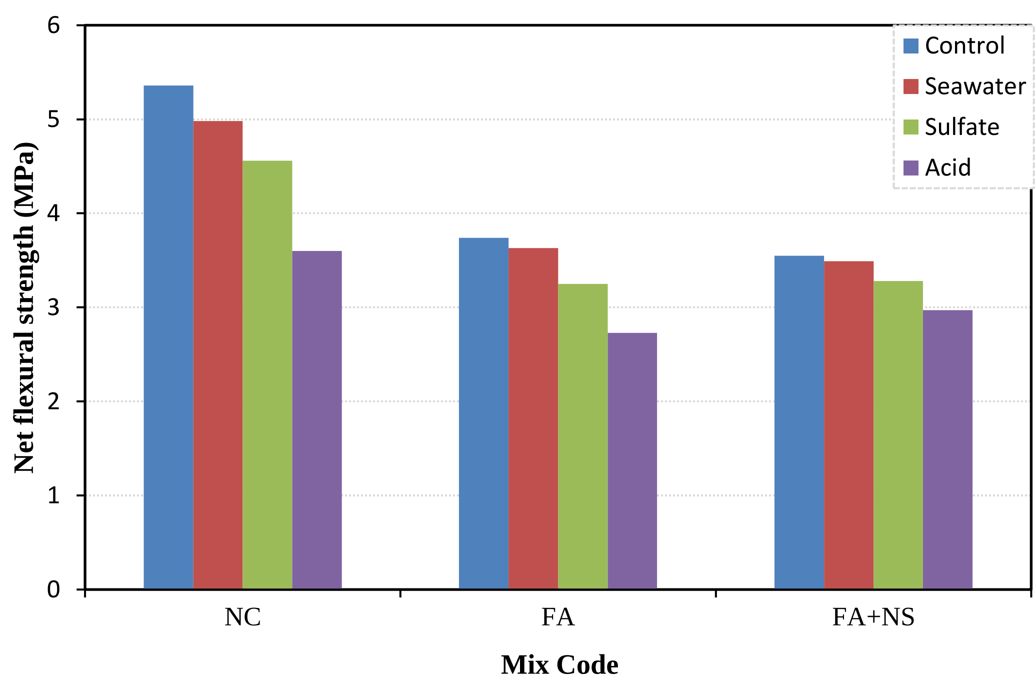


Figure 4.15 The net flexural strength of GPC and NC specimens according to the mixes

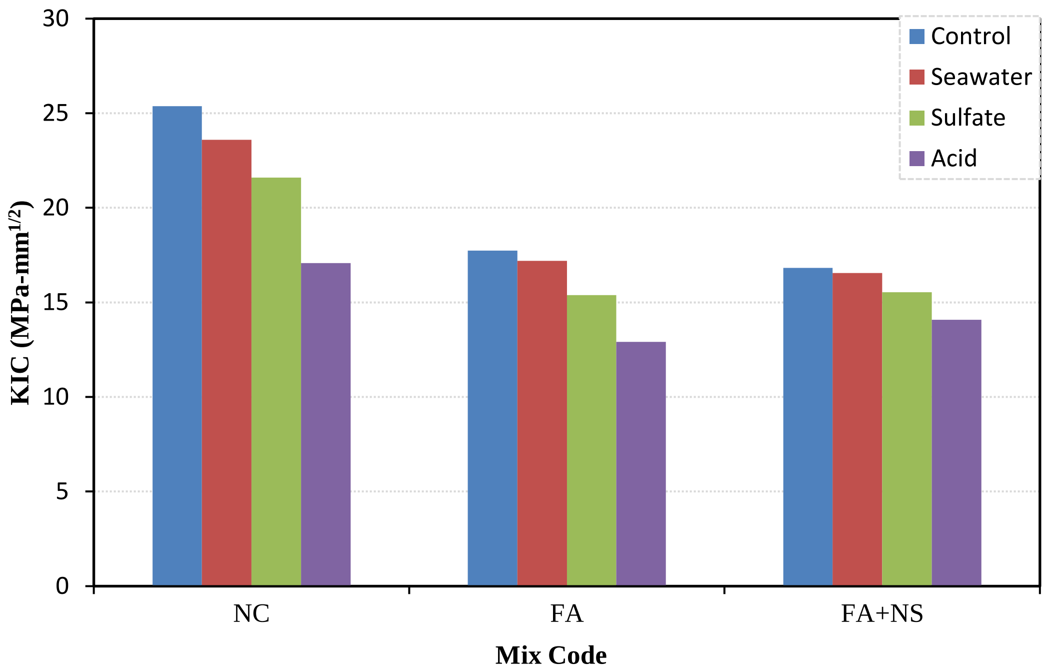


Figure 4.16 the stress intensity factor of GPC and NC specimens with mixes

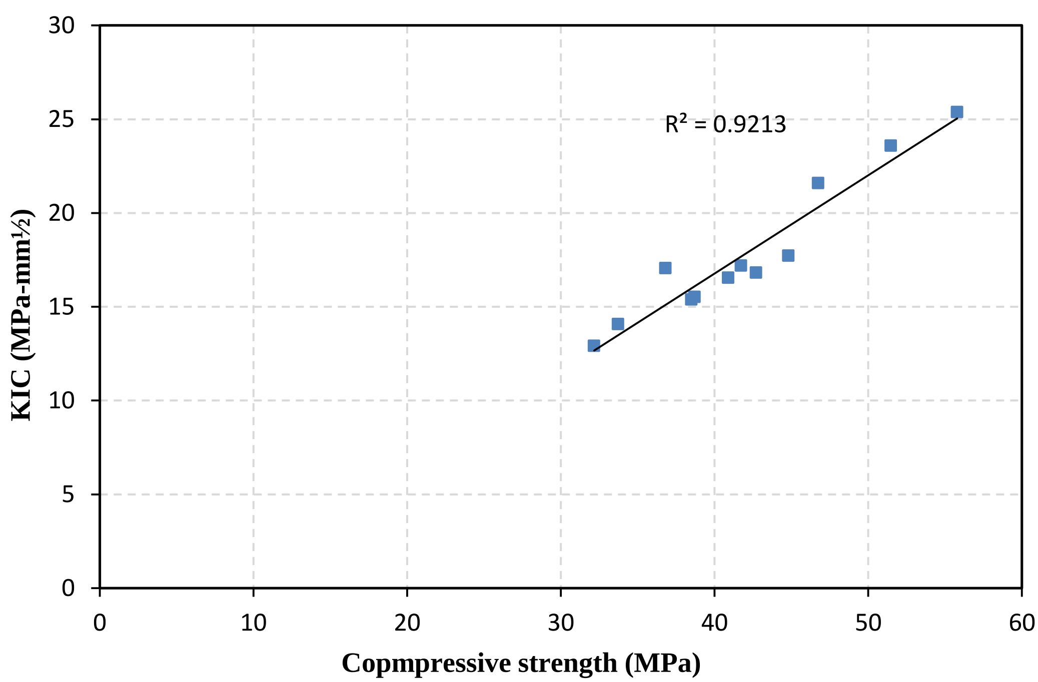


Figure 4.17 Relationship of critical stress intensity factor with compressive strength

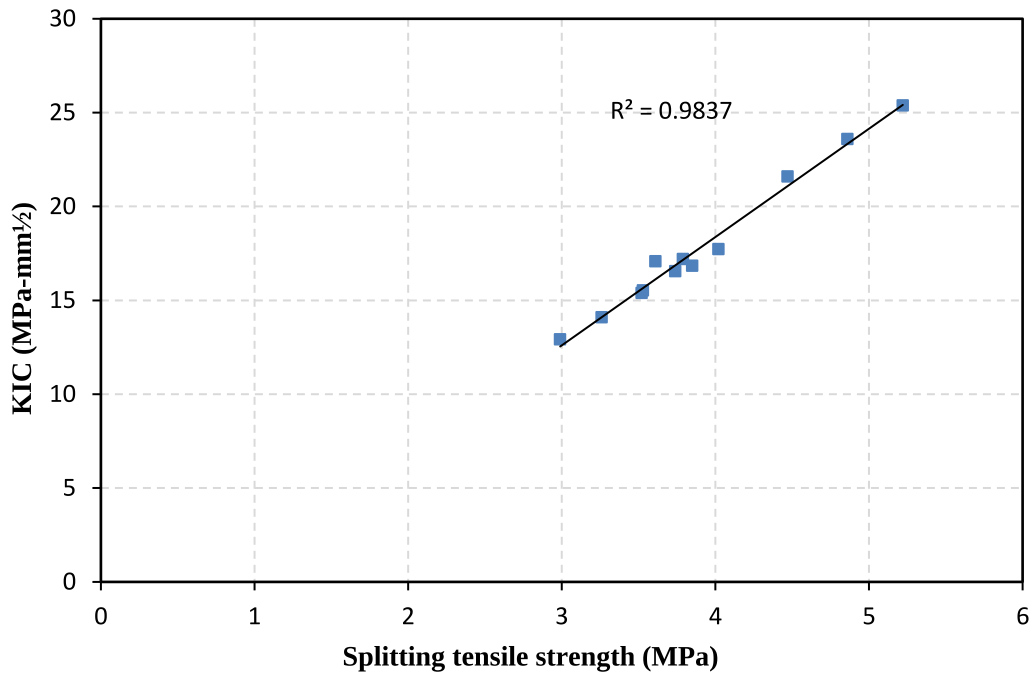


Figure 4.18 Relationship of critical stress intensity factor with splitting tensile strength

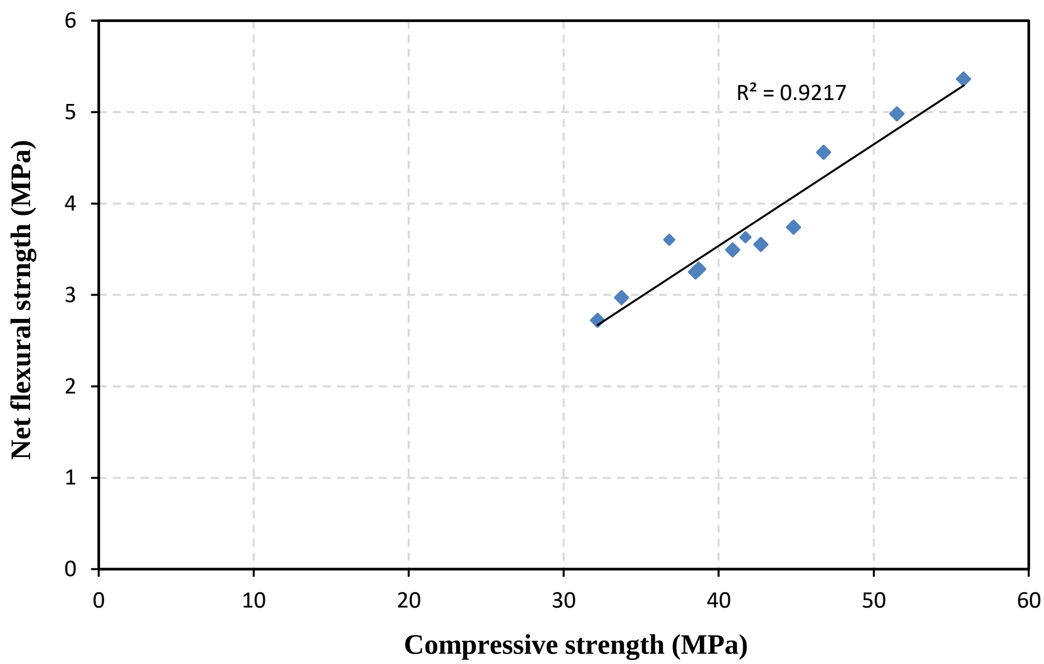


Figure 4.19 Relationship of net flexural strength with compressive strength

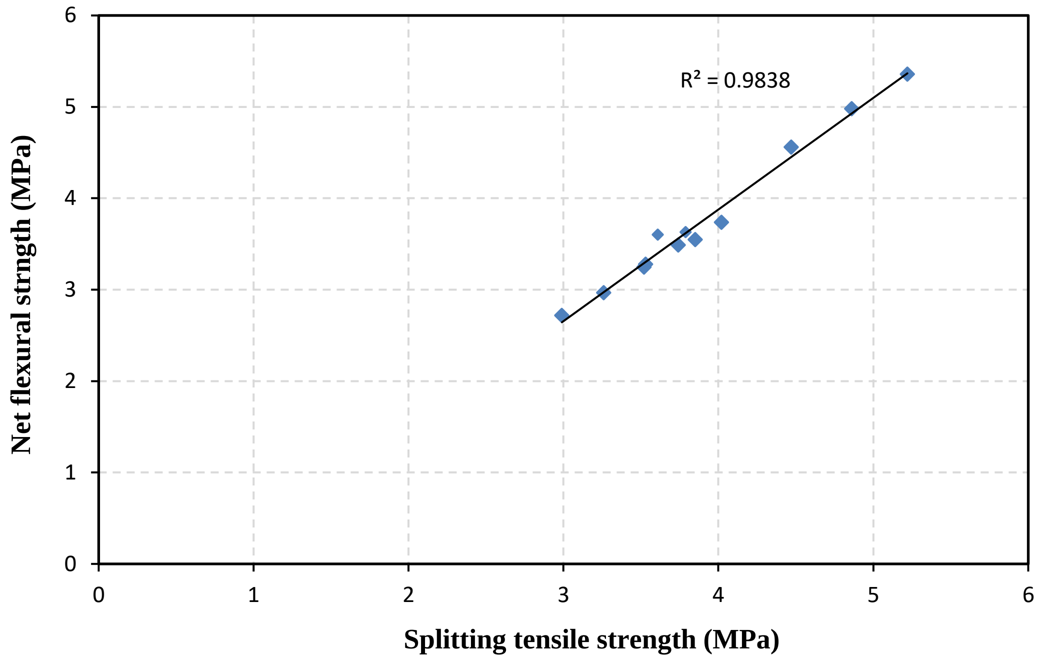


Figure 4.20 Relationship of net flexural strength with splitting tensile strength

CHAPTER 5

CONCLUSION

The mechanical and durability properties of fly ash based geopolymer concretes with and without Nano silica was investigated under chemical attacks (5% sulfuric acid, 5% magnesium sulfate and 3.5% sea water) and the results were compared with NC. In addition to this, the applicability of geopolymer concretes for structural use was also investigated. The following findings were summarized below;

- Visual inspection results of the specimens exposed to sulfuric acid solution indicated that GPC specimens showed moderate surface erosions at their surfaces, while NC specimens showed severe surface erosions due to higher CaO content. Fly ash based GPC samples maintained their initial conditions under magnesium sulfate and sea water attack, whereas the color of the NC concrete changed from gray to white. The favorable effect of Nano silica on durability performance of GPC can be clearly observed even in the short term period.
- The weight loss of NC specimens due to hydration reactions in ambient condition (control specimens) was more than 3-times than the weight loss of heat cured FAGPC specimens. Results also indicated that Nano silica addition (3% by binder weight) had no or negligible effect on weight change of the specimens.
- The weight enhancement was found for almost all specimens under chemical environment during first 15 days of chemical exposure due to solution absorption and expansion occurred by gypsum formation and highest weight gain was obtained under sulfuric acid solution.
- After one-month exposure to the chemical solution, the weights of the all fly ash based GPC specimens were above from the initial weights. The weight gain further continued for specimens under sea water and magnesium sulfate attack, however, the weight of the specimens decreased from the further 15 day exposure to sulfuric acid

attack. Sulfuric acid attack became hazardous in earlier exposure times. Nano silica including mixes showed less weight reduction under sulfuric acid and lower weight gain under sea water and magnesium sulfate attack due to the more dense structure and decreased porosity and permeability.

- Compressive strengths, splitting tensile strength, flexural strength, fracture energy and stress intensity factor results were decreased in the order of sulfuric acid > magnesium sulfate > sea water > control (ambient) environments, respectively for all concrete types. Sulfuric acid and sea water attacks were observed to be the most and least dangerous environments for all concrete types, respectively.
- Mechanical strength (compressive, splitting, flexural, i.e.) results indicated that NC specimens performed slightly better performance than fly ash based GPC specimens at same water to cement or alkaline solution to binder ratio. However, mechanical strength deterioration was observed to be highest for NC specimens under chemical attacks, especially under sulfuric acid environment due to high CaO content.
- The lowest mechanical strength reduction under chemical attack was observed in FA+NS specimens than FA specimens as materials included the lowest amount of calcium, which demonstrated that even low amount of calcium is adequate for the chemical reactions and therefore, CaO can be responsible for the deterioration of concrete under chemical attacks even in the short term chemical exposure. FA+NS type of GPC concrete was appropriate for the structures exposed to harsh environment.
- Nano silica addition into FA GPC specimens improved the residual mechanical strengths and its contribution was observed to be highest under severe chemical environment (sulfuric acid), which can be attributed to lower porosity and permeability and more dense structure. Nano silica especially increased the durability resistance of the fly ash based GPC specimens and its use in structures under chemical environment should be widespread and hence the life span of the structures can be improved further.

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