EFFECTS OF CRYSTALLIZED CAPILLARY IMPERMEABILITY ADMIXTURES ON MECHANICAL AND DURABILITY PROPERTIES OF CONCRETE AND MORTAR

KRİSTALİZE KAPİLER GEÇİRİMSİZLİK SAĞLAYAN BETON KATKILARININ BETON VE HARÇLARIN MEKANİK VE DURABİLİTE ÖZELLİKLERİNE ETKİLERİ

DİLARA ULUDAĞ

PROF. DR. MUSTAFA ŞAHMARAN

Supervisor

2022

ABSTRACT

EFFECTS OF CRYSTALLIZED CAPILLARY IMPERMEABILITY ADMIXTURES ON MECHANICAL AND DURABILITY PROPERTIES OF CONCRETE AND MORTAR

Dilara ULUDAĞ

Master of Science, Department of Civil Engineering

Supervisor: Prof. Dr. Mustafa ŞAHMARAN

September 2022, 82 pages

Concrete is the most used building material today. It has many advantages as well as disadvantages. One of the most important disadvantages is that concrete has a permeable structure. Good concrete must be durable. The condition of durability is that the concrete is impermeable.

The permeability of concrete is related to its porous structure. The small void makes the concrete impermeable. Harmful substances such as sulfate and chloride are transported with water to the concrete. These substances damage the concrete over time and shorten its service life of the concrete. Today, many studies are carried out to reduce the permeability of concrete. In these studies, the concrete has been studied to have the minimum permeability by using mineral and chemical additives. Thus, it is aimed to increase the service life by minimizing the permeability of the concrete.

In this thesis, the effects of concrete admixtures providing capillary impermeability on the mechanical and durability properties of concrete and mortars were investigated. The purpose of the experiment is to determine how effective the additives are against impermeability and strength. Experiment (I) started by preparing samples by adding different admixture ratios to CEM-I 42.5R Portland cement. (II) The flexural and compressive strengths of the samples, which were kept in water for 28 days by adding 1% and 2% liquid and powder additives, were measured. Scanning Electron Microscopy (SEM), X-Ray Diffraction Analysis (XRD), and Thermogravimetric Analysis (TGA) analyses were performed to determine the microstructural characterizations of the specimens after the resistance tests. (III) Analysis and test results showed that the addition of crystalline admixture increased the compressive strength but did not affect the flexural strength. However, the analysis results showed that both liquid admixtures and powder admixtures play an important role in durability as they support crystal formation, fill the voids, and increase impermeability.

Keywords: Crystalline admixtures, SEM, XRD, TGA, Durability, Permeability

ÖZET

KRİSTALİZE KAPİLER GEÇİRİMSİZLİK KATKILARININ BETON VE HARÇLARIN MEKANİK VE DURABİLİTE ÖZELLİKLERİNE ETKİLERİ

Dilara ULUDAĞ

Yüksek Lisans, İnşaat Mühendisliği Bölümü

Tez Danışmanı: Prof. Dr. Mustafa ŞAHMARAN

Eylül 2022, 82 sayfa

Beton günümüzde en çok kullanılan yapı malzemesidir. Birçok avantajının yanı sıra dezavantajları da vardır. Bu dezavantajların en önemlilerinden biri ise betonun geçirimli bir yapıya sahip olmasıdır. İyi bir beton durabil olmalıdır. Durabilitenin şartı ise betonun geçirimsiz olmasıdır.

Betonun geçirimliliği boşluklu yapısı ile ilgilidir. Boşluğun az olması betonun geçirimsiz olmasını sağlar. Suya maruz kalan betona su ile sülfat ve klorür gibi zarar verici maddeler taşınır. Bu maddeler zaman içerisinde betona zarar vererek betonun servis ömrünü kısaltır. Günümüzde betonun geçirgenliğini azaltmak için birçok çalışma yapılmaktadır. Bu çalışmalarda mineral ve kimyasal katkı maddeleri kullanılarak, betonun en az geçirimliliğe sahip olması için çalışılmıştır. Böylelikle betonun geçirimliliği en aza indirgenerek servis ömrünü arttırmak hedeflenmiştir.

Bu tez çalışmasında kristalize kapiler geçirimsizlik sağlayan beton katkılarının beton ve harçların mekanik ve durabilite özelliklerine etkileri araştırılmıştır. Deneyin amacı, katkıların geçirimsizliğe ve dayanımına karşı ne kadar etkili olduğunu saptamaktır.

Deney (I) CEM-I 42.5R portland çimentosuna değişik katkı oranlarının eklenmesi ile numune üreterek hazırlanarak başlanmıştır. (II) %1 ve %2 oranlarında sıvı ve toz katkılar eklenerek 28 gün suda bekletilen numunelerin eğilme ve basınç dayanımları ölçülmüştür. Numunelere dayanım testlerinden sonra laboratuvar ortamında mikroyapısal karakterizasyonlarının tespiti için Taramalı Elektron Mikroskobu (SEM), X-Işını Difraksiyon Analizi (XRD) ve Termogravimetrik Analiz (TGA) analizleri yapılmıştır. (III) Analiz ve test sonuçları kristalize katkı eklenmesinin basınç dayanımını arttırdığını fakat eğilme dayanımına etki etmediğini göstermiştir. Bununla birlikte analiz sonuçları sıvı katkının da toz katkının da kristal oluşumunu destekleyip boşlukları doldurduğunu ve geçirimsizliği arttırdığından ötürü durabilite üzerinde önemli bir rol oynadığını göstermiştir.

Anahtar Kelimeler: Kristalize katkı, SEM, XRD, TGA, Durabilite, Permeabilite

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to Prof. Dr. Mustafa ŞAHMARAN, who supervised my thesis and stood by me with his valuable knowledge and experience during the thesis.

I would like to express my sincere gratitude to Hüseyin ULUGÖL, who has supported me throughout the process of writing my thesis, to whom I always get answers when I need, and who lights my way.

I would like to express my gratitude to my precious teacher Ertuğrul ASİLOĞULLARI for their moral support throughout the thesis period.

Finally, I would like to extend my respects to my dear grandmother Süheyla ULUDAĞ and uncle Müjdat ULUDAĞ who gave me all the support during my graduate program.

Dilara ULUDAĞ

September 2022, Ankara

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SYMBOLS AND ABBREVIATIONS

Abbreviations

SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction Analysis
TGA	Thermogravimetric Analysis
PC	Portland Cement
ASR	Alkali-Silica Reaction
ACR	Alkali-Carbonate Reaction
ASV	Average Strength Value
Ref	Reference Specimen
LA-1	Specimen with 1% Liquid Admixture
LA-2	Specimen with 2% Liquid Admixture
PA-1	Specimen with 1% Powder Admixture
PA-2	Specimen with 2% Powder Admixture

1. INTRODUCTION

Cementitious composites, first used in the Ancient Roman period, have taken their place among the popular building materials in the construction industry since then and are still the most widely used building materials today. Concrete is a cement-based composite consisting of binder and filler. Concrete materials are the most used among cement composites. When global concrete production is considered, annual concrete production per capita is around 4.7 tons. Its low cost, good fire resistance, and high compressive strength make concrete unrivalled in the industry, with an annual consumption of 33 billion tons (Hou et al., 2014).

The porous nature of cementitious composites may be one of the main sources of degradation tendencies. Because of porous structures, aggressive substances can be carried by water and pass-through pores and microcracks, compromising the composite's microstructure and reducing its overall durability. There is growing interest in innovative and sustainable approaches to reduce cementitious materials' permeability naturally. Cement-based materials and chemical admixtures are widely used (Cheung et al., 2018; Zhan et al., 2019). These chemical admixtures include the permeability reducing admixtures (PRA) recommended by the American Concrete Institute (ACI) Committee 212 and used by the construction industries for decades to fulfil these purposes.

Liquid or powder waterproofing admixtures with different mechanisms are used to reduce the permeability of concrete mixtures. Some of these admixtures (permeability reducing admixtures) are added to the concrete when fresh and provide impermeability by filling the capillary spaces. The working principle of these additives is to provide impermeability by imparting water-repellent properties to the concrete (Rixom,1999).

The most important parameter needed in producing concrete with a high service life is the low void ratio of the concrete (Uyan et al., 2003). The void structure and ratio of the concrete are directly related to the permeability of the concrete. Due to the high permeability of concrete, harmful substances may enter the concrete. For example, in a sulfate attack, sulfate waters penetrate the concrete in the concrete cavities and cause some harmful chemical reactions (Akman, 1989 and Young ,1998).

Concrete admixtures are organic or inorganic-based materials added to the mixture in certain proportions before mixing in concrete production (Topçu et al., 2004). As it is known, concrete admixtures are divided into two, mineral and chemical admixtures. Concrete's resistance to sulfate, acid, carbonation, reinforcement corrosion, freeze-thaw, and alkali-silica reaction depends on its permeability to a significant extent (Mehta, 2006). Therefore, the permeability of concrete is the most important factor affecting the service life of the concrete structure.

The durability of the concrete needs to be void and impermeable, that is, its microstructure. Therefore, all the properties that affect the void and impermeable elements directly affect the durability. The first of these is the cracks that occur due to shrinkage in the concrete and pose an important problem for durability. In this thesis, the effects of chemical additives on the mechanical and durability properties of concrete and crosses were investigated. For this purpose, concrete samples were prepared by mixing powder and liquid chemical admixtures homogeneously into the dough prepared in two different ratios (1%, 2%). The prepared samples were exposed to the standard curing effect in the curing pool and subjected to various tests at the end of 28 days and compared with the reference concrete.

2. LITERATURE REVIEW

2.1. Concrete as a Building Material

2.1.1. Cement

Portland cement: it is a hydraulic binder obtained by fine grinding the clinker obtained by mixing the raw materials consisting of lime, alumina, iron oxide and silica in certain proportions and firing in a blast furnace (Neville, 1996). Primitive materials of Portland cement are limestone (limestone, marl) and clay. These materials are finely ground and fired in rotary kilns at 1350 ^{0}C-1400 ^{0}C temperatures. With the decomposition of limestone, CaO is formed, with the decomposition of clay, silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) are formed. These components combine at high temperature to form silicates and aluminates (Mills et al., 1955).

The most important of these are:

- Dicalcium silicate (C_2S) $2CaO.SiO_2$
- Tricalcium silicate (C_3S) $3CaO.SiO_2$
- Tricalcium aluminate (C_3A) $3CaO.Al_2O_3$
- Tetracalcium alumino-ferrite (C_4AF) $4CaO.Al_2O_3.Fe_2O_3$

These silicates and aluminates are found in Portland cement at approximately 16.6% C_2S, C_3S 54.1%, C_3A 10.8%, and C_4AF 9.1% ratios, respectively (Neville, 1996).

2.1.2. Aggregate

It is the name given to materials such as gravel, sand, and crushed stone used in concrete production. Its volume in concrete is between 60% and 80%. Aggregates are classified as fine and coarse according to their particle size. The properties sought in aggregates are to be hard, durable, and void-free, and resistant to pressure and abrasion. It should not contain substances that can damage dust, soil, and concrete. It should not be flat and long; it should be in cubic form. It should not enter harmful reactions with cement (Usta, 2012).

2.1.3. Water/Cement Ratio

It is expressed as the mass ratio of water to cement in the concrete mix. The lower the w/c ratio in the concrete, the greater the strength of the concrete (Abrams, D., 1918). W/c is directly related to the space between cement particles. The smaller the void in the cement, the faster the hydrates will fill the voids, the stronger the hydrates will be, the more durable the concrete will be. The w/c ratio required for the cement to complete its hydration varies between 0.22 and 0.25 (Ramachandran, V., 1995).

2.1.4. Water

Structures exposed to the effects of atmosphere or groundwater are damaged over time. Protecting the structure from water means prolonging the service life of that structure. In the porous materials used in the production of structures with the effect of water, moisture, bleeding, efflorescence, melting, cracking, etc., events occur. Water also causes corrosion on metals; damage occurs in the structure. That is why impermeability is one of the basic properties sought in high-performance concrete (Aköz, 2005).

As a result of the reactions of the main components of calcium silicate in the cement with water, besides the C-S-H gels that give the cement paste binding property, calcium hydroxide ($Ca(OH)_2$) crystals that are not resistant to water are also formed (Neville, 1990; Akman, 1987; Baradan et al., 2002). Water leaking into the concrete by any means from the outside causes $Ca(OH)_2$ to dissolve (Aköz, 2005). With the infiltration of water, the salts in the concrete turn into a molten state, and the water containing these salts and dissolved $Ca(OH)_2$ moves towards the surface of the concrete through the capillary spaces. As a result of the evaporation of the water on the concrete surface, $Ca(OH)_2$ and salts in the water form a thin layer of precipitate on the surface. $Ca(OH)_2$ combines with carbon dioxide in the air and turns into calcium carbonate ($CaCO_3$); this event is called efflorescence. Since most of the precipitate formed is $CaCO_3$, the accumulation layer is seen in white colour. In this chemical event, besides $CaCO_3$, very small amounts of sodium sulfate, sodium carbonate, sodium bicarbonate, sodium silicate, potassium sulfate, calcium sulfate, and magnesium sulfate may also be present. The efflorescence event, which develops rapidly in the first months after the concrete is placed, decreases over time, and almost ends after three to four years. However, as the efflorescence event continues in permeable concrete, which is exposed to the effect of water, the concrete becomes more porous, and in this case, the strength of the concrete, especially its durability, is adversely affected. In summary, it is easier for harmful waters to leak into the hollow concrete and cause damage to the concrete (Erdoğan, 2003; Akman, 1992).

2.2. Durability of Concrete

The durability of concrete is closely related to the amount of voids and their structure. As the amount of space and the connections of the spaces with each other increase, the penetration and transportation of harmful materials and water into the concrete becomes easier. As a result, the concrete is more easily damaged. In order to obtain structures with longer service life by increasing the durability of concrete, first, the amount of voids in the concrete must be reduced. The determining factor in many durability problems is the penetration of water, harmful substances, and gases carried in the water into the concrete. The production quality of impermeable concrete is considered the first and most important measure.

The fact that the concrete is void and impermeable is beneficial in terms of durability. In other words, durability and permeability are two closely related events. The more void-free the concrete, the lower its permeability; This ensures that the steel in the concrete provides a healthy service throughout the service period without being exposed to chemical effects in reinforced concrete structures.

2.2.1. Durability Issues in Concrete

Owners demand a long service life for the structure, as it is challenging and expensive to construct. It is vital for national economies that the structures be thick (Memon et al., 2002). This situation clearly shows the importance of thick buildings to ensure sustainable development in the sector (Baradan et al., 2002; Arıoğlu, 1989).

Apart from mechanical effects, the main factor controlling deterioration processes in concrete is the presence of water or moisture in the environment; because water carries harmful substances into the concrete and accelerates the formation of chemical reactions. The stone of water depends on the type of voids in the concrete, their diameter, and the presence of micro or macro cracks. For this reason, it is necessary to control the gaps in the concrete from the outside and prevent the formation of cracks to ensure a thick layer. The temperature, humidity, and the transport mechanism of chemical substances in the concrete or its immediate surroundings are important factors affecting the permanence of the concrete (Baradan et al., 2002). Some important chemical and physical events that adversely affect the durability of concrete; dissolution of calcium hydroxide in the concrete and efflorescence on the concrete surface, sulfate effect, acid effect, carbonation, alkali-aggregate reaction, corrosion of the reinforcement in the concrete, freeze-thaw effect, corrosion of the concrete surface (Erdoğan, 2003). These events, which adversely affect the durability of concrete, are explained below.

2.2.1.1. Corrosion

Corrosion is a slowly developing physical and mechanical event. The forces that come to the concrete surface in the form of friction or impact create an effect like rasping the concrete surface and causing the surface to collapse. To measure the wear of the concrete surface, the depth of the loss on the concrete surface showing the wear is measured, or the weight loss-based tests are applied (Erdoğan, 2003). The compressive strength of concrete is the main factor determining its resistance to compression. It is recommended to keep the curing period twice as long as normal to obtain a good abrasion resistance in concrete (Felekoğlu et al., 2003).

2.2.1.2. Freeze-Thaw Effect

With the effect of salts that can be dissolved in water in concrete cavities, it freezes at temperatures slightly below ^{0}C, and the volume of water that turns into ice increases by about 9%. When the capillary spaces are completely or more than 91% filled with water, the volume increase that occurs with the onset of freezing and the transformation of some of the water into ice creates hydraulic pressure on the water that has not yet frozen in the spaces, the water is pushed out of the spaces, the forced water around the spaces is cemented. It creates stresses large enough to cause the paste to crack (Şahin et al., 2003; Felekoğlu et al., 2003). In the study by Johnson (2002), it is stated that the use of blast furnace slag up to 70% in concrete production provides excellent freeze-thaw resistance.

Since the crystalline admixtures prevent water ingress into the concrete structure, they also reduce the freeze-thaw damage. At the same time, since the $Ca(OH)_2$ output from the concrete decreases, it reduces the efflorescence in the surface appearance (Baradan 2015).

2.2.1.3. Alkali-Aggregate Reaction

Another reaction that creates an expanding product in concrete is the alkali-aggregate reaction. The alkali-silicate-hydrated gel formed as a result of the alkali-aggregate reaction (AAR) absorbs water from the cement paste, creates micro-cracks in the paste, and increases the water absorption of the concrete. Gel formation, which increases with water absorption, enlarges the cracks, especially the aggregate-cement interface damage, leading to the concrete's fragmentation. The fact that the alkali content of the cement exceeds 0.6% of the Na_2O value calculated with the equation shown in 2.2.1.3 and the presence of active silica in the aggregate is insufficient for the alkali-aggregate reaction to start because the reaction only takes place. The total alkalis and the alkali ions can dissolve in the intermediate place and have different effects from each other (Baradan et al., 2002; Akman, 2002).

$(Na_2O)_{eq}= Na_2O+0.658K_2O$ (2.2.1.3.)

Two types of reactions are mentioned: alkali-silica reaction (ASR) in siliceous aggregates and alkali carbonate reaction (ACR) in calcitic dolomites and dolomitic limestones (Neville, 1990). The characteristic composition of the gel formed in the alkali-silica reaction has not been determined yet, but it is thought that the gel contains silicon, sodium, potassium, calcium, and magnesium compounds (Baradan et al., 2002). In some sources, this product was similar to zeolite in XRD analysis, and its chemical composition was $(NaAlSiO_4)_{12.27}$ H_2O or $Ca(Al\text{-}SiO_4)_{12.27}$ H_2O, gel and crystal products occurred at the aggregate mortar interface and air spaces. It has been stated (Marfil and Maiza, 2001). Studies on the subject have shown that pozzolan materials with low alkali content are more effective in reducing alkalinity in the cavity solution and reducing the expansion resulting from ASR compared to those with high alkaline content (Duchesne and Berube, 2001) in cases where it is necessary to use cement with a high alkaline oxide value and aggregates containing active silica and causing the alkali-silica reaction, it is necessary to add to the binding material. It is stated that the reaction rate can be reduced by adding a pozzolan material such as slag (Baradan et al., 2002; Postacıoğlu, 1987; Shehata and Thomas, 2002).

2.2.1.4. Acid Effect on Concrete

The corrosive effect of acids in the water that affects the structure and seeps into the hardened concrete is called an acid attack (Uğurlu, 2003). As a result of the dissolution of $Ca(OH)_2$ and C-S-H gels in the hardened concrete exposed to acid attack, a soft, thin layer like mud forms on the concrete surface, the concrete becomes more porous, and its strength and durability decrease (Erdoğan, 2003; Neville, 1990; Akman, 1987). Carbonic acid (H_2CO_3) in the air, which is one of the acids affecting the structure, is formed by the dissolution of CO_2 in water. Streams and snow waters in the countryside may contain such weak acids. In addition, acids released due to production or used in production in different branches of industry affect industrial structures and discharge units. These acids are, for example, hydrochloric acid (HCl) in the chemical industry, nitric acid (HNO_3) and phosphoric acid (H_3PO_4) in the fertilizer industry, acetic acid (CH_3CO_2H) in the fermentation process, formic acid ($H.CO_2H$) in the food and dye industry, lactic acid in the dairy industry. ($C_2H_4(OH).CO_2H$), tannic acid ($C_{76}H_{52}O_{46}$) in the leather industry, and tartaric acid $[CH(OH).CO_2H]_2$ in the winemaking industry (Erdoğan, 2003).

2.2.1.5. Sulfate Attack

In a normal concrete, ettringite, and gypsum are formed by the reaction of calcium hydroxide formed as a result of cement hydration and sulfate ions in the environment. Since the volume of these materials is large, they cause the concrete to expand. The pH value of a normal concrete should be around 13. The hydroxides formed in cement hydration react with sulfate ions and reduce the pH level of the environment, which causes serious damage to the concrete. Sulfate ions also disrupt the structure of C-S-H gel, which is formed as a result of cement hydration and gives concrete durability. As a result of this, the compressive strength of concrete decreases (Uyan, 2003).

C_3A and C_4AF, which are the main components of cement, play an important role in the resistance of cement, therefore concrete, against sulfate. High amounts of C_3A pave the way for monosulfoaluminates that will form over time, and they form ettringite, which causes expansion and spillage in concrete in advanced ages. However, keeping the amount of C_3A low alone is not enough for the concrete to be resistant to the effect of sulfate. The permeability of concrete is one of the most important factors in its resistance to the effect of sulfate. Sulfate, which meets with the concrete in groundwater, soil, or other factors, will penetrate the concrete in concretes with high permeability and will increase the harmful effects and strength losses of sulfate to higher levels (Erdoğan and Karakaş, 2003). Durability needs to produce as much impermeable concrete as possible to increase the resistance of concrete against the effect of sulfate (Uygunoğlu et al., 2006).

Another important effect of the sulfate effect is reinforcement corrosion in reinforced concrete structures. If the concrete falls below the normal pH level, the layer that protects the reinforcement in reinforced concrete structures also decreases, and reinforcement corrosion begins with the presence of water and oxygen in the environment. This corrosion causes expansion and cracks the concrete rust. Thus, the equipment is exposed to all external dangers (Ilıca et al., 2008).

2.2.1.6. Carbonation

Carbonation is the neutralization of the concrete as a result of the reaction between the alkali components of the cement paste and the carbon dioxide (CO_2) gas in the atmosphere (ACI 222R, 2001). This event, which reduces the pH of the concrete, which is at the value of 12-13, and causes the reinforcement to rust, is accepted as one of the important factors determining the service life of reinforced concrete elements (Baradan et al., 2002).

The alkalinity of concrete is largely provided by the dissolved calcium hydroxide $Ca(OH)_2$ in the pore water resulting from the hydration of the cement (Philipose et al., 1992; Neville and Brooks, 2001). In the carbonation event, the air's carbon dioxide dissolves in the pore water in the non-carbonated region, turning it into bicarbonate.

Another substance that dissolves in the void water is $Ca(OH)_2$, the dissociated $Ca(OH)_2$ reacts with carbonic acid (H_2CO_3) and turns into stable $CaCO_3$ and water (Pereira, 2003). The pH value of the environment, which is 12.6 before carbonation, decreases to 8.3 after carbonation.

2.2.2. Permeability of Concrete

The permeability of concrete is a function of the microcracks at the interface between the voids in the concrete and the cement paste-aggregate. It is important in terms of durability that the concrete is void and impermeable. Durability and permeability in concrete are two closely related events. Liquid permeability of concrete consists of pressurized water permeability, capillary water absorption and vapor permeability. If the necessary measures are not taken in terms of impermeability, these three permeability values in concrete reach high values in the same direction and negatively, and this leads to problems in terms of durability.

Some harmful physical and chemical events caused by the water leaking into the concrete and the foreign substances in these waters in the concrete are as follows:

- Calcium hydroxide, which is in the structure of the hardened cement paste, dissolves under the influence of the water leaking from the outside and rises to the surface. Thus, the amount of space increases. With the evaporation of the calcium hydroxide and salt water that comes to the surface, calcium carbonate and salt deposits are white spots on the concrete surface.
- Sulphates and acids in the water leaking into the concrete lead to the formation of products that create expansion in the concrete.
- Water, oxygen, and chlorine leaking into the concrete environment cause corrosion of the iron reinforcements in the concrete. As a result of corrosion, the cross-sections of iron reinforcements become smaller. In addition, corrosion products on the reinforcements cause an expansion in the concrete.
- In concretes whose capillary spaces are filled with water, large expansions occur as a result of freezing of the water in the voids.

2.2.3. Admixtures

Mineral and chemical admixtures are used to reduce the permeability of concrete. Since mineral admixtures are thinner and have a pozzolanic reaction, when used as fillers or instead of cement in concrete, they improve the permeability properties of concrete by reducing capillary voids and improving the aggregate-dough interface (Gruber et al., 2001; Asbridge et al., 2001). Today, with the development of concrete technology, chemical admixtures that provide water impermeability are produced in liquid or powder form with different mechanisms apart from mineral admixtures. Some of these admixtures (permeability reducing admixtures) are added to the concrete when it is fresh and provide impermeability by blocking the capillary spaces. The other part (anti-humidity admixtures) can be applied to the surface of the concrete as well as incorporated into its structure. These admixtures impart water-repellent properties to the concrete and provide impermeability (Roger Rixom, 1999).

2.2.3.1. Mineral Admixtures

According to ASTM C 615, siliceous and aluminous substances that have little or no self-binding properties but react with lime and gain binding properties under appropriate conditions, are called pozzolans. With the use of pozzolans in concrete, there is a decrease in the void structure and impermeability of the concrete. This improves the durability properties of concrete. As it is known, during the hydration of the C_2S and C_3S components of the cement, besides the calcium silicate hydrates (C-S-H), the main hydration product, $Ca(OH)_2$, which is the weakest part of the concrete, is also released. Pozzolans react with this weak part, gaining their binding property and providing the opportunity to obtain more dense and durable concrete. Pozzolans such as fly ash, silica fume, and blast furnace slag are used to fill the aggregate-cement interface, which is one of the important parameters for impermeability and the voids in the cement paste (ASTM C 618, 1991).

2.2.3.1.1. Silica Fume

Silica fume is obtained from flue gases formed as a result of reduction reactions in electric furnaces during the production of metal silicon and silicon alloys. It contains 90-95% amorphous silicon dioxide. Silica fume reduces aggregate cement paste interface defects. Therefore, it improves the strength and durability of concrete. For hardened concrete, it reduces water permeability, alkali silica reaction, and permeability against harmful chemicals such as chloride and sulfate leaking into the concrete from the environment (Saran, 2007). According to the studies, researchers attribute the positive effect of silica fume on strength and durability to the strengthening of the aggregate-cement paste interface. Experiments with mercury porosimetry showed that silica fume created more small pores by reducing coarse pores in hardened cement paste and mortars, and these new pores were distributed more homogeneously. However, this situation did not change the total porosity in the internal structure. The homogeneous structure is associated with the slower and controlled water evaporation in the small pores. For this reason, water absorption of silica fume-added concretes also decreases compared to non-admixed concretes (Yeğinobalı, 2009).

2.2.3.1.2. Fly Ash

Fly ash, a fine waste material of power generation facilities and contains large amounts of solid waste in these facilities, is obtained after the burning of the coal. This mineral generally has a pozzolanic feature and contributes to the development of concrete strength (Abbas et al., 2017; Munir et al., 2016; Oner et al., 2005). The addition of fly ash to concrete not only reduces the amount of cement and fine aggregates but also reduces water consumption. While fly ash improves the workability, impermeability, and modification of concrete, it reduces the heat of hydration and thermal expansion (Dinakar et al., 2008; Ukwattage et al., 2013; Wang et al., 2017).

Because of these important benefits, this mineral has been widely used in many research and projects. Fly ash with its finer particles can be used instead of silica fume as a complementary cement material in the production of high strength concrete. A lower average pore diameter can be achieved when blended cement paste containing classified fine fly ash particles is compared to Portland cement paste and cement paste containing ordinary fly ash (Chindaprasirt et al., 2005). Choi et al. (2012), Chindaprasirt et al. (2005), and many other researchers (Givi et al., 2008) reported higher compressive strength in blended cement pastes, mortars, and concretes containing finer fly ash particles. In addition, according to the results stated, concrete containing ultrafine fly ash can achieve longer durability due to the increased surface area and smaller particle size of the ultrafine fly ash (Shaikh and Supit, 2015). Finally, significant reductions in autogenous shrinkage and a higher shrinkage crack resistance were observed in concrete containing ultrafine fly ash compared to concrete containing silica fume (Hossain et al., 2007).

2.2.3.1.3. Blast Furnace Slag

Iron oxide (mineral ore, pellets, sinter), fluidity regulators (limestone, dolomite), and fuel (coke) are used in blast furnaces in iron and steel production facilities. Blast furnace slag is the residue floating on the molten iron collected in the lower part of the furnace obtained from the post-treatment furnace using this furnace.

The strength of slag added concrete depends on the slag's fineness, the slag/cement ratio in the mixture, and the activity index of the slag. When used in finely ground concrete, it is seen that workability increases, absorbs less water, and reduces bleeding (Mehta, 2006).

The use of slag is used in the concrete industry to increase the workability of the concrete, extend the setting time, reduce bleeding and permeability, and reduce the heat of hydration. At the same time, the use of slag as a binder with cement provides durability against acid and sulfate attacks in improving the mechanical properties of concrete (Erdoğan, 2003; Eren and Yılmaz, 2004).

2.2.3.1.4. Metakaolin

Metakaolin consumes calcium hydroxide very quickly, and many studies in the 1980s showed that adding it to the cement matrix in fiber-reinforced composites protects the glass fibers. In the 1990s, the use of metakaolin in concrete became widespread, and it was noted that it was effective in improving a number of concrete properties such as improving sulfate resistance, reducing ASR expansion, eliminating efflorescence. The use of metakaolin as a pozzolanic additive in mortar and concrete has become an important research topic in recent years. Most of these studies have focused on the removal of portlandite (CH), a hydration product that adversely affects durability. Removal of portlandite has a significant effect on sulfate strength and ASR, as well as an increase in strength as a result of the reactions of portlandite and metakaolin in the cement phase.

Jamal et al. (2003) investigated the effect of the use of metakaolin on the mechanical and durability properties of concrete samples. For this purpose, concrete samples containing different proportions of metakaolin were produced. According to the test results, it was stated that the use of metakaolin positively affected the durability and mechanical properties of concrete.

2.2.3.1.5. Glass Powder

The glass powder is another important mineral additive used instead of cement to increase the strength and durability of concrete and reduce environmental problems. Glass has an amorphous structure and high silica (SiO_2) content (Vijayakumar et al., 2013). When the particle size of the glass powder is 0.075 mm or less than 0.038 mm, the glass powder exhibits pozzolanic properties and adds to the concrete or mortar to achieve the desired strength and durability (Soliman and Tagnit-Hamou, 2016).

2.2.3.1.6. Other Mineral Admixtures

Apart from silica fume, fly ash, blast furnace slag, metakaolin, and glass powder, there are many other mineral additives such as rice husk ash, marble powder, natural zeolite, and limestone flour. However, these minerals are not as widely used as others. Therefore, studies on these minerals are limited. Apart from all these mineral additives, there is another special mineral, which is calcium meta silicate ($CaSiO_3$), which attracts attention with its acicular particle structure, which occurs naturally and can also be produced synthetically. This mineral is wollastonite. Wollastonite, which is theoretically composed of up to 50% CaO and up to 55% SiO_2, is a special mineral that also contains elements such as aluminium, iron, magnesium, manganese, potassium, and sodium. Wollastonite is a calcium meta silicate ($CaSiO_3$) formed by the interaction of calcite-containing limestone ($CaCO_3$, limestone) and silica (SiO_2) at high temperatures, usually in hot magma (Haner and Çuhadaroğlu, 2013). This mineral is found together with apatite, andradite, diopside, epidote, garnet, sphene, plagioclase feldspar, tremolite, calcite, and quartz in contact with metamorphic limestones and volcanic rocks (Kalla et al., 2013).

2.2.3.2. Chemical Admixtures

Along with the developing technology in impermeable concrete solutions, a common method in recent years is the use of chemical additives. Positive results are obtained in the use of impermeable chemical additives, especially in structures with the high ground water level, water structures, or structures requiring deep foundations.

Since the waterproof admixtures prevent water ingress into the concrete structure, they also reduce the freeze-thaw damage. At the same time, since the Ca(OH)2 output from the concrete structure decreases, it reduces the efflorescence in the surface appearance (Baradan et al., 2015)

Permeability reducing admixtures are added to the mixture in amounts less than 5% of the weight of the cement. In order for permeability-reducing admixtures to fulfill their functions, first, the quality of the concrete produced must comply with the standards.

Ertem et al. (2002) observed that cement-based impermeable admixtures crystallize and do not have the ability to fill the voids and cracks in the concrete. Due to its inflexible structure, it cannot move with the applied concrete surface and causes the formation of structural cracks over time. The smallest damage that may occur in the structure of the insulation causes water ingress and thus deterioration of the material. For this reason, the long-term performance of cement-based waterproofing materials is low.

In the study of Tsai-Lung (2013), the tensile, flexural, and compressive strength values were determined by adding the crystallized water-impermeable additives to the mixture at the rate of 3%, 5%, 7% by weight of the cement. Scanning electron microscope (SEM) imaging was performed. According to the findings, the mechanical properties of the mixture with additive used at the rate of 3% of the cement weight were the highest, and it was observed in the SEM images that a large number of needle-like crystalline structures were formed in all mixtures and filled the void structures.

García (2019) observed that the use of crystalline additives makes cement-based materials more durable and fills the pores. Thanks to the formation of crystals that prevent water ingress in capillary channels and micro-cracks, liquids are prevented from entering the concrete structure. Crystallized additive ratios of cement were put into production as 1%, 1.5%, and 2% by weight. After being kept in H_2SO_4 solution for 90 days, the mechanical properties were investigated. After exposure to acid, as the crystallized mixing ratio increased, more compressive strength was obtained than the control sample, as well as lower mass loss. However, it was observed that there was no significant effect on capillary water absorption as the rate of crystalline admixture increased.

Pazderka and Hájková (2016) stated that the admixtures with crystalline properties prevent water vapor transmission between 16-20%. In the waterproof tests applied to the concrete specimens, it was observed that the crystallized admixture started to fill the voids in the concrete structure at the end of the 12th day. It has been observed that the crystallized admixture has a 2% positive effect on the concrete compressive strength.

Aghabaglou et al. (2019) carried out studies on the specimen with an alkaline content of less than 10%, chloride content of less than 0.1%, and 3 liquid impermeable admixtures with a pH value of 10-11. While it is necessary to add a superplasticizer of 1.3% of the cement weight to produce 20 slumps worth of concrete with the control sample. However, this rate was calculated as 0.8% in the concretes with impermeable admixture. It was observed that the loss of consistency at the end of 45 minutes was higher in waterproof admixtures than in the reference specimen. According to the results of water absorption, capillarity, and permeability, it was observed that impermeable additives gave better results in mixtures with w/c less than 0.6.

Al-Kheetan et al. (2018) used crystalline and hydrophobic admixtures to increase the impermeability against chloride and harmful chemicals. In this study, crystallized and water-repellent chemical admixtures were added at the rates of 1%, 2%, and 3% by weight of the cement. Despite the high dispersion in the produced mixtures, no dispersion was observed in the concrete. While the optimum performance was determined in mixtures containing 2% additive, higher strength values were observed in the mixture containing 2% hydrophobic admixture compared to the mixture containing 2% crystallized admixture. However, in water impermeability tests, it was concluded that mixtures with crystalline admixtures showed more positive effects.

Crystalline admixtures are considered by a pore blocked protection system, which means that pores are filled (Cappelesso et al., 2016). Since the admixtures used to support the formation of crystalline products, crystalline admixtures were used in this study.

As a result of the ever-increasing population in the world, the need for structural elements with higher performance is increasing due to the constantly developing construction and advancing construction technology. The desire to produce materials for high-performance structural elements that are more resistant to environmental factors and have higher strength depending on engineering applications has brought additives to the fore. Even though the use of mineral additives is high, there has been a trend towards chemical additives with the developing technology. Chemical admixtures constitute a large part of the additives that increase the performance of structural elements in terms of both durability and strength. Chemical admixtures used in the production of cement-based materials aim to develop some early or final properties in line with the needs of the produced structural element. As an example of the properties of cement-based materials that chemical additives can improve and develop; Increasing the workability without increasing the amount of water in the mixture or reducing the amount of mixing water without changing the workability, adjusting the workability loss rate, delaying or accelerating the set start, reducing segregation, reducing sweating, increasing pumpability, increasing the strength increase rate can be given. The reason for the wide growth in the use of chemical additives in the production technology of cement-based materials, especially concrete, is the physical and economic benefits of chemical additives in concrete production. Chemical admixtures have effects on the early and final properties of cement-based materials such as desired workability, set control, strength and durability (Mindess et al., 2002). It is expected that the crystalline capillary impermeability additives used in this study will increase the strength of concrete and mortars, decrease the permeability of the samples by supporting the formation of C-S-H gels, and support other mechanical properties of the specimens.

3. MATERIALS AND METHODOLOGY USED IN EXPERIMENTAL STUDIES

3.1. Materials Used in Experimental Studies

3.1.1. Cement

The CEM I 42.5 R Portland Cement (PC) was used as the major binder material for all mixtures. The PC complies with ASTM C150 (2007) and TS-EN-197-1 (2012) standards. The physical and chemical properties of PC are given in Table 3.1.

Table 3. 1. Chemical and physical properties of CEM I 42.5 R Portland Cement

Chemical Composition, %										**Physical Properties**	
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl	Loss on ignition	Density (g/cm^3)	Specific Surface, Blaine (cm^2/g)
19.60	5.07	2.48	64.00	1.33	2.90	0.12	0.80	0.08	3.14	2.98	3135

3.1.2. Admixtures

One of the options to reduce the permeability of concrete is to use chemical admixtures. In this study, the mixture used liquid and powder admixture, which are chemical admixtures that form crystalline structures.

3.1.3. Water

In all mixtures, Ankara mains water in accordance with TS-EN-1008 (2003) was used. Mains water was taken from without being waited and used.

3.1.4. Aggregate

Aggregate ratios used in all specimens are given in Table 3.2.

Table 3. 2. Granulometric properties of aggregate

Aggregate Type	**Sieve Mesh Dimensions (mm), Sieve (%)**						
	25	**19**	**12.5**	**9.5**	**4.75**	**2**	**0.075**
Natural Sand	100	100	100	100	99	98	97
Coarse Aggregate	100	100	100	74.5	5	3	0

3.2. Methodology Used in Experimental Studies

Preparation of mixtures, casting, and molding phases are described in this chapter.

3.2.1. Preparation of Mixtures

The materials used in mixtures were added by weighing on a 0.1 gr precision scale. Cement and chemical admixtures were mixed with mains water in the mixer at the ratio specified in the Table 3.3. Mixtures are poured into molds and left to dry under room conditions for 1 day.

Table 3. 3. Ratios and materials used in experimental studies for 1 m^3

Specimen	**Specimen Acronym**	**Quantity (kg/m^3)**			
		Cement	**Water**	**Liquid Admixture**	**Powder Admixture**
Reference	Ref	1.6	0.4	-	-
Liquid Admixture 1%	LA-1	1.6	0.4	0.016	-
Liquid Admixture 2%	LA-2	1.6	0.4	0.032	-
Powder Admixture %2	PA-2	1.6	0.4	-	0.032
Powder Admixture %1	PA-1	1.6	0.4	-	0.016

3.2.2. Casting and Placing

For the mixtures to be homogeneous, the cement and admixtures were mixed with a mixer for 1 minute. After 1 minute, water was added, and the mixture continued to be mixed until it became smooth and homogeneous. After the mixing process was done, the pasta was poured into pre-oiled molds. To place the paste in the mold properly, the mold shook gropely. Since the vibration process was not performed properly in field conditions, this placement method was used considering the most adverse conditions.

3.2.3. Curing Conditions

Water curing was applied for produced specimens. The specimens were left in the water tank for 28 days in water under room conditions. At the end of the 28 days, they were removed from water and left to dry. After drying, flexural and compressive strength tests were performed on the specimens.

3.2.4. Preparation of Concrete and Mortar Specimens

In this experiment, both liquid and powder admixtures were used in concrete and mortar mixtures shown in Table 3.4 at the rate of 2% of cement weight. Compressive strength test, pressurized water permeability test and mass loss test in sulfuric acid and length change test after mass loss test experimented on the specimens.

Table 3. 4. Mixing ratios for 1 m^3 of concrete

Component (kg)	**Reference**	**Concrete with Liquid Admixture**	**Concrete with Powder Admixture**	**Specific Weight (gr/cm ^{3})**
Cement	300	300	300	3.15
Natural Sand	930	930	930	2.51
Coarse Aggregate	930	930	930	2.67
Water	165	165	165	1.00
Powder Admixture	-	6	-	1.06
Liquid Admixture	-	-	6	1.13

3.2.5. X-Ray Diffraction Analysis (XRD)

The X-Ray Diffraction Analysis (XRD) method is based on the principle that each crystal refracts X-rays in a characteristic pattern, depending on the phase's unique atomic arrangement. These diffraction profiles for each crystal phase identify that crystal, somewhat like a fingerprint. XRD method does not destroy the specimen during the analysis and allows analysis of even very small specimens. Qualitative and quantitative investigations of rocks, crystalline materials, thin films, and polymers can be made with the XRD device.

3.2.6. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) Analysis

EDX, EDAX, or EDS, energy dispersive X-ray spectroscopy provides additional comprehension of the surface material in due course of the SEM analysis process. EDX analysis is used to obtain the elemental composition of a specimen and authorizes for a more quantitative result that can be provided by SEM analysis alone. The combination of EDX and SEM analysis offers chemical composition and fundamental research and provides a comprehensive metallurgical assessment.

3.2.7. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. This measurement provides information about physical phenomena, such as phase transitions, absorption, adsorption, and desorption; chemical phenomena, including chemisorption, thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction).

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1. Flexural and Compressive Strength Test

Flexural and compressive strength tests gave different results in all mixtures. The specimens' 28-day flexural and compressive strength test results are shown in Table 4.1. As a result of the tests, it was seen that there was no relationship between the flexural strength and the admixture, the addition of admixtures did not change the strength. The 28-day flexural strength results of the specimens ranged from 1.5 MPa to 2.6 MPa.

According to Mehta (2006), as the permeability of the systems increases, the strength decreases. It can be said that the permeability decreases due to the increased C-S-H gels and amorphous structures due to the admixture, and the strength increases with the decrease of the permeability. When the results of the tests performed on the specimens are examined, it can be said that the compressive strengths increase slightly with the admixture, and the results were consistent and approximate. It agrees with the test results of Pazderka and Hájková, who had previously performed compressive strength tests with crystalline admixtures, that the compressive strength test results were very close to each other. From the highest to smallest, strength results are LA-2, LA-1, PA-1, PA-2, Ref. Average strength value (ASV) for Ref is 75.4 MPa, ASV for LA-1 is 80.9, ASV for LA-2 is 83 MPa, ASV for PA-2 is 79.1 MPa and ASV for PA-1 is 80.7 MPa. The specimens with liquid admixtures have the highest strength values, while those with powder admixtures have smaller strength values than those with liquid admixtures.

Table 4. 1. Flexural and compressive strength test results

Specimen No	**Flexural Strength (MPa)**	**Compressive Strength (MPa)**
Reference	1.8	80.4
	2.4	72.8
	1.7	73
Specimen with %1 Liquid Admixture	1.6	77.4
	1.6	78.9
	1.5	86.3

Specimen with %2 Liquid Admixture	2.6	76.5
	1.9	87.4
	1.8	85.2
Specimen with %1 Powder Admixture	1.7	74.4
	2	83.1
	1.5	84.5
Specimen with %2 Powder Admixture	1.8	78.5
	1.7	74.8
	2.4	84

4.2. Compressive Strength Test of Hardened Concrete

Crystalline admixtures added to the concrete can negatively affect one feature while improving another. The compressive strength, which is the most important characteristic of concrete, is also affected by the type and ratio of admixtures. Apay et al. (2016), as a result of the compressive strength test applied to the specimens prepared by using 0.5%, 1.0%, 1.5%, and 2.0% water-reducer admixtures by weight of the cement, the highest compressive strength was 36.1 MPa, and the highest water impermeability rate was the specimen with 2% observed chemical admixtures. Calcium silicate hydrate (C-S-H) gel is the primary hydration product of cement and constitutes 60% of the volume of Portland cement and it is responsible for durability and strength of concrete and paste (Alizadeh, R. et al., 2011; Pellenq,R et al., 2008; Nonat, A., 2004). In this study, the addition of admixtures increased the strength as it supported the formation of the C-S-H gel. Pazderka (2017) investigated the effects of crystalline admixtures on compressive strength. In the compressive strength tests performed at the end of 28 days, it was observed that the results of the specimens with 2% of the cement amount added to the crystallization were close to each other with the specimens without admixture, and the compressive strength of the specimens produced with 1% of the crystallized admixture was higher than the specimens without admixtures.

The compressive strength test results of the specimens with admixtures and reference specimens are given in Table 4.2. Since both admixtures have an effect that fills the concrete voids, it is seen that the final strength of the blended concrete mixtures is higher than the reference concrete.

The effects of the admixtures added to the concrete to provide water impermeability on the compressive strength were examined experimentally at 3, 7, and 28 days and are presented in Table 4.2. It can be said that the crystalline admixtures relatively increase the strength of the concrete with the crystallized products formed as a result of the hydration of the cement. However, when the values are examined, it can be said that there are no significant increases compared to the reference concrete. While the 3-day compressive strength value of the reference concrete was 14.6 MPa, it reached a maximum of 26.1 MPa at the end of 28 days. On the other hand, while the 3-day strength was 18.1 MPa in liquid-added concrete, it reached 26.5 MPa at the end of 28 days. While the powder-added concrete gave a strength result of 20.4 MPa on the 3rd day, this value reached 28.8 MPa at the end of the 28th day. With the use of powder admixture, its effect on concrete compressive strength was better at 28 days compared to liquid admixture and reference concrete. Accordingly, both admixtures increase the final strength values of concrete mixtures with relatively low target strength values by around 15-20%. The crystallized hydrated products formed in concrete cavities over time also provided a positive effect on concrete strength, providing strength gain compared to the reference concrete. As a result, it can be stated by examining the values in Table 4.2 that the use of crystalline admixtures affects the compressive strength positively, but this does not make a significant difference.

Table 4. 2. Compressive strength test results of concrete

Day	**Strength (MPa)**		
	Reference	**Liquid Admixture**	**Powder Admixture**
3 days	14.6	18.1	20.4
7 days	22.5	21.9	23.4
28th day	26.1	26.5	28.8

4.3. Pressurized Water Permeability Test

Concrete cube specimens of 15 cm-sized were produced by using chemical admixtures at the rate of 1% and 2% of the cement weight. Pressurized water permeability test was performed by leaving the first group of the produced specimens in the curing pool for 7 days. The second group was left in the curing pool for 28 days and the third group was cured in the pool for 7 days and left under laboratory conditions for 21 days and then tested. The pressurized water permeability tests of concrete specimens with and without admixtures were carried out in accordance with the standard TS-EN-12390-8 Concrete – Hardened Concrete Tests – Part 8: Determination of Water Penetration Depth under Pressure.

The results and measurements after the experiment are shown in Table 4.3.

Figure 4. 1. Pressurized water experiment setup

Table 4. 3. Pressurized water permeability test results

Specimens	**7 days water cure (5 & 7 bars)**	**7 days water cure + 21 days of air cure (7 bars)**	**28 days water cure (7 bars)**
	Average Water Depth (mm)	Average Water Depth (mm)	Average Water Depth (mm)
Reference	35 (5 bars)	36	25
LA-1 (%1)	22 (7 bars)	17	15
PA-1 (%1)	20 (7 bars)	17	13
LA-2 (%2)	15 (5 bars)	13	12
PA-2 (%2)	13 (5 bars)	12	9

The voids in the aggregate grains are structural voids that vary between 0% and 20% of the aggregate solid volume. The size and number of aggregate voids negatively affect strength and durability. As a result of drying and shrinkage of the cement paste, it loses some of the water in it and shrinks. However, since the aggregates do not change in volume at the same rate, they restrict the free shrinkage of the cement paste, and cracks occur in this case (Erdoğan, 2015).

There is a clear difference in the water treatment depth between the cases of the specimens with crystalline admixtures. While 25 mm water depth is measured in the reference specimen without admixture, this rate is almost half in the other specimens with admixtures. When the void ratios appearing in the specimens containing admixtures are examined, it is seen that all the specimens with admixture contain less voids compared to the reference specimen. It can be said that both powder and liquid crystalline admixtures that provide water impermeability have reduced the void ratio in the specimens. The water absorption values by weight of reference and concrete specimens with admixture are given in Table 4.3. A decrease is observed in the water absorption values of the concretes in the specimens with admixture. The reason for this is that crystalline products form in the concrete voids and fill these voids, and as a result, the water absorption rate decreases. While the best result was obtained in the specimen with 2% powder admixture, the lowest result was obtained in the specimen with 1% liquid admixture. This is because the admixtures change the microstructure and reduce the void ratio in the structure.

4.4. Length Changes of Mortars in Sulfate Solution

25×25×285 mm^3-sized mortars were produced in accordance with the ASTM C1012 standard in order to see the length change in the specimens with admixture and the specimen without admixture mortars exposed to sulfate. While preparing the mortar mixtures, mortars were prepared to contain 1 part cement, 2.75 parts sand, 0.485 parts water by weight, in accordance with the ASTM C1012 standard. Admixtures were added in the mixture by the admixture ratio is 2% of the cement weight. After the mortars were cured for 7 days, the lengths of the samples were measured and then placed in a 290 g/l Na_2SO_4 solution at 30 °C. After the mortars remained in the solution for 30 days, the lengths of the mortars were measured again and the change in length was determined according to the ASTM C1012 standard. Figure 3 shows the height measurement process of the mortars before and after they are left in the sulfate solution. The results are presented in Table 4.4.

The formation of gypsum and calcium sulfoaluminate occurs as a result of the reactions of sulfates with hydrated cement components, especially with $Ca(OH)_2$ and tricalcium aluminate (C_3A), which are described below. These salts occupy much more volume than the components they replace. The resulting expansion causes damage to the concrete.

The reactions of sodium sulfate with $Ca(OH)_2$ can be written as:

$$Ca(OH)_2 + Na_2SO_4.10H_2O \rightarrow CaSO_4.2H_2O + 2NaOH + 8H_2O$$

As a result of this reaction, the volume of the solid phase increases by 124%. With continuous water washing, $Ca(OH)_2$ can be completely removed from the body. When the reaction reaches equilibrium as a result of the accumulation of NaOH, only some of the SO_3 is converted to gypsum (Malhotra, 1991).

The measured length changes were expressed as % with respect to the initial changes. As shown in previous studies and standards, the critical height extension limit value was accepted as 0.1% in this study (Ouyang et al., 1988). In the measurements made, it was determined that there was an increase in length in all samples, while the results were found to be negligibly low. The percentage changes in length of the specimens are given in Table 4.4 and before and after photographs are given in Figures 4.2 – 4.4. However, it is said that mortars with admixture change less in length; this can be explained by the higher 28-day compressive strength and less permeability compared to the reference specimen.

The reason for the elongation is the realization of five reaction mechanisms in the cement. The mechanisms depend on the SO_3, free CaO and MgO amounts in the cement. Other effects are specific surface and delayed ettringite formations (Santhanam et al., 2006). In the study, it is thought that the elongation in mortar samples is caused by the effect of some of these mechanisms.

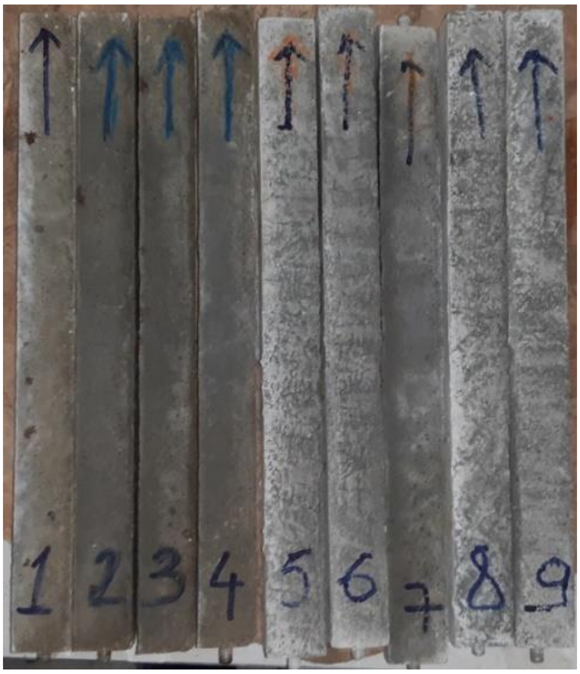

Figure 4. 2. Length measurement process of mortars before the test

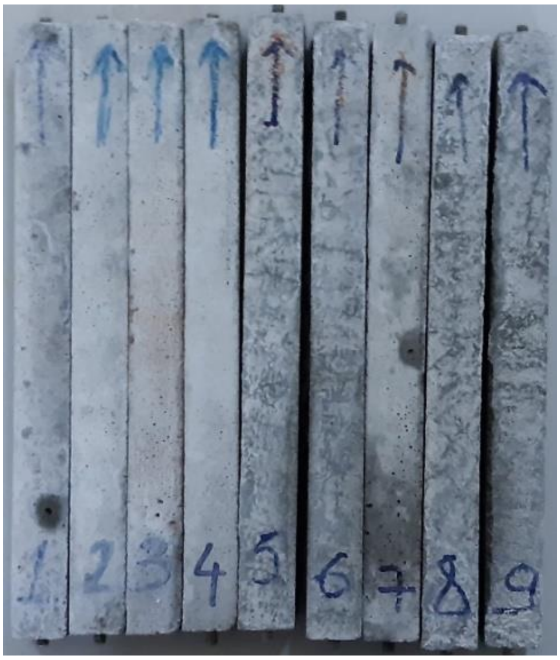

Figure 4. 3. Length measurement process after the test

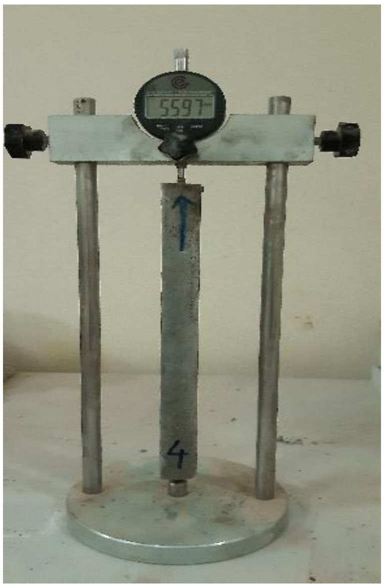

Figure 4. 4. Left in 290 g/L Na_2SO_4 solution for 30 days

Table 4. 4. Length change results for mortars

Mixture	**Length Change**
Reference	0.022%
Liquid Admixture	0.007%
Powder Admixture	0.009%

4.5. Mass Loss in Acid Solution of Concrete

In order to compare the mass losses of the concrete specimens with admixtures and the reference concrete in the sulfuric acid solution, the specimens were kept in a 7% sulfuric acid. It was renewed once a week to keep the sulfuric acid solution concentration constant and clean the dissolved concrete pieces, and the mass changes were measured weekly. Accordingly, the mass values and mass loss values at the beginning and end of the experiment are given in Table 4.5.

When the weights of the concrete specimens produced within the scope of the study were measured and compared one by one, it was observed that there were changes in the weights of the concretes. These changes indicate deterioration in concrete specimens. The increases and decreases in the weights of the specimens after they are exposed to the sulfuric acid solution indicate that the produced concrete has been damaged due to chemicals.

The cement matrix's resistance to acid corrosion is essentially determined by the properties of its pore structure, the matrix's components' capacity to neutralize acid, and the end products of acid corrosion (Shi and Stegemann 2000). Mineral acids including hydrochloric acid, nitric acid, and sulfuric acid are the most harmful for concrete among the main factors causing acidic attack. Because sulfate ions often start sulfate attack in addition to the dissolving brought on by hydrogen ions, sulfuric acid is quite corrosive (Hewayde *et al.* 2007; Attiogbe and Rizkalla 1988; Ichitsubo *et al.* 2006; Kawai *et al.* 2005).

When the results in Table 4.5 are examined, changes in specimen weights are seen due to the ongoing hydration reactions. The highest weight reduction due to acid was observed in the reference specimen. When the specimens with admixture were examined, the least weight reduction was observed in the powder-added specimen. The reason for this is that sulfates (SO_4) in sulfuric acid penetrate the concrete by diffusion and react with C_3A and CaOH in the cement, causing the formation of gypsum ($CaSO_4$) and ettringite (C_4A_3S) (Attiogbe et al., 1988). These reactions cause an increase in the volume of the concrete, and the weight of the concrete sample increases. However, in more time and chemical concentrations, this increase in volume may cause cracking of the concrete, softening the outer surface and pouring the outer surface of the concrete, and reducing the weight of the concrete (Sanni et al., 2012).

Table 4. 5. Mass loss results for concrete in acid solution

	Mass (gr)		**Loss (%)**
	Beginning	**Final**	
Reference Concrete Specimen	7940	3957	50.2
Concrete Specimen with Liquid Admixture	8049	6490	19.4
Concrete Specimen with Powder Admixture	8017	6592	17.8

4.6. X-Ray Diffraction (XRD) Analysis

According to Mehta (2001), as hydration proceeds, the voids in the cement particles begin to fill with hydration products. As a result of the hydration of calcium, sulfate, aluminate, and hydroxyl ions with cement, crystals called ettringite begin to form. After a couple of hours, calcium hydroxide ($Ca(OH)_2$) crystals, and small fibrous calcium silicate hydrate (C-S-H) crystals begin to fill the voids (Mehta, 2001). Sauman (1979) has expressed that the carbonation of calcium silicate hydrate (C-S-H) points to the formation of silica gel and valerite, which is turned into calcite.

XRD analysis is one of the test methods that determine the mineral components such as calcium silicate hydrate (C-S-H), aluminosilicate hydrate (C-A-S-H), portlandite ($CA(OH)_2$), ettringite. The following figures show the XRD analysis results of the specimens cured in water for 28 days.

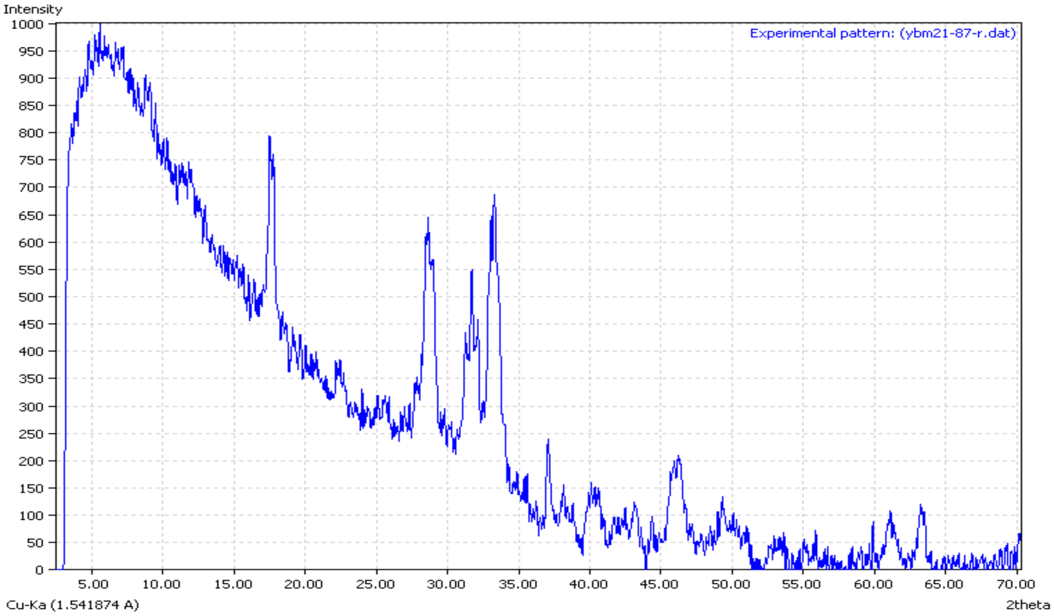

Figure 4. 5. XRD analysis of reference specimen

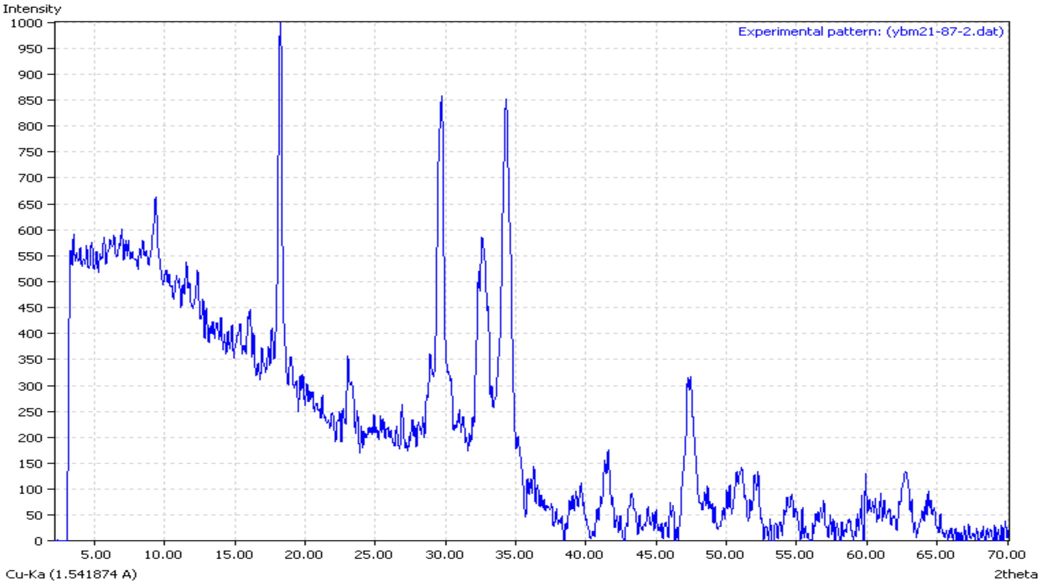

Figure 4. 6. XRD analysis of the specimen with 1% liquid admixture

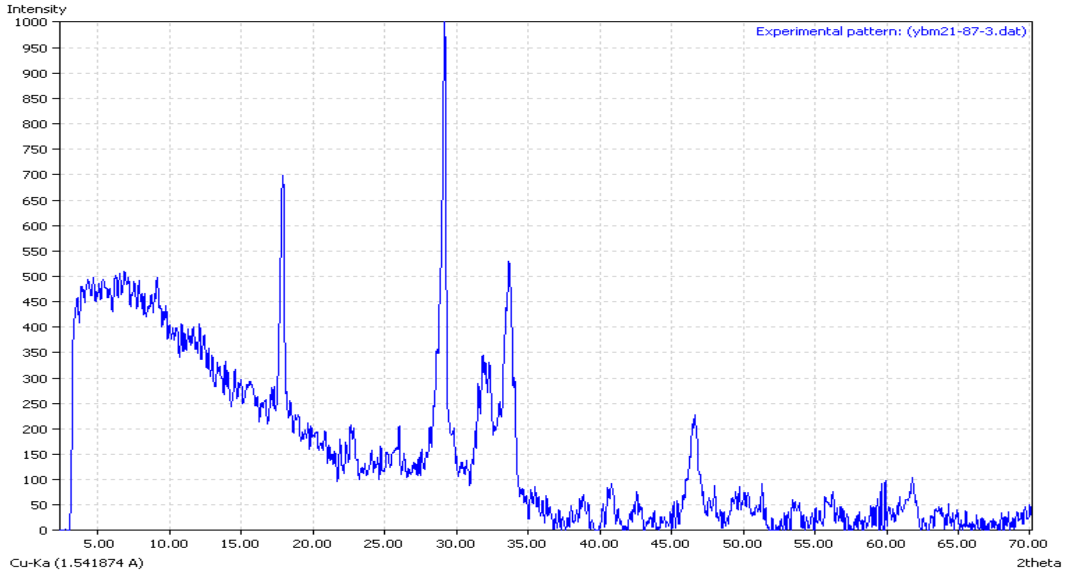

Figure 4. 7. XRD analysis of the specimen with 2% liquid admixture

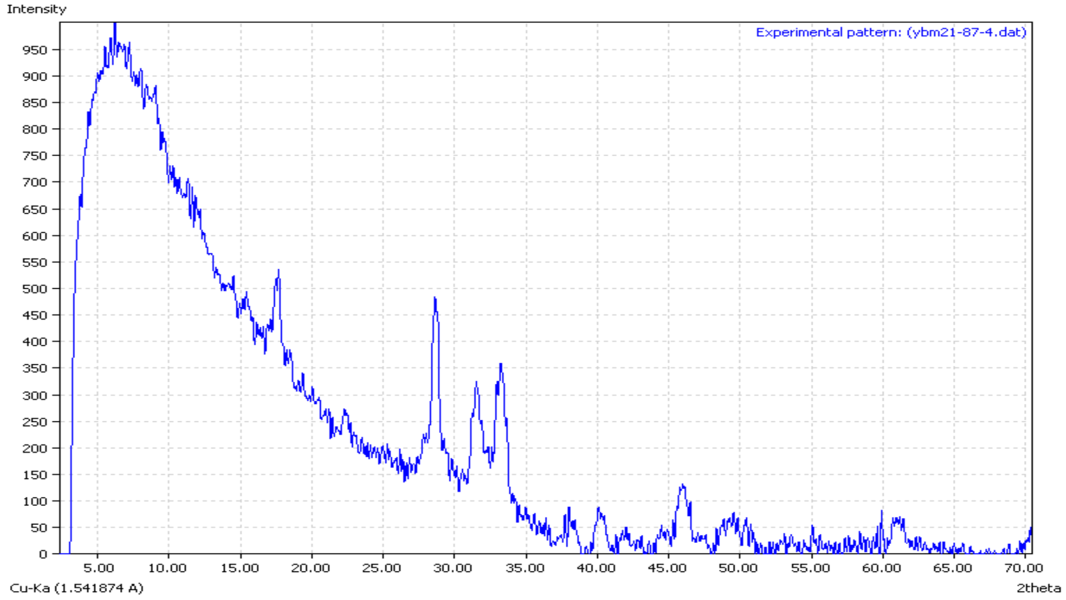

Figure 4. 8. XRD analysis of the specimen with %2 powder admixture

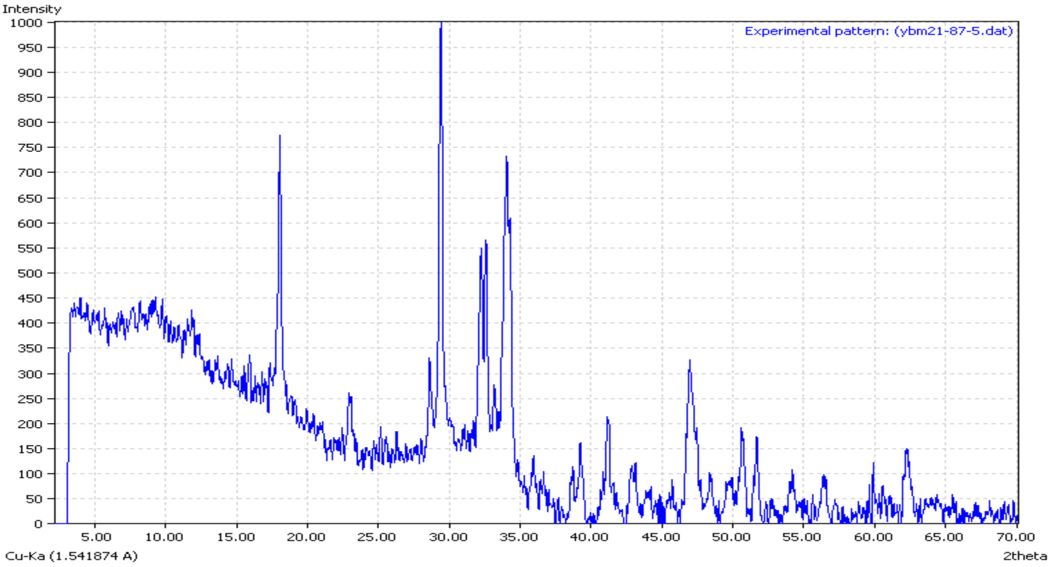

Figure 4. 9. XRD analysis of the specimen with 1% powder admixture

As a result of X-ray diffractometry analysis performed separately for 5 samples, graphs were prepared by grouping so that each additive group could be evaluated within itself. In this context, XRD Analysis results of the specimens are given in Figure 4.5 to 4.9, respectively. As a phase in the analysis, C_3S, C_2S, celite C_3A, portlandite, in other words, C-H and ettringite were observed. In order to obtain graphics; First, the specimens were ground into powder. The powder specimen was placed in the specimen holder of the device and analyses were made for each specimen separately.

In this analysis, the main hydration products, ettringite and calcium hydroxide peaks formed in all specimens, including the reference specimen, are significantly seen. In addition to ettringite and $Ca\ (OH)_2$, the contribution was observed in the admixture added specimen in the calcites, alite, and belite peaks. The products observed as a result of XRD in specimens are compatible with TGA/DTA analysis results. When the second specimen is examined, similar crystal peaks were observed with the third sample, which shows that the amount of calcium hydroxide is higher in powder-added specimens. However, in the third sample, it is seen that ettringite gives a higher peak than the sample of 1 %contribution. It can be said that the increase in hydration products is due to the increase in the contribution rate, and therefore the cracks are filling more intensely. When the XRD results of the fourth sample were examined, it was seen that more intense ettringite occurred than in the fifth sample. When the samples are compared, dust contribution can be subjected to ettringite formation, and fluid contribution positively supports calcium hydroxide formation.

After 28 days, ettringite was determined in all specimens. As seen in the Figure 4.5 to Figure 4.9, the specimens with admixtures have higher amounts of ettringite than the reference specimen. The densest ettringite has been shown in the LA-2 specimen.

4.7. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) Analysis

Garcia et al. (2017), it has been observed that the use of crystalline admixtures makes cement-based materials more durable and fills the pores. With the formation of crystals that prevent water intake in capillary channels and micro-cracks, liquids are prevented from entering the concrete structure. Pazderka (2017) investigated the effects of crystallized admixtures on compressive strength as well as concrete impermeability. In this study, the optimum level of crystalline admixture was investigated.

SEM images were taken from the specimens that were crushed after the strength test, and the microstructure of the specimens was analysed. Different phases such as calcite, alite, ettringite, calcium silicate hydrate (C-S-H) formed in concrete can be used to analyse SEM images. In the 28-day SEM images, it was seen that the C-H phases were crystallized and replaced by C-S-H gels. Crystallized admixtures bind C-H to itself, accelerating the formation of new C-S-H gels, and with the effect of this situation, the structure became more impermeable and durable over time. When the SEM analysis results were examined, significant changes and concentrations were observed in the reference specimen without admixture and the specimens with admixtures. It was observed that many needle-shaped crystals formed in all mixtures and filled the voids.

EDX analysis was performed to identify existing compounds formed after the addition of admixtures. Different peak densities were observed for Si, Ca, Al, O. These elements show that the reactions occur significantly and correlate well with the results. It has been proven that the Si element increases in the specimens with admixtures. As a result of the experiment, the importance of the elements in the specimen is very high. The ratios of the elements in the specimen, the structures that emerge as a result of hydration, for example, It also allows us to have an idea about calcium silicate hydrate (C-S-H), calcium hydroxide (Ca(OH)2), calcium sulfoaluminate (C6AS3H32 also called ettringite).

When the SEM analysis results and EDX graphics of the reference specimen without admixture shown in Figure 4.10 are examined, the porous and non-crystalline structure of the specimen and its microcracks can be seen. According to the EDX graphics of Figure 4.10, there is 40.36% calcium (Ca), 33.59% oxygen (O), and 18.02% carbon (C), which are the main hydration products in the specimen. In addition, a silicon peak was observed in the reference specimen, indicating that the crystalline admixture also stimulated the production of new calcium silicate hydrates. There is 3.52% silicon (Si) in the specimen. When looking at the values, it can be seen from the ratios of the elements that the specimen is crystallized to a certain extent, but the lack of amorphous structures that provide impermeability and the presence of microcracks that can be seen from time to time prove the permeability of the specimen.

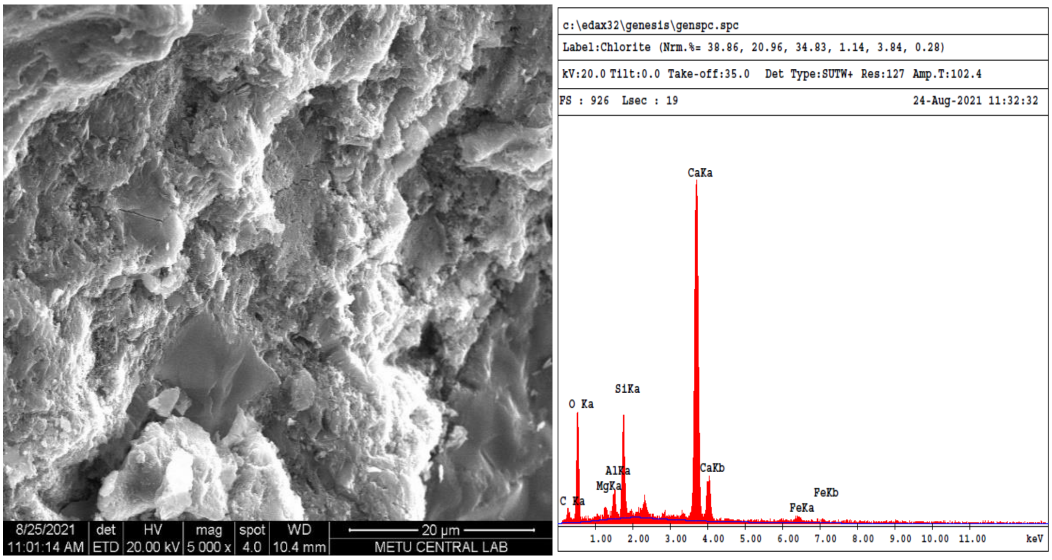

Figure 4. 10. SEM/EDX analysis of the reference specimen of the cement paste

When the results of the SEM analysis shown in Figure 4.11 are examined, it is seen that the cracks in the specimen with 1% liquid admixture have partially disappeared, and crystals are formed in voids. According to the EDX results, 35.59% of the specimen with 1% liquid admixture contains calcium, 38.83% oxygen, and 18.60% carbon. It is seen that C-S-H gels are formed, and CH formations are covered with C-S-H gels in the 28-day-specimen with 1% liquid admixture. In addition, a silicon peak was observed in the specimen with a 1% liquid admixture shown in Figure 4.11, indicating that the crystalline admixture also stimulated the production of new calcium silicate hydrates, which contained 3.62% silicon (Si) in the specimen. Compared to the reference specimen given in Figure 4.10, it is remarkable that the admixture fills the hydration products and capillary voids formed in Figure 4.11.

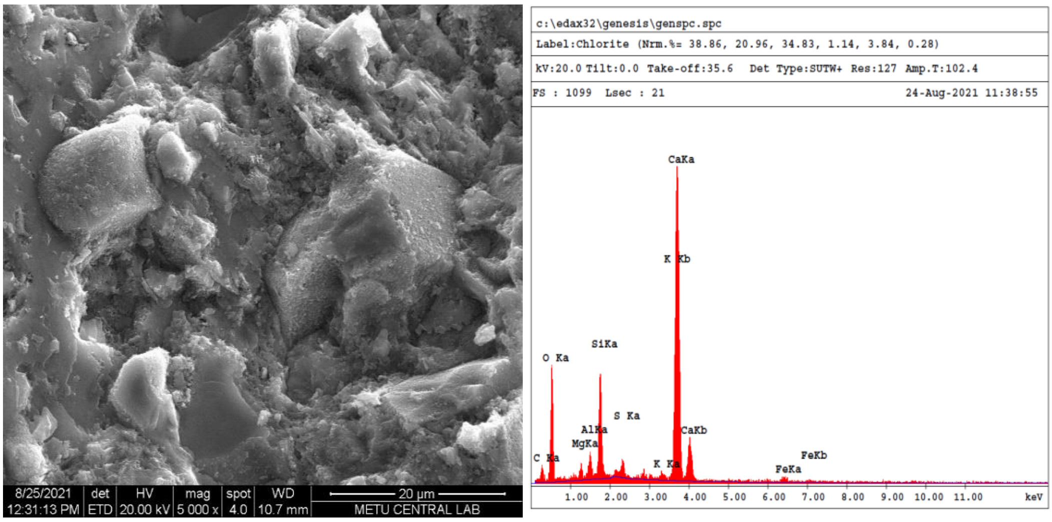

Figure 4. 11. SEM/EDX analysis of the specimen of the cement paste with 1% liquid admixture

Figure 4.12 presents the specimen's SEM image and EDX analysis with a 2% liquid admixture. Results show that amorphous structures, needle-like ettringites, and few cracks appear in the specimen with 2% liquid admixture. According to the EDX results, 39.50% of the specimen with 2% powder admixtures contains calcium, 37.49% oxygen, and 13.56% carbon. It is seen that C-S-H gels are formed, and CH formations are covered with C-S-H gels in the 28-day-specimen with 2% liquid admixture. Moreover, a silicon peak was detected in the specimen with a 1% liquid admixture shown in Figure 4.11, indicating that the crystalline admixture also stimulated the production of new calcium silicate hydrates, which contained 4.42% silicon (Si) in the specimen. Compared to the specimen with 1% liquid admixture given in Figure 4.11, more needle-like ettringite and less amorphous structure are striking in the specimen with 2% liquid admixture shown in Figure 4.11.

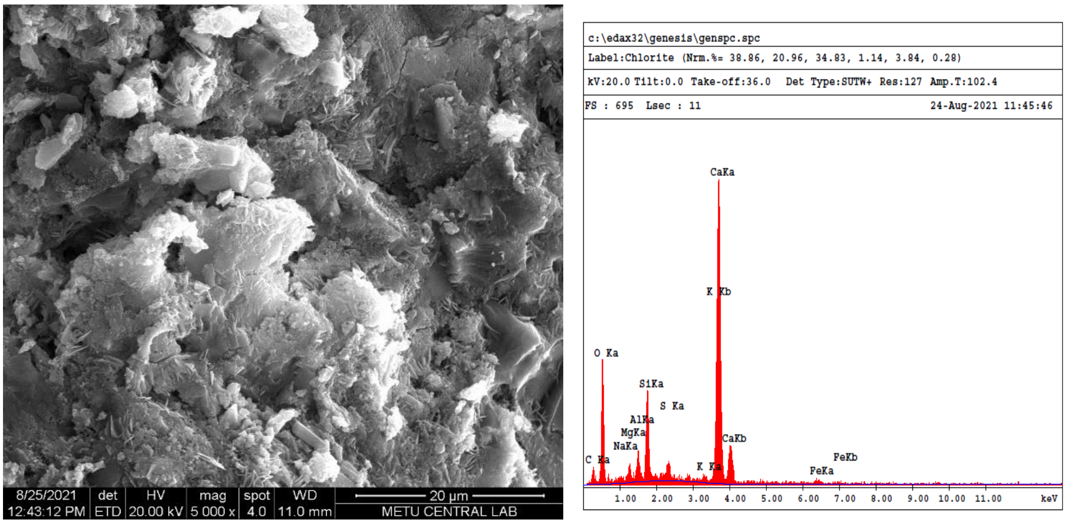

Figure 4. 12. SEM/EDX analysis of the specimen of the cement paste with 2% liquid admixture

The specimen with 2% powder admixture exhibits amorphous structures and needle-like ettringites, according to the results of the SEM analysis. Data from EDX graphics have demonstrated that there is a large amount of O (oxygen), Ca (calcium), and C (carbon), which are mainly the hydration products of cement, in the specimen. According to the EDX results, 38.04% of the specimen with 2% powder admixtures contains calcium, 38.80% oxygen, and 13.76% carbon. In addition, small amounts of aluminum (Al) and iron (Fe) peaks were also observed. It contains 1.51% aluminum and 1.56% iron. In the sample, a silicon peak was also seen, proving that the crystalline admixture promoted the synthesis of new calcium silicate hydrates. In the specimen, silicon (Si) accounts for 1.06%. It is seen that C-S-H gels are formed, and CH formations are covered with C-S-H gels in the 28-day-specimen with 2% powder admixture. As seen in Figure 4.13, ettringite structures formed by the admixture and a more void-free structure stand out.

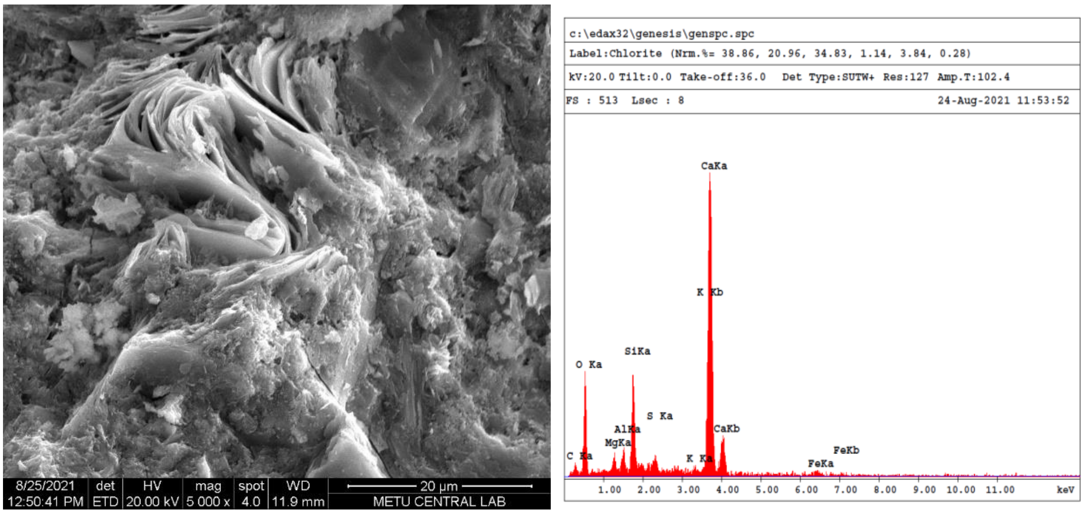

Figure 4. 13. SEM/EDX analysis of the specimen of the cement paste with 2% powder admixture

According to the findings of the SEM analysis, the specimen with 2% powder admixture displays amorphous structures and needle-like ettringites. According to the EDX results, 31.63% of the specimen with 2% powder admixtures contains calcium, 15.35% oxygen and 52.11% carbon. In addition, small amounts of iron (Fe) peak were also observed. It contains 0.19% iron. When the values are examined, it is understood that the changed values are used in the formation of C-S-H and $CaCO_3$. As a result, it is seen that C-S-H gels are formed, and CH formations are covered with C-S-H gels in specimen with 2% powder admixture. As seen in Figure 4.14, ettringite structures formed by the admixture and a more void-free structure stand out.

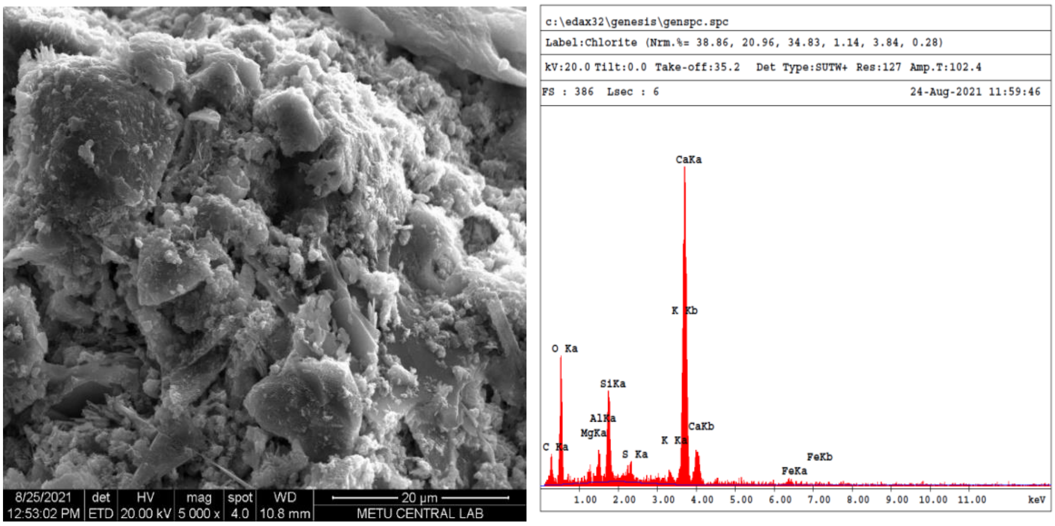

Figure 4. 14. SEM/EDX analysis of the specimen of the cement paste with 1% powder admixture

4.8. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) Analysis for Concrete Specimens

SEM and EDX analyzes were performed on the sections taken from the produced control and chemically added mortar specimens. Since the variable in concrete specimens is the crystalline admixture, the void structure and the state of the hydration products were mainly investigated in the examinations.

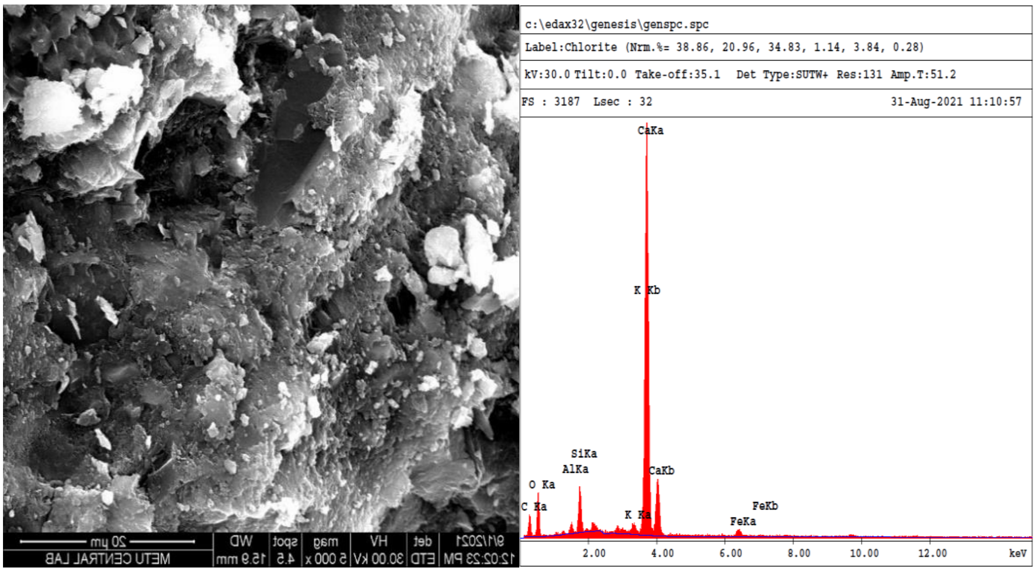

Figure 4. 15. SEM/EDX analysis of reference specimen of concrete

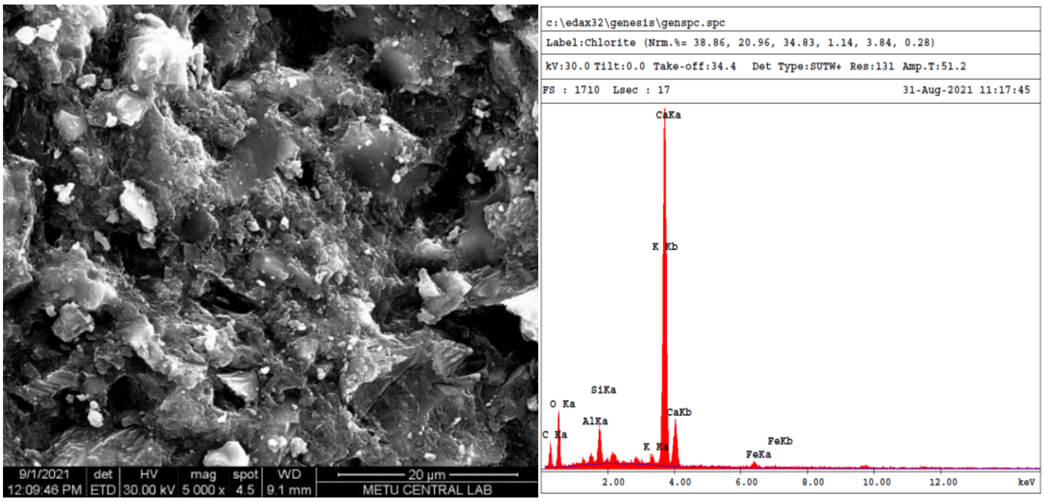

Figure 4. 16. SEM/EDX analysis of the specimen of concrete with 1% liquid admixture

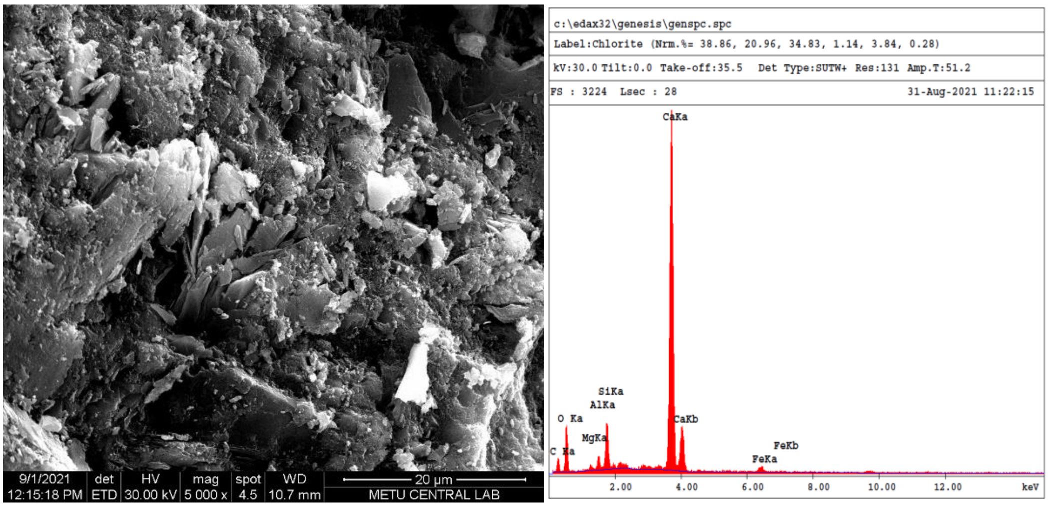

Figure 4. 17. SEM/EDX analysis of the specimen of concrete with 2% liquid admixture

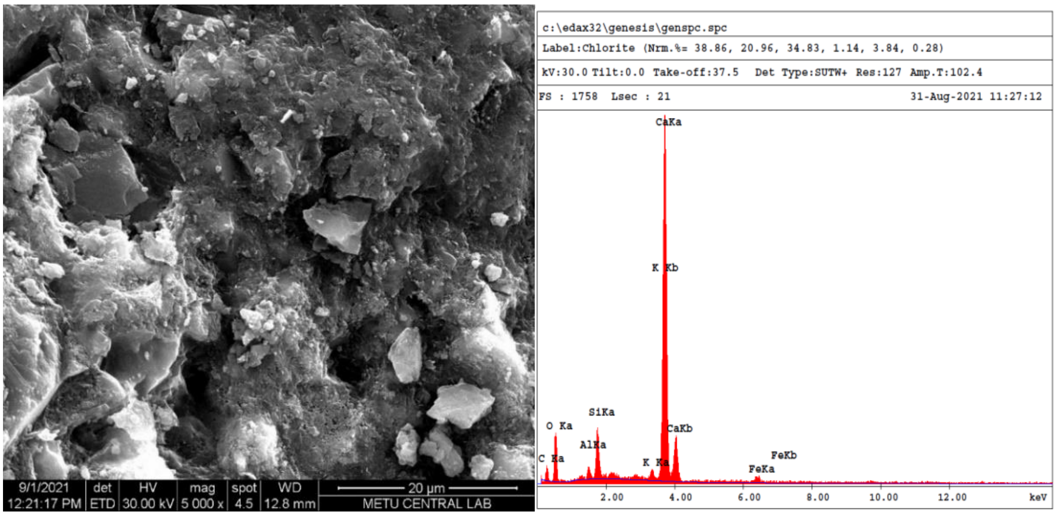

Figure 4. 18. SEM/EDX analysis of the specimen of concrete with 2% powder admixture

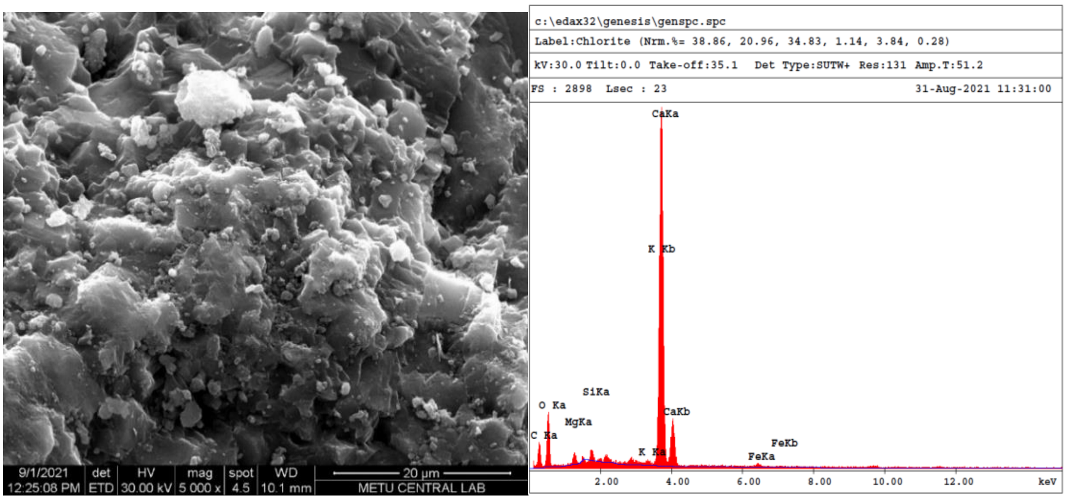

Figure 4. 19. SEM/EDX analysis of the specimen of concrete with 1% powder admixture

Figure 4.15 shows the reference specimen, Figure 4.16 shows the specimen with 1% liquid admixture, Figure 4.17 shows the specimen with 2% liquid admixture, Figure 4.18 shows the specimen with 2% powder admixture, and Figure 4.19 shows the specimen with 1% powder admixture.

According to EDX graphics, the reference specimen shown in Figure 4.15 contains 39.09% oxygen (O), 40.57% calcium (Ca), 6.68% carbon (C), 7.76% silicon (Si). The specimen with 1% liquid admixture shown in Figure 4.16 contains 33.89% oxygen (O), 41.93% calcium (Ca), 7.88% carbon (C), 8% silicon (Si). The specimen with 2% liquid admixture shown in Figure 4.17 contains 35.91% oxygen (O), 27.56% calcium (Ca), 21.55% carbon (C), 6.66% silicon (Si). The specimen with 2% powder admixture shown in Figure 4.18 contains 38.34% oxygen (O), 38.44% calcium (Ca), 7.33% carbon (C), 7.86% silicon (Si). The specimen with 1% powder admixture shown in Figure 4.19 contains 35.18% oxygen (O), 36.07% calcium (Ca), 16.35% carbon (C), 5.27% silicon (Si). The high amount of Ca and Si values can be associated with the formation of CaCO3 and C-S-H gel.

As seen in the figures, powder admixture and liquid admixture were quite effective in filling the voids in all specimens. When the EDX graphs of the specimens were examined, it was observed that the calcium (Ca) peaks were much more prominent. This can be attributed to the formation of C-S-H gels and different calcium carbonate products.

When the SEM analysis of the specimens with admixture is compared with the reference specimen, it can be said that the amorphous structures in the specimens with admixture are generally more homogeneous and more regularly distributed. It is supported by the SEM graphics that the specimens with admixture show higher strength performance compared to the reference specimen. According to EDX analysis, calcium (Ca) is abundant in all specimens in general.

4.9. Thermogravimetric Analysis (TGA)

According to Kucharczyk, mass changes below 550 °C are due to dehydration and dehydroxylation, while mass changes above 550 °C are due to decarbonation. The temperature rise in the concrete evacuates the water in the concrete. First, the free water in the capillaries evaporates, then the capillary water, and finally the physically bound water in the C-S-H. It is seen that among the specimens in Figures, it has the most lost free water.

The water loss of the specimens with admixtures in all specimens is expected to be less than the reference specimen with no admixture. Each phase was characterized by its temperature range and a certain mass loss. The temperature ranges are clearly defined by the curve. Together with the temperature, ettringite dissolves first when the temperature reaches 100 °C.

When the TGA curves of specimens were examined, it was observed that the thermal decomposition process basically took place in two stages for all specimens. The weight loss seen in the first stage temperature range is due to moisture and crystalline water removal. Weight loss in the temperature is due to dihydroxylation. The reason for this increase in weight loss is due to its decomposition with the admixture attached to the structure. It is seen that the mass losses in the powder-added specimens are less than the mass losses in the liquid-added specimens. However, there is no significant difference in mass loss between specimens with powder admixture and liquid admixture.

Five specimens were observed by thermogravimetric analysis (TGA). The specimens were taken in a ceramic crucible and heated from 18 °C to 878 °C in thermoanalyzer at a heating rate of 10 °C min-1 using air as a medium under static conditions.

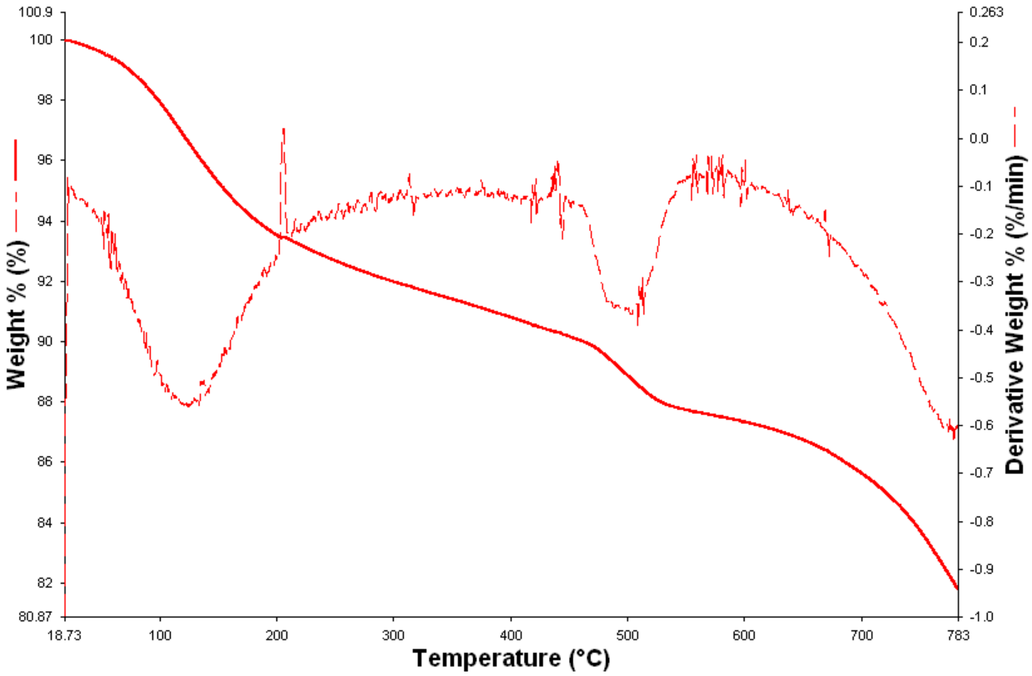

Figure 4. 20. TGA analysis of reference specimen

The TGA analysis result is presented in Figure 4.20, as weight loss with respective temperature range and peak temperature for the characteristic specimens. The total weight loss of the reference specimen shown in Figure 4.20 because of heating from 25 °C to 878 °C was 19.7 %. The four characteristic endothermic effects are noticed. The first effect, in the temperature range from 18 °C to 100 °C is due to evaporation of surface adsorbed water because specimens adsorbed water from the air during its cooling to the room temperature after drying at 104 °C and according to the result, it can be said that the free water rate in the specimen is 1.3%. The second effect, in the temperature range from 100 °C to 350 °C, is attributed to the dehydration of C–S–H and ettringite and calcium aluminate hydrate, and the weight loss was 6.3% in this range. The temperature at which these compounds lose water depends upon the available $CaO:SiO_2$ ratio in the hydrated cement matrix. The third effect, the temperature range between 450 °C and 550 °C shows the degradation of $Ca(OH)_2$ formed during hydration, and it can be said that the loss of $Ca(OH)_2$ is 2.8% in this range according to the graph.

Finally, the temperature ranges from 750 °C to 850 °C, indicating that calcium carbonate is decarbonized in the hydrated compound. It was observed that the decarbonized calcium carbonate in this range was 5.6%.

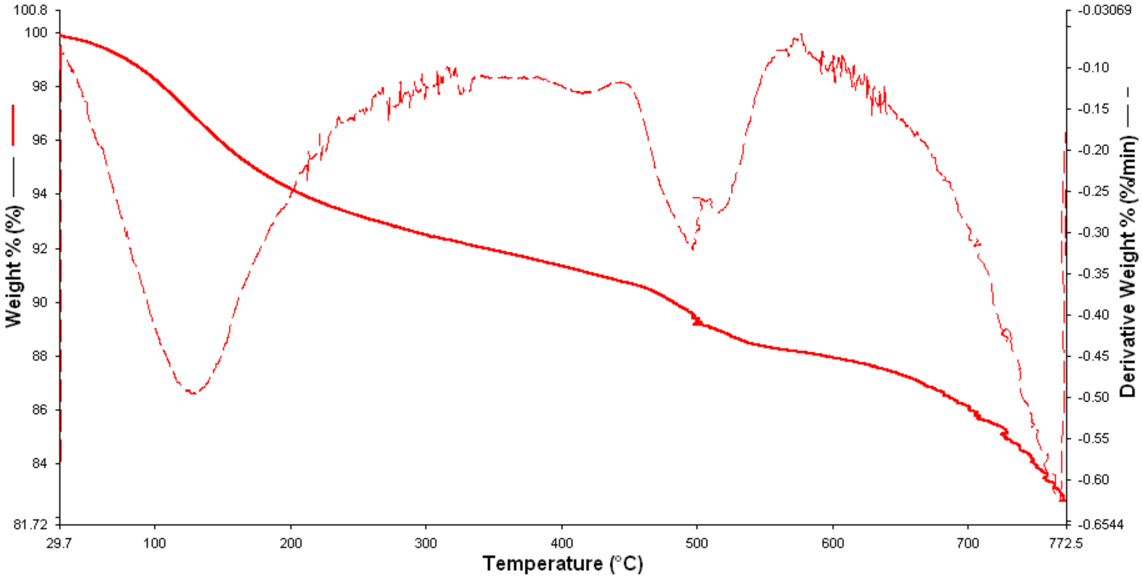

Figure 4. 21. TGA analysis of the specimen with 1% powder admixture

The specimen with the 1% powder admixture in Figure 4.21 lost 17.37% of its entire weight as a result of being heated from 29 °C to 775.5 °C. Figure 4.21 shows the weight loss from the TGA study and the typical specimens' temperature range and peak temperature. The first effect, which occurs in the temperature range of 29 °C to 100 °C, is caused by the surface-adsorbed water evaporating because specimens absorbed water from the air during their cooling to room temperature after drying at 104 °C. As a result, it can be concluded that the specimen's free water rate is 3.11%. The dehydration of C-S-H, ettringite, and calcium aluminate hydrate is responsible for the second effect, which occurs in the temperature range of 100 °C to 350 °C. In this range, weight loss was 8%. The ratio of CaO to SiO_2 in the wet cement matrix determines the temperature at which these compounds begin to lose water. According to the TGA graph, the third effect, the temperature range between 450 °C and 550 °C, displays the degradation of $Ca(OH)_2$ generated during hydration. The loss of $Ca(OH)_2$ in this range is estimated to be 3%.

Finally, the temperature range from 550 °C to 775.5 °C indicates that calcium carbonate is decarbonized in the hydrated compound. It was observed that the decarbonized calcium carbonate in this range was 1%.

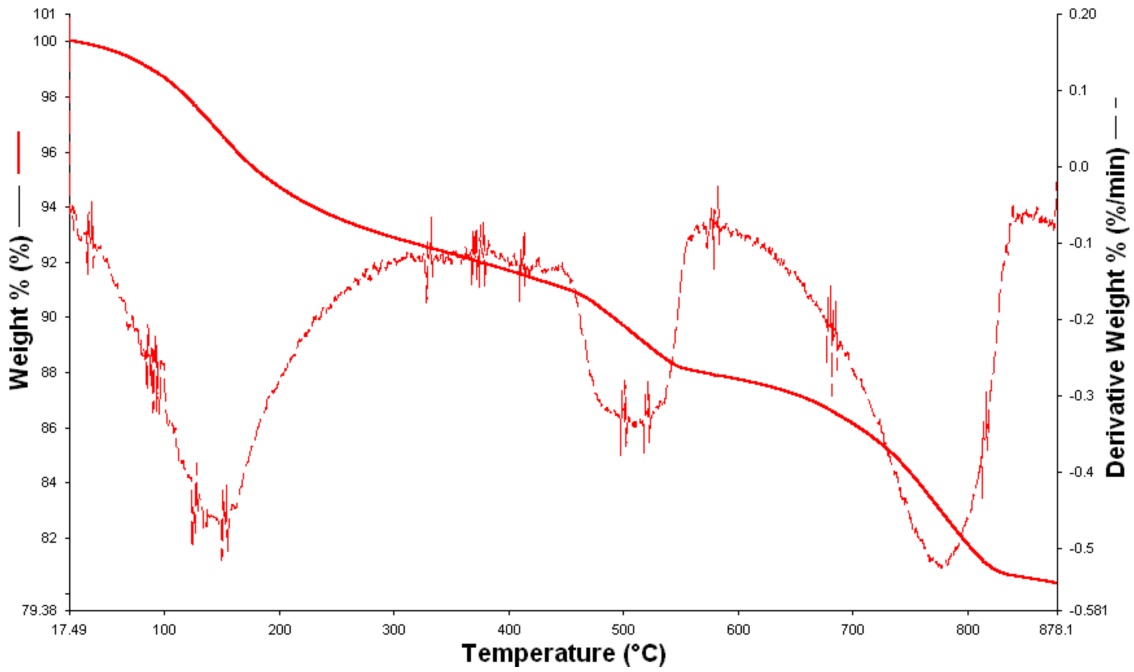

Figure 4. 22. TGA analysis of the specimen with 2% powder admixture

When heated from 17 °C to 878 °C, the specimen in Figure 4.22 with the 2% powder admixture lost 19.65% of its total weight. The weight loss from the TGA analysis, as well as the temperature range and peak temperature for the typical specimens, are shown in Figure 4.22. Specimens absorbed water from the air during their cooling to room temperature after drying at 104 °C, which results in the first effect, which happens in the temperature range of 17 °C to 150 °C. The specimen's free water rate is therefore calculated to be 6%. The second effect occurs between 150 and 350 °C and is caused by the dehydration of C-S-H, ettringite, and calcium aluminate hydrate. The weight loss in this range was 3%. The temperature at which these compounds start to lose water depends on the ratio of CaO to SiO_2 that is present in the wet cement matrix. The degradation of $Ca(OH)_2$ produced during hydration is seen by the third effect, which occurs in the temperature range between 350 °C and 600 °C, on the TGA graph. In this range, 4% of the $Ca(OH)_2$ is thought to be lost. The temperature range of 600 °C to 878 °C further suggests that calcium carbonate is decarbonized in the hydrated molecule. The decarbonized calcium carbonate in this range was observed to be 5%.

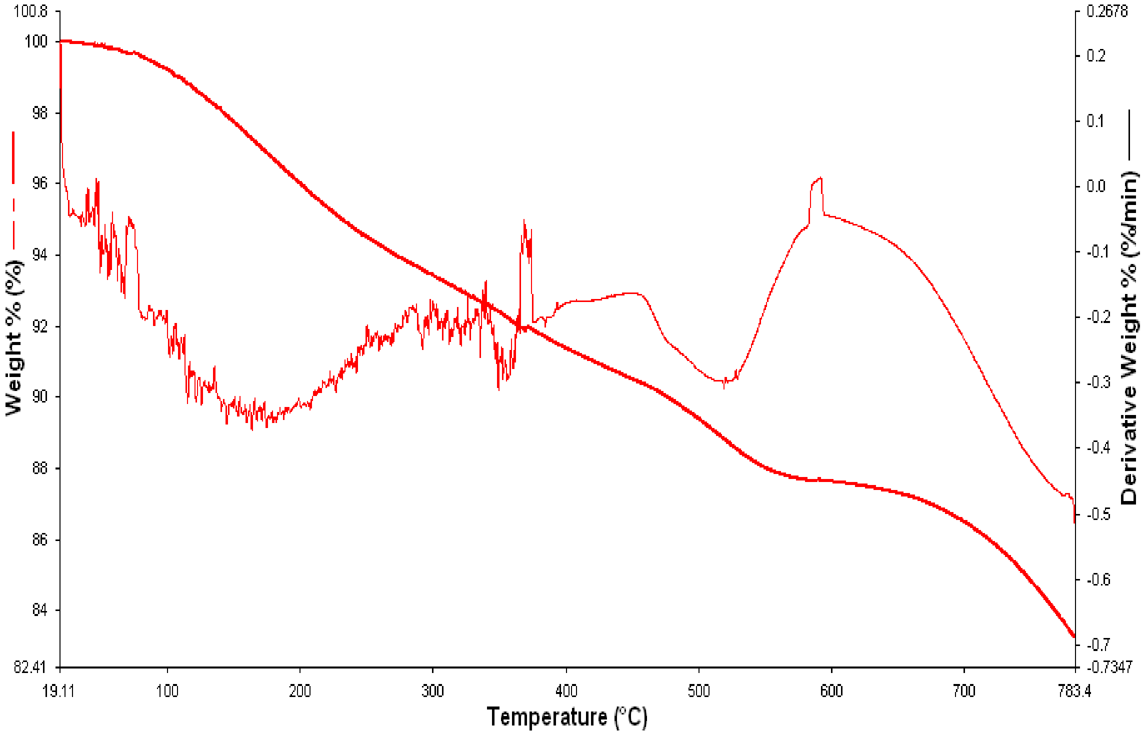

Figure 4. 23. TGA analysis of the specimen with 1% liquid admixture

Figure 4.23 shows that the specimen with the 1% liquid admixture lost 16.73% of its total weight when heated from 19 °C to 783 °C. Figure 4.23 displays the weight loss determined by the TGA analysis as well as the temperature range and peak temperature for the representative specimens. The first effect, which takes place in the temperature range of 19 °C to 150 °C, is caused by specimens absorbing water from the air during their cooling to room temperature after drying at 104 °C. Therefore, a 3% free water rate for the specimen is estimated. The second effect is brought on by the dehydration of C-S-H, ettringite, and calcium aluminate hydrate, which takes place between 150 °C and 350 °C. In this range, there was a 3% weight loss. The ratio of CaO to SiO_2 in the wet cement matrix determines the temperature at which these compounds begin to lose water. The third impact on the TGA graph, which takes place in the temperature range between 350 °C and 600 °C, represents the degradation of $Ca(OH)_2$ created during hydration. In this range, 3% of the $Ca(OH)_2$ is thought to be lost. The temperature range of 600 °C to 783 °C further suggests that calcium carbonate is decarbonized in the hydrated molecule. The decarbonized calcium carbonate in this range was observed to be 3%.

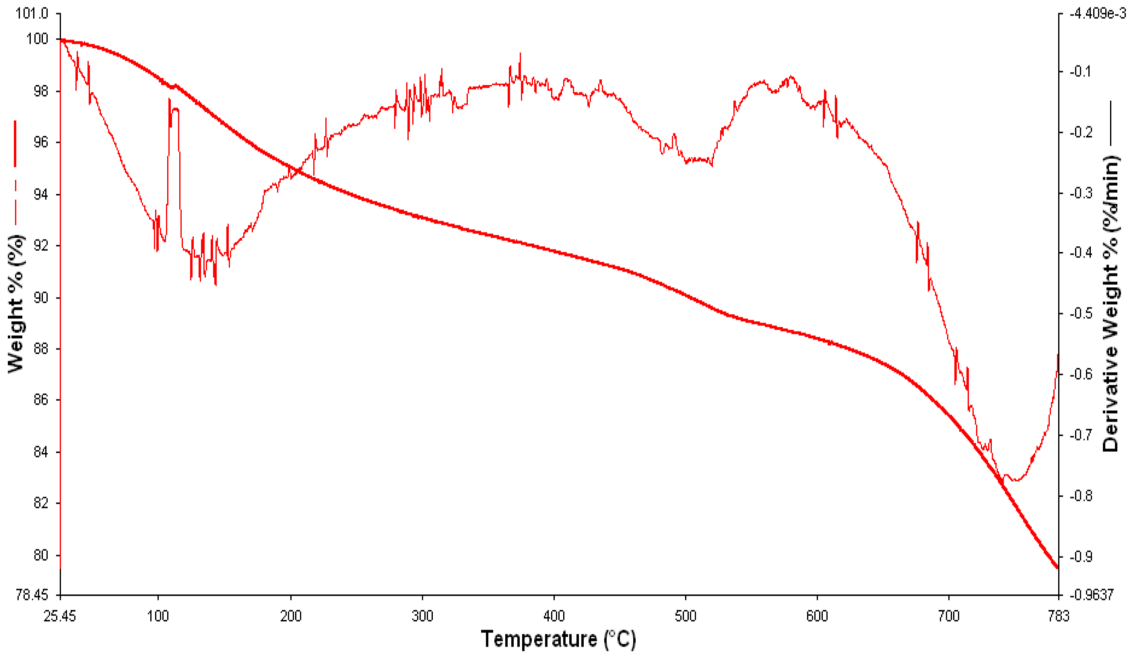

Figure 4. 24. TGA analysis of the specimen with 2% liquid admixture

Figure 4.24 shows that when heated from 25 °C to 783 °C, the specimen with the 2% liquid admixture lost 20.52% of its total weight. Figure 4.24 shows the TGA analysis's estimated weight loss as well as the representative specimens' temperature range and peak temperature. Specimens absorb water from the air when they cool to room temperature after drying at 104 °C, resulting in the first effect, which occurs in the temperature range of 25 °C to 150 °C. As a result, the specimen's estimated free water rate is 3%. The second effect occurs between 150 and 350 °C and is caused by the dehydration of C-S-H, ettringite, and calcium aluminate hydrate. There was a 4% weight loss in this range. The temperature at which these compounds start to lose water depends on the ratio of CaO to SiO_2 in the wet cement matrix. The third influence on the TGA graph, which occurs in the 350 °C to 600 °C temperature range, is the decomposition of $Ca(OH)_2$ produced during hydration. It is estimated that 3% of the $Ca(OH)_2$ is lost in this range. A further indication that calcium carbonate is decarbonized in the hydrated molecule is the temperature range of 600 °C to 783 °C. In this range, 7% decarbonized calcium carbonate was found.

5. CONCLUSION

In this study, in which the effect of the use of crystalline capillary impermeability admixtures in concrete production on the mechanical and durability properties of concrete was investigated, admixtures in different proportions were added to the cement and conducted into various tests, and the results obtained in the study are summarized below.

1. During the reaction time of the Portland cement in the admixture-added specimens, the silicates reacted with the free calcium hydroxide to form the amorphous calcium silicate hydrate gel. For this reason, the amount of calcium hydroxide, which is harmful to the strength and durability of the concrete, has decreased depending on the admixtures used. The crystalline admixture which used in this study supported the formation of C-S-H gel and ettringite, making the specimens more impermeable and durable. In this case, it can be said that the admixture reduces the water penetrating the specimens by forming amorphous structures, increases the strength of the specimens, makes the damage in the environment more resistant to acids and reduces the permeability of the specimens.

2. At the end of 28 days, while the admixtures did not change the flexural strength, there was a noticeable increase in the compressive strength of the specimens. It has been shown that admixtures improve the microstructure of cement paste by contributing to crystal formation in the aggregate-cement and cement interface region. The specimen with a 2% liquid admixture showed the highest compressive strength.

3. In the mass loss experiments, the change in the total weight loss increased during the decomposition of the crystals formed by the addition of admixtures. The reason for this increase in weight loss is due to its decomposition with the admixture attached to the structure. The highest mass loss was observed in the specimen with a 2% liquid admixture.

4. SEM images showed that the admixture plays a positive role in filling the microcracks in the specimens. When the EDX graphs of the products on the

surface of the microcracks were examined, it was shown that all specimens had high levels of oxygen (O), calcium (Ca), and carbon (C), aluminum (A). Besides these elements, silica (Si) peaks were also observed. This reveals the presence of C-S-H and C-A-S-H gels, which are hydration products. The TGA and XRD analyses show that the formed products such as C-S-H and ettringite fill the cracks.

5. Powder admixtures showed less functionality than liquid admixtures. Compressive strength ratios and analysis results gave a more positive response in specimens with liquid admixtures.

As a result, it has been observed that the admixtures added to provide impermeability change the compressive strength regardless of powder or liquid. Compared to the powder admixture, the liquid admixture gave better results. Both types of admixtures supported ettringite formation and filled the cracks and voids in the sample. The importance of crystalline capillary impermeability in the anticipated crystallized formation process cannot be denied, but studies on strength should continue.

6. REFERENCES

Abrams, D. A. (1918). Design of concrete mixtures. Bulletin, 1, 2071-1050.

ACI Committee 212—American Concrete Institute. Report on Chemical Admixtures for Concrete; American Concrete Institute (ACI): Michigan, MI, USA, 2016; ISBN 978-1-942727-80-4.

ACI 222R-01, Protection of Metals in Concrete Against Corrosion, American Concrete Institute, Detroit, Michigan

Akman, M.S., (1989), Concrete durability and its importance, I. National concrete congress. Congress Proceedings, 24 May 1989, Istanbul.

Akman, M.S., (2002), “Effects of the Content and Kind of Soluble Alkalis in Cements on Different Properties of Concrete”, Cement and Concrete World, December-November 2002, 7: 35-52.

Alizadeh, R., Beaudoin, J. J., & Raki, L. (2011). Mechanical properties of calcium silicate hydrates. Materials and Structures, 44(1), 13-28.

Al-Kheetan J.M. Rahman M.M. Chamberlain A.D. (2018). Structural Concrete; 19.

Arıoğlu, E., (1989), “Prefabrikasyon Endüstrisinde Beton Kalitesinin ve Denetiminin Mevcut Durumu”, 1. Ulusal Beton Kongresi, 24-25-26 Mayıs 1989, İstanbul, 199-208.

Asbridge A.H., Chadbourn G.A., Page C.L., (2001), “Effects of metakaolin and the interfacial transition zone on the diffusion of chloride ions through cement mortars”, Cem Concr Res, Vol. 31, 2001, pp. 1567–1572.

ASTM C 618, Specification for Fly Ash and Raw or Calcined Pozzolan for Use As a Mineral Admixture in Portland Cement Concrete, 1991.

Attiogbe, E. K. and Rizkalla, S. H. (1988). “Response of concrete to sulfuric acid attack.” *ACI Materials Journal*, 84(6), 515-526.

Bakharev, T. (2005). Resistance of geopolymer materials to acid attack. *Cement and Concrete Research,* 35, 658-670.

Baradan, B., Yazıcı, H. ve Ün, H., (2002), Betonarme Yapılarda Kalıcılık, Dokuz Eylül Üniversitesi Mühendislik Fakültesi Yayınları, Yayın No:298, ISBN: 975-441-189-1, İzmir.

Baradan, B., Türkel, S., Yazıcı, H., Ün, H., Yiğiter, H., Felekoğlu, B., Tosun, K., Aydın, S., Yardımcı, Y., M., Topal, A. ve Öztürk, A. U., (2012), Beton, D.E.Ü. Mühendislik Fakültesi Yayınları, İzmir, 2012.

Baradan, B. Yazıcı, H. Aydın, S. Aydın, (2015), Concrete. Dokuz Eylül Engineering Faculty Publications, 2015.

Cappellesso, V. G., dos Santos Petry, N., Dal Molin, D. C. C., & Masuero, A. B. (2016). Use of crystalline waterproofing to reduce capillary porosity in concrete. Journal of Building Pathology and Rehabilitation, 1(1), 1-12.

Cementing Materials Against Alkali-Silica Reaction", Cement and Concrete Research, 31: 1057-1063.

Cheung, J.; Roberts, L.; Liu, J. Contributions and sustainability. Cement Conc. Res. 2018, 114, 79-89.

Duchesne, J. ve Berube, M.A., (2001), "Long-term Effectiveness of Supplementary

Eren Ö., Yılmaz, Z., (2004), "Değişik sıcaklıklarda kür edilen salt Portland çimentolu, yüksek fırın cürufu veya uçucu kül katkılı betonlarda dayanım gelişimi1", İMO Teknik Dergi, 23 (1): 3311-3322.

Erdoğan, T.Y., (2003), "Beton", ODTÜ Geliştirme Vakfı Yayıncılık ve İletişim AŞ., Ankara.

Erdoğdu, Ş., Karakaş, E., (2003), Sülfat İyonu Konsantrasyonu Düşük Ortamlara Maruz Betonun Durabilitesinin Karşılaştırılmalı Olarak İncelenmesi, *5. Ulusal Beton Kongresi*, sf. 555-565, İstanbul.

Ertem, E. (2002). Yeraltı Su Seviyesi Altında Kalan Bodrum Kabuklarında Karsılasılan.

Felekoğlu, B., Yardımcı, M. Y. ve Baradan, B., (2003), "Kendiliğinden Yerleşen Betonların Isınma ve Donma-Çözülme Direnci", 5. Ulusal Beton Kongresi, 1-2-3 Ekim 2003, İstanbul, 365-374.

Garcia, D. C. S., Soares, M. M. N. D. S., Bezerra, A. C. D. S., Aguilar, M. T. P., & Figueiredo, R. B. (2017). Microstructure and hardness of cement pastes with mineral admixture. Matéria (Rio de Janeiro), 22.

Gruber K.A., Ramlochan T., Boddy A., Hooton R.D., Thomas M.D.A., (2001), "Increasing concrete durability with high-reactivity metakaolin", Cem Concr Compos., Vol. 23, 2001, pp. 479–484.

Hewayde, E., Nehdi, M., Allouche, E. and Nakhla, G.(2007). “Effect of mixture design parameters and wetting – drying cycles on resistance of concrete to sulfuric acid attack.” *Journal of materials in Civil Engineering,*
19(2), 155-163.

Hou, D., Ma, H., Zhu, Y., & Li, Z. (2014). Calcium silicate hydrate from dry to saturated state: Structure, dynamics and mechanical properties. *Acta materialia , 67,* 81-94.

Ichitsubo, M., Tamaguchi, T., Horiguchi, I. and Takemura, K. (2006). “The Resistance to Sulfuric Acid Attack in Cementitious Materials with Ironblast- furnace Slag.” *Concrete Journal,* 44(3), 19-25.

Jamal, M.K and Roger, M.C., (2003). Absorption characteristics of metakaolin concrete. Cement and Concrete Research, 34(1): 19-29.

Johnson, J. A., (2002), “Durability and Temperature Related Characteristics of High Performance Concrete”, PhD Thesis, Purdue University, UMI Number: 3104967.i

Kawai, K., Yamaji, S. and Shinmi, T. (2005). “Concrete deterioration caused by sulfuric acid attack.” *10th DBMC International Conference On Durability of Building Materials and Component,* Lyon, France 17- 20 April 2005

Malhotra V.M., 1991. Durabily of concrete, Second International Conference, Montreal, Canada

Mardani-Aghabaglou, A., Yüksel, C., Beglarigale, A., & Ramyar, K. (2019). Improving the mechanical and durability performance of recycled concrete aggregate-bearing mortar mixtures by using binary and ternary cementitious systems. Construction and Building Materials, 196, 295-306.

Marfil, S.A. ve Maiza, P.J., (2001), “Deteriorated Pavements Due to the Alkali-silica-Reaction, A Petrographic Study of Three Cases in Argentina”, Cement and Concrete Research, 31:1017-1021.

Mehta, P. K., Monteiro, P. J. M., (2006), Concrete Microstructure Properties and Materials, McGraw Hill, 2006.

Mindess, S., Young J.F., ve Darwin, D. (2002). *Concrete (2nd edition)*. New
York: Prentice Hall.

Mills, A. P., Hayward, H. W. and Rader, L. F., (1955), Materials of Construction, John Wiley and Sons, New York, 1955.

Neville, A. M., (1996), Properties of Concrete, Fourth Edition, John Wiley & Sons. Inc., New York, 1996.

Neville, A.M. ve Brooks, J.J., (2001), Concrete Technology, Revised Edition, Pearson Education Limited.

Nonat, A. (2004). The structure and stoichiometry of CSH. Cement and concrete research, 34(9), 1521-1528.

Ouyang, C., Naani, A., Chang, W.F., 1988. Internal and external sources of sulfate ions in Portland cement mortar: Two types of chemical attack. Cement and Concrete Research, V.18, pp. 699-709.

Parron-Rubio, M. E., Perez-Garcia, F., Gonzalez-Herrera, A., Oliveira, M. J., & Rubio-Cintas, M. D. (2019). Slag substitution as a cementing material in concrete: Mechanical, physical and environmental properties. Materials, 12(18), 2845.

Pazderka, J., & Hájková, E. (2016). Crystalline admixtures and their effect on selected properties of concrete. Acta Polytechnica, 56(4), 306-311.

Pazderka, J., (2017), The Crystalline Admixture Effect on Concrete and Cement Mortar Compressive Strength, Key Engineering Materials, 722:87-91.

Pellenq, R. M., Lequeux, N., & Van Damme, H. (2008). Engineering the bonding scheme in C–S–H: The iono-covalent framework. Cement and Concrete Research, 38(2), 159-174.

Pereira, R. M. S., (2003), “Accelerated Corrosion Testing, Evaluation and Durability Design of Bonded Post-Tensioned Concrete Tendons”, PhD Thesis, The University of Texas at Austin, UMI Number: 3118069.

Philipose, K. E., Beaudin, J. J. ve Feldman, R. F., (1992), “Degradation of Normal Portland and Slag Cement Concrete Under Load Due to Reinforcement Corrosion”, Fourth Canmet/ACI, Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Vol 2,1491- 1508.

Ramachandran, Vangipuram Seshachar. Concrete admixtures handbook: properties, science and technology. William Andrew, 1996.

Roger Rixom R., Mailvaganam N., (1999), Chemical admixtures for concrete. 3th ed., E & FN Spon, London, England, 1999.

Santhanam, M., Cohen, M. and Olek, J., “Differentiating seawater and groundwater sulfate attack in Portland cement mortars”, Cement and Concrete Research, 36 (12): 2132-2137 (2006)

Saran, A. G., (2007), Öğütülmüş Granüle Yüksek Fırın Cürufunun Beton Durabilite Özelliklerine Etkisi, Yüksek Lisans Tezi, İ. T. Ü., Fen Bilimleri Enstitüsü, İstanbul,2007.

Sata, V., Sathonsaowaphak, A., Chindaprasirt, P., (2012), Resistance of lignite bottom ash geopolymer mortar to sulfate and sulfuric acid attack. *Cement & Concrete Composites*, **34**, 700-708.

Sauman Z., (1979), Carbonization of porous concrete and its main binding components, 1979

Shi, C. and Stegemann, J. A. (2000). “Acid corrosion resistance of different cementing materials.” *Cement and Concrete Research*, 30(5), 803-808.

Shiru S. (2015). Experimental Ġnvestigations Of The Permeability Characteristics of Self Compacting Concrete Mixes Made With Varying Constituents. Yüksek Lisans Tezi, Near East University.

Şahin, R., Taşdemir, M.A., Gül, R. ve Çelik, C., (2003), “Betonun Don Hasarının Mekanik Deneylerle Analizi”, 5. Ulusal Beton Kongresi, 1-2-3 Ekim 2003, İstanbul, 333-343.

Topçu, İ.B., Demir, A. and Boğa, A.R., (2004), Effects of plasticizer and super plasticizer additive usage on fresh concrete properties. Turkey Engineering News.

Uğurlu, A., (2003), “Sulama Kanallarında Sülfat Problemi ve Çözüm Önerileri”, 5. Ulusal Beton Kongresi, 1-2-3 Ekim 2003, İstanbul, 567-574.

Uyan, M., Pekmezci B.V. ve Yıldırım H. 2003. Akışkanlaştırıcı katkı ve kür koşullarının betonun geçirimlilik özelliklerine etkisi 10-12, İstanbul.

Uygunoğlu, T., Yücel, K. T., Yurtçu, Ş., 2006. Betonun Zararlı Ortamlardaki Durumu: Yeraltı Suyu Etkisi, *Yapı Teknolojileri Elektronik Dergisi*, sf. 29-35.

Weng, T. L., Lin, W. T., & Cheng, A. (2013). Effect of metakaolin on strength and efflorescence quantity of cement-based composites. The Scientific World Journal, 2013.

YAZICI, H. YÜKSEK HACİMDE C SINIFI UÇUCU KÜL İÇEREN BETONLARIN MEKANİK ÖZELLİKLERİ VE SÜLFÜRİK ASİT DAYANIKLILIĞI. Pamukkale Üniversitesi Mühendislik Bilimleri Dergisi, 11(3), 443-448

Yeğinobalı, A., (2009), Silis Dumanı ve Çimento ile Betonda Kullanımı, TÇMB, Ankara, 2009.

Young, J.F., (1998), A Review of The Pore Structurc of Cement Paste and Concrete and Its Influence On Permeability . S.P.108, Permeability of Concrete. ACI.

Zhan, P.; He, Z., (2019),Shrinkage reducing admixture application in concrete: A review. Constr. Build. Mom. 2019, 201, 676–690.